ABSTRACT

BHAUMIK, ANAGH. Structure-Property Correlations of Undoped and B-doped Q-Carbon. (Under the direction of Professor Jagdish Narayan).

Recently there is a potential interest in synthesizing new phases of carbon by utilizing highly non-equilibrium techniques. These novel phases of carbon have unique properties which lead to potential applications in multifunctional electronic devices. The present research is focused on the structure-property correlations of Q-carbon (quenched-carbon) and B-doped Q-carbon. The Q-carbon phase having over 75% sp$^3$-bonded carbon (and the rest sp$^2$) is formed by nanosecond pulsed laser melting of amorphous carbon and subsequent quenching of highly undercooled molten carbon. The laser parameters and thermal conductivities of the substrate and thin film play important roles in determining the degree of undercooling which dictates the formation of amorphous Q-phases. The isothermal field-dependent magnetization plots confirm room-temperature ferromagnetism in Q-carbon with a finite coercivity and saturation magnetization at 300 K, and a Curie temperature ($T_C$) of 570 K. We have also found n-type conductivity in Q-carbon in the entire temperature range from 10 - 300 K from extraordinary Hall effect (EHE) measurements. The analysis of the EHE in Q-carbon follows a non-classical “side-jump” electronic scattering mechanism. We have experimentally observed an electrochromic effect in Q-carbon thin films, where the optical absorption can be increased up to ~48% at 265 nm with the application of 10 V. The detailed structure-property measurements in undoped Q-carbon show an excess amount of unpaired electrons near the Fermi energy level ($E_F$), which causes the room-temperature ferromagnetism, extraordinary Hall effect, and electrochromic effect. The ferromagnetic property of Q-carbon can be completely destroyed upon B-doping to form high-temperature superconductors. We have achieved superconducting transition temperatures ($T_c$) of 36 and 55 K in two distinct phases of B-doped Q-carbon having 17 and 27 at% B, respectively.
The temperature-dependent magnetic susceptibility and resistivity measurements indicate type-II Bardeen-Cooper-Schrieffer (BCS) superconductivity in the B-doped Q-carbon thin films. The superconducting phases also exhibit high values of critical current density (~10⁸ A/cm²) and upper critical field (~10 T). By employing the magnetic flux creep measurements, we have shown the applicability of B-doped Q-carbon thin films in MRI and NMR inserts. The critical fluctuation measurements show a crossover from 2D to 3D nature of Cooper pair transport near $T_c$ in the high-temperature superconducting phases. By utilizing the detailed structure-property correlations, we have proved that the increased B concentrations beyond thermodynamic solubility limits, moderate to stronger electron-phonon coupling, and higher density of states near the $E_F$ cause high-temperature superconductivity in B-doped Q-carbon. We have also used our novel pulsed laser annealing technique to synthesize Q-BN and c-BN structures from nanocrystalline h-BN, convert amorphous carbon nanofibers (CNFs) into diamond nanofibers (DNFs), and form nitrogen-vacancy (NV) centers in diamond for ultrafast quantum technology. The multiple pulse laser shots on the quenched phases (Q-carbon and Q-BN) form nanoneedles, microneedles, and single-crystal thin films of diamond and c-BN. This formation is dependent on the nucleation and growth times which are controlled by laser energy density and thermal conductivities of substrate and as-deposited thin film. Highly concentrated NV centers in diamond are synthesized by pulsed laser annealing of N-doped amorphous carbon films which are grown by pulsed laser deposition in an atmosphere of $N_2^+$ plasma. This ultrafast technique generates fewer surface traps thereby forming ~75% NV⁻ centers at room-temperature which are optically and magnetically distinct as compared to NV⁰ centers. We have also achieved tuning of these centers in the highly concentrated NV-diamonds by using photons, phonons, and electrons, which is a prerequisite condition for next-generation quantum sensing, communication, and computing. This discovery of interesting
properties of amorphous quenched phases shows that non-equilibrium synthesis which employs undercooling process can be used to fabricate new materials with greatly enhanced physical properties and functionalities.
Structure-Property Correlations of Undoped and B-doped Q-Carbon

by
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DEDICATION

To My Wife, Mom, and Dad

Monalisa Acharjee, Asha Bhaumik, and Professor G. C. Bhaumik
BIOGRAPHY

Anagh Bhaumik was born in Durgapur, West Bengal, India. After completing his high school from St. Xavier’s, St. Peter’s, and Bidhan Chandra Institution, Durgapur he earned his B.Tech degree in Metallurgical and Materials Engineering from National Institute of Technology, Rourkela. After that, he worked in MECON Limited (a public sector undertaking) for four and half years where he designed and commissioned wire rod mill-2 at Vizag Steel Plant and hot dip galvanizing line at Bokaro Steel Plant, India. He got his M.S degree in Materials Science from Missouri State University. For his M.S thesis, he worked with solar cells and ferroelectric devices under the guidance of Prof. Kartik Ghosh, and his thesis title is “An Atomistic Approach to Integrate Two-Dimensional Thin Film and Nanostructures For Solar Cell Application: Reduced Graphene Oxide and Copper Oxide Nanostructures.” Then he joined the Ph.D. program (Materials Science and Engineering) at North Carolina State University.
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1. Introduction

Carbon being the sixth most abundant element in the Earth’s crust, its direct conversion into novel solid phases of carbon and crystalline diamond at ambient conditions have immense scientific and technological benefits. The discovery of carbon nanotubes and graphene have triggered a substantial interest in synthesizing new phases of carbon having distinct entropy which can be used in potential spintronics, optoelectronics, and high-speed electronic applications. Among other solid phases of carbon, diamond has immense practical wide-range applications ranging from biomedical to heat sinks for electronic components. The formation of diamond nanoneedles and microneedles is scientifically challenging with tremendous impact on field emission-based devices and biomedical applications, including drug delivery. The diamond nanoneedles and microneedles will lead to minimally invasive transdermal medical devices used for various applications, including drug delivery, fluid sampling, micro-dialysis, and electrochemical sensing. From equilibrium thermodynamic considerations, the formation of diamond nuclei (using conventional bulk processing) is only viable at high temperatures and pressures. Carbon nanotubes (CNTs) can be converted to crystalline diamond by shock wave, high-pressure high-temperature (HPHT) and hydrogen plasma techniques. Previous attempts on the formation of microneedles have focused on reactive ion etching of nanocrystalline diamond thin films, where the length is limited by the deposited thickness of diamond and diameters of microneedles are limited to larger sizes by reactive ion etching. The resulting microneedles are polycrystalline with a significant concentration of defects which can provide traps and recombination centers. In another approach, the dependence of diamond growth rates during chemical vapor deposition (CVD) of diamond thin films have been used to get single-crystal microneedle of limited sizes. By controlling the CVD parameters, enhanced growth either along $<111>$ direction or along $<100>$ direction can be
achieved and microneedles, albeit limited sizes and aspect ratios, can be formed. Besides the limitations on size and aspect ratio, the CVD requires high temperatures with overall low throughput, as the process occurs in solid state.\textsuperscript{12} Hexagonal-BN and c-BN have similar structure and properties with graphite and diamond, respectively. The BN thin films can be doped (both \textit{p} and \textit{n}-type) and can also be used at high temperatures with ferrous alloys (unlike diamond).\textsuperscript{13} Therefore, the formation of phase-pure diamond, c-BN, and new phases of carbon and BN will have tremendous technological applications.

Non-equilibrium processing techniques have been widely used to synthesize novel materials having a wide range of functionalities.\textsuperscript{14,15} In this thesis, we have reported the formation of a novel quenched solid phase of carbon (Q-carbon) and its direct conversion into nano and microstructures of crystalline diamond (at room temperature and atmospheric pressure) using pulsed laser annealing. The Q-carbon was formed as a result of nanosecond pulsed laser melting and subsequent quenching of super undercooled molten carbon. This new phase of carbon has exciting properties, namely room-temperature ferromagnetism, extraordinary Hall effect, and electrochromic effect. We have also shown that nanocrystalline h-BN can be converted directly into quenched-BN (Q-BN) by using the pulsed laser annealing. Subsequent pulsed laser annealing of these quenched phases formed nanoneedles, microneedles and single-crystal thin films of diamond and phase-pure c-BN. The texture of diamond and c-BN crystals was \textit{<110>} thereby confirming the liquid-phase mediated growth. Q-carbon contains 75-85\% \textit{sp}^3 bonded carbon and the rest is \textit{sp}^2. The diamond nuclei present in the Q-carbon structure could be grown into \textasciitilde 5 \mu m diamond by using the equilibrium hot filament chemical vapor deposition (HFCVD) process. In the CVD grown diamond (from Q-carbon), diamond attained a \textit{<111>} out-of-plane orientation, as a result of epitaxial growth on \textit{<0001>} sapphire substrates. We have also shown the direct
conversion of the tip of amorphous carbon nanofibers into diamond nanofibers by using the pulsed laser annealing. Therefore, our novel laser processing technique which is based on the super undercooling process will ultimately pave the pathway to highly efficient and commercially viable solid-state devices.

The superconductivity in diamond and carbon-based materials has generated tremendous theoretical and experimental interests. Superconductivity in boron-doped diamond is well-established with an observed superconducting transition temperature ($T_c$) ranging from 4 K to 11 K with an increasing boron concentration in the substitutional lattice sites of the diamond.\textsuperscript{16,17} With the increase in hole concentration, strong attractive interactions are induced which cause an increase in $T_c$. From electron-phonon coupling (theoretical) calculations in B-doped diamond over a wide range of boron concentrations, Moussa and Cohen had predicted $T_c$ of over 55 K for substitutional B concentrations in the range of 20-30\%.\textsuperscript{18} These calculations did not take into account electron anisotropy and phonon anharmonicity in improving the accuracy of electron-phonon coupling calculations, nevertheless, provide an important guide for the synthesis of materials with increasing boron concentrations by non-equilibrium techniques. It should be mentioned that B concentration beyond which B starts clustering to form dimers and precipitates is the upper limit for obtaining the highest $T_c$ in B-doped diamond. The bonding and anti-bonding states in B dimers consist of symmetric and anti-symmetric combinations of the bound state in B. The symmetric and antisymmetric states lie deeper in the band gap and above the isolated B energy level, respectively.\textsuperscript{19} These energy states do not contribute to the density of states near the Fermi level, thereby reducing the value of $T_c$. Since the thermodynamic solubility limit for (substitutional) B in diamond is 2.0\%, higher concentrations can be attained only by highly non-equilibrium techniques. It should be noted that substitutional B atoms generate hole carrier
concentration which enhances superconductivity. On the other hand, interstitial B atoms in the diamond lattice donate three electrons which adversely affect superconductivity by compensating holes and reducing the carrier concentration. Similarly, atomic hydrogen atoms create B-H complexes which neutralize holes and reduce \( T_c \). High-temperature and high-pressure (equilibrium) synthesis of B-doped diamond leads to \( T_c \) of 4 K.\(^{16}\) The increase in \( T_c \) has been achieved by non-equilibrium MPCVD (microwave-plasma enhanced chemical vapor deposition) synthesis of B-doped diamond, where the non-equilibrium aspect is derived from the energetics of plasma beyond equilibrium energy (\( k_B T \)) of the CVD process. The highest \( T_c \) of 11 K has been achieved for B-concentration of 5.0% in (111) MPCVD films.\(^{17}\) The (111) oriented B-doped diamond films exhibited higher \( T_c \) than the (100) thin films.\(^{20}\) This was due to the higher lattice expansion resulting from unrelaxed strains in (111) B-doped diamond thereby giving rise to higher density of states which cause an increase in the onset of \( T_c \) from 6.3 K (in (100) B-doped diamond) to 11.4 K.\(^{17}\) The B dimers can form easily along the <100> direction as compared to <111> direction which can also be a reason for the directional-dependence of \( T_c \). Another motivation for superconductivity in amorphous B-doped Q-carbon was derived from the increased superconducting transition temperature in amorphous bismuth (6.8 K) as compared to single-crystals of Bi (0.53 mK).\(^{21}\)

In this thesis, we have used a non-equilibrium method based upon melting (by using nanosecond laser) of amorphous B-doped carbon films in a super undercooled state and quenching subsequently to form B-doped Q-carbon. In this process, B-doped Q-carbon thin films were formed without the presence of hydrogen which reduces \( T_c \) by forming B-H complexes.\(^4\) In addition, much higher concentrations of B could be achieved (beyond thermodynamic solubility limits) by rapid quenching from melt via solute trapping. We have achieved \( T_c \) of 36 K and 55 K...
in two distinct phases of B-doped Q-carbon having a B concentration of 17 and 27 at%, respectively. We have also performed detailed magnetic and electrical characterizations, and structure-property correlations of these novel carbon-based superconducting phases.

Pure and nitrogen-doped nano- and microdiamonds are non-toxic, and have excellent electronic, magnetic, optical, and mechanical properties with applications ranging from drug delivery and fluorescent biomarkers to single-photon sensors and quantum computing, nanoscale electronic and magnetic sensing, single-spin nuclear magnetic resonance, nanoscale thermometry and nanosensors. The nitrogen-vacancy (NV) center in diamond is a point defect with C$_{3v}$ symmetry consisting of substitutional nitrogen and vacancy pair along <111> directions. These NV centers in diamond are quite stable, and are ideally suited for reliable and robust electronic, optical, and magnetic nanoscale devices operating at room temperature. The NV center is a deep-level defect, and it exists in neutral NV$^0$ state and magnetically active NV$^-$ state with a trapped electron. The unique features of NV center are derived from spin triplet ground state and dependence of fluorescence on spin orientation. The magnetically active NV$^-$ defects are characterized by optical zero-phonon line (ZPL) at 1.945 eV (637 nm), whereas NV$^0$ has ZPL at 2.156 eV (575 nm). Since NV$^-$ is magnetically active, its luminescence can be controlled by the magnetic field for various applications including single-photon sensors, nanoscale electronic and magnetic sensing, single-spin nuclear magnetic resonance, nanoscale thermometry, fluorescent biomarkers, quantum computing, and nanosensors. The above applications require precisely controlled synthesis of pure and NV-doped diamonds, where NV defects can be located individually in various diamond structures, such as nanodiamonds (4-10 nm), nanoneedles, microneedles, and thin films. Current methods of introducing NV defects in diamond have many problems and challenges. The CVD-based techniques produce large-grain polycrystalline films, and nanodiamonds produced by CVD
are embedded into amorphous carbon from which extraction of individual nanodiamond is quite cumbersome and expensive. Since nitrogen doping in CVD is controlled by thermodynamic solubility limit, the number density of NV centers per unit volume is quite limited. The second technique involves nitrogen ion implantation. The nitrogen ion implantation produces high concentration of Frenkel (vacancy-interstitial pairs) defects. Annealing of these defects and putting nitrogen into substitutional sites represent many challenging problems, including high-thermal budgets. Therefore, the controlled introduction of nitrogen centers exceeding thermodynamic solubility limits in diamond nanostructures is still extremely challenging. With the emerging trend towards high-speed quantum technology, synthesizing highly concentrated (high-quality) NV-centers and their precise modulation by electrons and photons are essential criteria for quantum devices to perform optimally.

In this thesis, we have also reported a direct conversion of N-doped amorphous carbon into highly concentrated NV-centers in diamond. The nanodiamonds having NV centers were formed by homogeneous nucleation from the undercooled melt, where the size was dictated by the melt lifetime. Nanoneedles and microneedles were formed as a result of interfacial instability of the crystallizing interface, which was controlled by laser and substrate variables, particularly thermal conductivities of the thin films and substrate. On the other hand, single-crystal films were also created when substrate could act as a template for the epitaxial growth. These nanodiamonds were also arranged periodically in a self-organized fashion which is needed for quantum devices. Since the diamond growth occurred from a liquid phase under ultrarapid quenching and solidification with velocity of the order of 5 ms⁻¹, it was possible to trap NV defects beyond thermodynamic limits. It should be noted that, a single NV defect in 5 nm or lower size diamond will require a
higher concentration of nitrogen than its thermodynamic solubility limit of $2.0 \times 10^{18} \text{cm}^{-3}$. These high concentrations were achieved by rapid quenching from the liquid, utilizing the phenomenon of solute trapping. A deterministic control of the charge transitions between NV$^-$ and NV$^0$ centers was also achieved by using electrons, photons, and phonons. The synthesized NV centers in diamond can be used for various novel quantum nanotechnologies in physical and biological sciences.
1.1. References


2. Background

2.1. Undercooling

A phase is defined as a portion of a system whose properties and composition are homogeneous in nature and has a distinct entropy from other parts of the system. The components of the phase are the different elements or bonding structures such that the phase can be defined by the relative amounts of each component. The transformation of one phase into another is governed by the relative stability of the new phase which is determined by its Gibbs free energy ($G$) given by the equation (2.1):

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (2.1)

where, $\Delta H$, $\Delta S$, and $T$ denote a change in enthalpy, change in entropy (disorderliness), and temperature, respectively. The enthalpy is a measure of the heat content of the system and is dependent on the internal energy, pressure, and volume of the system. A system is in an equilibrium state when it has the lowest possible value of the Gibbs free energy. Therefore, it can be observed from equation (2.1) that low enthalpy and high entropy favor this condition. There can also be other configurations where the phase is at local free energy minima conditions (metastable states) but do not have the lowest possible value of the free energy (stable state). These states are shown in figure 2.1(a). The intermediate states are referred to as unstable and exist momentarily during the phase transformations. Therefore, it can be realized that by a change in temperature and pressure a system can be transformed from a stable (graphite) to metastable (diamond) state. Higher humps or energy barriers result in a slower transformation rate and therefore kinetics play an important role in the formation of metastable and new phases of a
material. The Clausius-Clapeyron equation helps us to characterize phase transformations between two phases of a material, and is given by the equation (2.2):

\[
\frac{dP}{dT_{eq}} = \frac{\Delta H}{T_{eq}\Delta V}
\]

(2.2)

For closed packed systems, \(\Delta V < 0\) and \(\Delta H > 0\) and therefore \(\frac{dP}{dT_{eq}}\) is negative. This indicates that an increase in pressure lowers the equilibrium transition temperature. This increase in pressure is triggered by a phenomenon known as undercooling which is mathematically represented by the difference between melting temperature and the temperature at which the nucleation occurs.

**Figure 2.1.** (a) Gibbs free energy vs arrangement of atoms showing metastable and stable phases, and (b) Gibbs free energy vs temperature showing the driving force for solidification (\(\Delta G\)) and undercooling (\(\Delta T\)).

Figure 2.1(b) indicates that the driving force for solidification is provided by the change in free energy. It can also be seen that below the melting temperature (\(T_m\)), the solid phase is more stable than the liquid phase and vice versa. At \(T_m\), the value of \(\Delta G = 0\). Therefore, the change in entropy can be defined by the equation (2.3):
\[ \Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m} \]  

(2.3)

where, \( L \) is the latent heat of fusion. For small values of undercooling (\( \Delta T \)) we can assume that \( \Delta H \) and \( \Delta S \) are independent of temperature (neglecting the difference between the specific heats between liquid and solid). Therefore, the change in free energy can be given by the equation (2.4):

\[ \Delta G = \Delta H - T^* \frac{\Delta H}{T_m} = \frac{\Delta H \Delta T}{T_m} \]  

(2.4)

Therefore, at any temperature below \( T_m \) there is a driving force for solidification. If the energy is added or removed quickly (non-equilibrium processes) the system can be significantly undercooled. Again, the change in total free energy is the sum of free energy change due to volume and surface. For a spontaneous forward reaction, the change in total free energy (\( \Delta G_T \)) should be negative and is calculated by using the equation (2.5):

\[ \Delta G_T = -\frac{4}{3} \pi r^3 \Delta G_V + 4\pi r^2 \gamma_S \]  

(2.5)

To calculate the values of critical radius (\( r^* \)) and critical nucleation barrier (\( \Delta G^* \)), \( d\Delta G_T/dr = 0 \).

Therefore, using the equation (2.5) we can find:

\[ \frac{d\Delta G_T}{dr} = -4\pi r^2 \Delta G_V + 8\pi r \gamma_S = 0 \; ; \; r^* = \frac{2\gamma_S}{\Delta G_V} \; ; \; \Delta G^* = \frac{16\pi \gamma_S^3}{3\Delta G_V^2} \]  

(2.6)

Again, by using equation (2.4), we can calculate the undercooling-dependent values of \( r^* \) and \( \Delta G^* \) represented in the equation (2.7):

\[ r^* = \frac{2\gamma_S T_m}{\Delta H \Delta T} \; ; \; \Delta G^* = \frac{16\pi \gamma_S^3 T_m^2}{3\Delta H^2 \Delta T^2} \]  

(2.7)
Therefore, it can be seen from the above equation (2.7) that $r^*$ and $\Delta G^*$ decrease with increasing undercooling.

2.1.1. Homogeneous Nucleation

In homogeneous nucleation, solid nuclei spontaneously appear within the undercooled phase. For the formation of the solid nuclei, large values of undercooling are required. To nucleate a solid of radius $r^*$ an energy barrier of $\Delta G^*$ should be overcome. The rate of homogeneous nucleation ($N$) is given by the equation (2.8):

$$N \approx \vartheta_D \exp\left(-\frac{\Delta G^*}{kT}\right)$$

(2.8)

where, $\vartheta_D$ denotes the frequency with which atoms from the liquid phase attach to the solid nucleus. This rearrangement of atoms follows the temperature-dependent diffusion formalism which is given by equation (2.9):

$$\vartheta_D \approx \exp\left(-\frac{Q_d}{kT}\right)$$

(2.9)

where, $Q_d$ denotes the activation energy. Therefore, for temperatures close to $T_m$, $\Delta G^* > Q_d$ and nucleation is suppressed. Since $\Delta G^*$ is inversely proportional to $\Delta T^2$, the value of $\Delta G^*$ decreases with increase in the value of $\Delta T$. Therefore, with increasing the value of undercooling, there is a sharp increase in homogeneous nucleation rate. It should also be noted that with larger values of undercooling (low temperatures) the diffusion is too small (low atomic mobilities) and the nucleation rates decrease sharply. Therefore, the nucleation rates in homogeneous nucleation are strongly dependent on temperature by the following equation (2.10):

$$N \approx \exp\left(-\frac{A}{\Delta T^2}\right)$$

(2.10)
There is a critical undercooling that is required for homogeneous nucleation. There is virtually no nucleation until $\Delta T_{cr}$ is reached. When $\Delta T_{cr}$ is reached, there occurs an “explosive” nucleation. Therefore, the solidification velocities in the case of homogeneous nucleation in the undercooling process are extremely large.

2.1.2. Heterogeneous Nucleation

The new phase can appear on the walls of the solid container, grain boundaries, and impurity particles by the process of heterogeneous nucleation. In this process, the values of undercooling are not as large as that required in homogeneous nucleation. The values of values of $r^*$ and $\Delta G^*$ for the case of heterogeneous nucleation can be calculated using the equation (2.11):

$$r^* = \frac{2\gamma S T_m}{\Delta H \Delta T}; \Delta G^* = S(\theta) \frac{16\pi \gamma S^3 T_m^2}{3\Delta H^2 \Delta T^2}$$

(2.11)

where, $S(\theta)$ is the angular component derived from the angle formed between the solid-container interface and liquid-container interface. The value of $S(\theta)$ can be calculated by using the equation (2.12):

$$S(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2 / 4 \leq 1$$

(2.12)

Therefore, in the case of heterogeneous nucleation, the values of $\Delta G^*$ and $\Delta T_{cr}$ are lower than in homogeneous nucleation. For temperatures closer to $T_m$, there is low nucleation and high growth rates (coarse microstructure). It can also be observed that for low temperatures (high undercooling), there is high nucleation rates but low growth rates (formation of amorphous and quenched structures). In the present research, the nucleation of diamond in the Q-carbon super
undercooled phase occurs by homogeneous nucleation whereas the nucleation of diamond on sapphire substrates occurs by heterogeneous nucleation.

2.2. Phase Diagram of Carbon

The phase diagram of carbon is of great interest in fundamental and applied research. According to the equilibrium (pressure vs. temperature) phase diagram (figure 2.2(a)), graphite, diamond, liquid, and vapor are the various phases of carbon. At low pressures, graphite converts into vapor above around 4000 K. According to the phase diagram, diamond synthesis from liquid carbon will require even higher temperatures and pressures as the graphite/diamond/liquid carbon triple point occurs at 5000 K/12 GPa, where 1 GPa = 9869 Atm. Therefore, it is consistent with the phase diagram that diamond can exist in the interiors of the outer planets (Uranus and Neptune) and Earth’s mantle, where pressure/temperature are 600 GPa/7000 K and 135 GPa/3500 K, respectively. Because of the high binding and activation energy of transformation, carbon polymorphs can exist as metastable phases in a P-T region, where a different phase is thermodynamically stable. As an example, diamond (metastable phase) survives indefinitely at room temperature, where graphite is the stable form. In the thermodynamically stable and metastable forms of carbon, graphite, diamond, liquid and vapor, we have introduced amorphous carbon with some $sp^3$ content and super undercooled state of liquid carbon. This can be accomplished by nanosecond laser melting of amorphous carbon, where undercooled state is at about 4000 K, some 1000 K below the melting point of graphite. This temperature is estimated by using simulation of laser interaction with materials (SLIM) program.$^1$ By quenching this super undercooled state, we are able to form nanodiamond and microdiamond by controlling the nucleation and growth times. The super undercooled state upon rapid quenching leads to the formation of new state of carbon (Q-carbon) with novel physical, chemical, and mechanical
properties. Our results clearly show that diamond can be formed at ambient pressure in air from super undercooled state of carbon, produced by nanosecond pulsed laser melting of amorphous carbon. Thus, amorphous state of carbon, laser parameters, and thermal conductivities of film and substrate determine the temperature distribution and undercooling and play a critical role in the nucleation and growth of diamond. By scaling with the melting point of carbon, we estimate the undercooling in carbon to be as high as 1000 K. This undercooling shifts amorphous carbon/diamond/liquid carbon triple point to 4000 K or lower at ambient pressures. This is rather a drastic change from graphite/diamond/liquid carbon triple point at 5000 K/12 GPa in the equilibrium phase diagram.

Figure 2.2. (a) Carbon phase diagram (P vs. T) which has amorphous diamondlike carbon melting at 4000 K at ambient pressures (dotted green line), and (b) Gibbs free energy as a function of temperature for graphitic carbon ($G_g$), liquid carbon ($G_{liq}$) and diamond ($G_d$). The amorphous Q-carbon is formed as result of quenching from $T^*$ and diamonds nucleate between $T^*$ and $T_{dl}$.

This shift of amorphous carbon/diamond/liquid carbon triple point to 4000 K or lower at ambient pressures leads to modification of equilibrium carbon phase diagram by Bundy et. al.\textsuperscript{2} to accommodate diamond processing under super undercooled state of carbon. At these transition temperatures, the Gibbs free energy of highly undercooled liquid equals that of metastable
diamond phase which is quenched and retained at room temperature. This transformation from super undercooled state of carbon into diamond, which can occur at 4000 K and ambient pressures, modifies the equilibrium carbon phase diagram, as shown in figure 2.2(a). The extension of the phase diagram (P vs. T) is based upon Simon equation, where \( P = P_0 + a[(T/T_r)^c - 1] \), where we have used \( P_0 = 10^{-4} \text{ GPa} \) at \( T_r = 4000 \text{ K} \) from our experiments and the experimental data of Bundy et al. to estimate the \( a \) and \( c \) parameters.\(^2\)\(^3\) From the Simon equation \( (dP/dT)_{T_r} = ac/T_r \) was determined and the results compared with the value estimated from Clausius-Clapeyron equation, where \( (dP/dT)_{T_r} = \Delta H_m/(T_r \Delta V) \), where \( \Delta V \) is the change in volume from super undercooled carbon into diamond. Figure 2.2(b) shows the variation of Gibbs free energy as a function of temperature for graphitic carbon (\( G_g \)), liquid carbon (\( G_{\text{liq}} \)), and diamond (\( G_d \)) near our ambient temperature of processing. According to this free energy diagram, amorphous Q-carbon is formed at the highest undercooling \( T^* \), and diamond is nucleated at a slightly higher temperature (between \( T^* \) and \( T_{\text{dil}} \)).

### 2.2.1. Diamond and Graphite

Diamond is a metastable allotrope of carbon containing 100% sp\(^3\) bonding. In diamond, each carbon atom shares electrons forming four strong covalent bonds. This renders the structure of diamond to have a very high melting point (5000 K at 10 GPa), high hardness (115 GPa), and large thermal conductivity (2200 W/m.K). The structure of diamond is a face-centered cubic Bravais lattice (Fd-3m space group). The diamond lattice can be seen as two interpenetrating FCC lattices separated by \( \frac{1}{4} \) of the width of the unit cell in each dimension. The atomic packing factor of diamond is 0.34. This shows that the diamond structure is mostly empty and therefore novel materials can be synthesized which are densely packed by using non-equilibrium synthesis. In graphite which is a stable allotrope of carbon, each carbon atom forms three covalent bonds with the neighboring carbon atoms (100% sp\(^2\) bonding). Therefore, a free electron is present for
electrical conduction in the structure of graphite. The delocalized electrons cause large diamagnetism in graphite. In graphite, the hexagonal (planar) sheets are connected to each other by a weak van der Waals force. Since the layers can slide easily on each other, graphite is slippery in nature and is used as a lubricant. The crystal structure of graphite is hexagonal and has a P63mc space group. However, it should also be noted that the in-plane carbon-carbon bond length in graphite (0.142 nm) is less than that in diamond (0.154 nm). Therefore, a single layer of graphite (graphene) can have a higher hardness than diamond. The key properties of diamond, c-BN, and graphite are given in table 2.1.

**Table 2.1.** Key properties of diamond, c-BN, and graphite.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Diamond</th>
<th>c-BN</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>Cubic Fd3m</td>
<td>Cubic F43m</td>
<td>P63mc</td>
</tr>
<tr>
<td>Lattice parameters (nm)</td>
<td>0.356</td>
<td>0.361</td>
<td>a=b=0.247; c=0.679</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>3.51</td>
<td>3.48</td>
<td>2.26</td>
</tr>
<tr>
<td>Reactivity with ferrous materials</td>
<td>High</td>
<td>Inert</td>
<td>High</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>2.417</td>
<td>2.117</td>
<td>2.675</td>
</tr>
<tr>
<td>Breakdown voltage (V/cm)</td>
<td>10^7</td>
<td>10^7</td>
<td>0</td>
</tr>
<tr>
<td>Bandgap (eV)</td>
<td>5.5</td>
<td>6.3</td>
<td>-0.04</td>
</tr>
<tr>
<td>Thermal conductivity (W/m.K)</td>
<td>2200</td>
<td>1300</td>
<td>398 (xy plane); 2.2(z plane)</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>100 GPa</td>
<td>70 GPa</td>
<td>295x10^{-3}</td>
</tr>
<tr>
<td>Oxidation temperature (°C)</td>
<td>600</td>
<td>1200</td>
<td>600</td>
</tr>
<tr>
<td>Graphitization (°C)</td>
<td>900</td>
<td>1500</td>
<td>-</td>
</tr>
<tr>
<td>Johnson figure of merit (High-power device)</td>
<td>8200</td>
<td>8200</td>
<td>-</td>
</tr>
<tr>
<td>Keyes figure of merit (Integrated circuits)</td>
<td>32</td>
<td>32</td>
<td>-</td>
</tr>
</tbody>
</table>

**2.2.2. Q-Carbon**

Direct conversion of carbon into diamond at ambient pressures and lower temperatures is scientifically challenging with immense technological significance. Conversion of carbon, one of
the most abundant materials in the Earth’s crust, into most precious material diamond has been a cherished goal of the scientists all over the world for the longest time. Diamond is one of the most desirable materials with many applications ranging from abrasives, protective coatings and biomedical applications to superior diamond electronics, photonics and display devices. Conventional bulk processing involves high pressures and temperatures, and chemical vapor deposition for thin films requires high temperatures in the presence of hydrogen. These requirements lead to low production volumes and high costs. More recently, another approach for the formation of nanodiamond from SiC has been reported at temperatures ~1000°C under flowing hydrogen and chlorine gases at ambient pressures. In this thesis, we have shown that the direct conversion of carbon into diamond can occur in air at ambient temperatures and pressures without any need for catalysts and hydrogen to stabilize sp³ diamond bonding. In addition, ferromagnetism in bulk carbon represents another scientific challenge with profound impact on magnetic storage, sensors, data processing and biomedical applications. These two challenging problems are solved by the discovery of a new state of carbon, referred to as Q-carbon or Quenched-carbon. In addition, the Q-carbon exhibits enhanced electrical conductivity, enhanced field emission, and super high hardness. The Q-carbon is formed as a result of quenching of super undercooled liquid carbon at the atmospheric pressure, which is found to be magnetic and it plays a critical role in diamond formation. It has been conjectured that liquid carbon may exist as a thermodynamically stable phase at high pressures and temperatures near the cores of Uranus and Neptune planets and contribute to their magnetism. Thus, our finding can also explain ferromagnetism in our planetary system and formation of natural diamonds in some planets. According to the equilibrium (P vs T) phase diagram (figure 2.2(a)) graphite, diamond, liquid and vapor are thermodynamically stable forms of carbon. At low pressures, graphite converts into vapor above around 4000 K. According
to the phase diagram, diamond synthesis from liquid carbon will require even higher temperatures and pressures as the graphite/diamond/liquid carbon triple point occurs at 5000 K/12GPa. Currently, diamond powders are synthesized by graphite to diamond conversion at high pressures and temperatures. Graphite can be transformed into diamond above about 2000 K at 6-10 GPa using a liquid metal (iron) catalyst which is used for commercial synthesis of diamond. In the thermodynamically stable forms of carbon, graphite, diamond, liquid and vapor, we have introduced amorphous carbon with some $sp^3$ content and super undercooled state of liquid carbon (figure 2.2(a)). This can be accomplished by nanosecond laser melting of amorphous carbon, where undercooled state is at about 4000 K (undercooling of 1000 K). The dotted extension to 4000 K in the phase diagram from the liquid-diamond-graphite triple point at 5000 K represents this super undercooled state, which upon quenching results in the formation of Q-carbon at a temperature slightly lower than 4000 K. Since the molten state of carbon is found to be metallic, the carbon atoms can be fully packed with mass density and hardness exceeding those of diamond. By quenching this super undercooled state, we are able to form Q-carbon, from which nanodiamonds, microdiamonds, and thin films are formed depending upon allowed nucleation and growth times. The new state of carbon (Q-carbon) has a very high fraction of $sp^3$ bonded carbon (>75%) and the rest $sp^2$, and possess novel physical, chemical, mechanical and catalytic properties. There is a considerable reduction in volume, when as-deposited amorphous carbon is melted in the undercooled state and quenched as Q-carbon. The formation of cubic diamond phase can occur if a sufficient time is allowed for homogeneous nucleation from the Q-carbon. The primary focus of this research is on nanosecond laser melting of amorphous carbon films on sapphire substrates. The irradiation of these films with ArF Excimer laser pulses (wavelength 193 nm or photon energy of 6eV and pulse duration of 20 ns) leads to confinement of laser energy and selective melting of
amorphous carbon films. These undercooling values for amorphous carbon are considerably higher than those achieved during melting of crystalline carbon such as HOPG (highly oriented pyrolytic graphite) samples, which did not lead to diamond formation. Our results show that under nanosecond pulsed laser melting, amorphous carbon can lead to a highly undercooled state which can be quenched into Q-carbon from which nanodiamonds, microdiamonds and large-area single-crystal diamond thin films are formed. The Q-carbon exhibits novel properties, including room-temperature ferromagnetism (RTFM), extraordinary Hall effect, and electrochromic effect which are described in detail in this thesis.

2.3. Non-equilibrium Techniques

Non-equilibrium techniques are the key to the synthesis of novel phases. Pulsed laser annealing has been widely used to synthesize new phases and anneal displacement damages in ion-implanted semiconductors.\textsuperscript{7,8} In the case of pulsed laser melting of amorphous Si layers, it has been observed that there exist two distinct microstructures near the surface. The fine-grained polycrystallites of Si are found in the region of the maximum melt-front penetration during annealing. The size of the crystallites is dependent on the random nucleation and growth in the highly supercooled melt. In the region from the surface to the fine-grains, large polycrystals of Si are formed with solidification velocities ranging from 4-6 m/sec.\textsuperscript{9} It has also been observed that the dopant distribution in the fine and large polycrystalline regions is consistent with the diffusion in liquid Si. During the pulsed laser irradiation process, the temperature in the fine-polycrystalline region is raised to \(~ 1350 \text{ K}\) which is \(330 \text{ K}\) (undercooling) lower than the melting point of Si. As discussed above, the rate of nucleation is extremely large in the highly supercooled state. The heat released from the crystallization process raises the temperature of the component and it leads to a stable growth. The explosive recrystallization occurs in the localized regions where the
temperature is raised so that the crystallization front is sustained when heat is liberated. In the fine-
polycrystalline region, the solidification velocity is controlled by the low thermal conductivity of
the underlying amorphous layers. The thermal conductivity of the fine-polycrystalline region is
close to the crystalline Si value and therefore large polycrystallites of Si are formed on the fine-
polycrystalline structure. The fine-polycrystalline Si structures are formed by nucleation and
growth in the super undercooled phase. This is due to the reason that: (a) there exists a sharp
boundary (first-order phase transformation) between the fine-polycrystalline and amorphous
regions, (b) the phases formed after the pulsed laser annealing have distinct entropy, (c) the time
for solid-phase crystallization only results in the formation of 10 nm crystallites not the large
polycrystalline grains, (d) the thermodynamic solubility limits can be exceeded due to diffusion of
dopants in the liquid phase, and (e) preliminary \textit{in situ} reflectivity measurements suggest that the
crystallization is completed within times comparable to the pulse duration of the laser used. It has
also been observed that for higher pulsed laser energy density, the width of the fine-polycrystalline
region is considerably smaller than the large-polycrystalline region. The linear increase in width
of the large-polycrystalline region is due to reason that this region melts and recrystallizes by
interface-controlled crystallization. The velocity of the liquid-solid interface is determined by the
rate of heat extraction from the interface into the bulk crystal. The interface velocity ($V$) can
therefore be expressed by using the equation (2.13):

$$ V = \frac{k}{L \rho} \left( \frac{dT}{dz} \right)_1 \approx \frac{k}{L \rho} \frac{T_m}{\sqrt{2DT}} $$

where, $k$, $L$, and $\rho$ indicate thermal conductivity of solid Si near the interface at the melting
temperature ($T_m$), latent heat, and specific density, respectively. In pulsed laser annealing, the
melt-in time is considerably smaller than the solidification (growth) time. The depth of melting is
directly proportional to interface velocity times pulsed laser width. The texture of the recrystallized grains in the large-polycrystalline region was found to be $<110>$ which indicates the unseeded nature of crystallization. The bulk nucleation can also be promoted if there are microcrystallites present in as-implanted amorphous Si layers. Therefore, the pulsed laser annealing also removes ion-implantation damage by melting the entire damaged layer. In this case, the defect-free substrate acts as the seed for the crystal growth. Detailed theoretical and experimental analyses have been carried out regarding melting of graphite by using 30 ns ruby laser. The regrowth kinetics of graphite from liquid carbon was also analyzed. It was also found that larger graphite crystals are formed by increasing the laser energy density. In the case of graphite, the 2$s$ and 2$p$ electrons absorb the energy of the incident laser. The absorbed energy is transferred to the graphite lattice via electron-phonon scattering. This melts the graphite structure. The electronic contribution to the thermal conductivity dominates the heat transport through the molten carbon. In the previous studies, melting of graphite (100% $sp^2$) was only performed which do not have the necessary undercooling to form new phases of carbon. In the present study, we have performed pulsed laser annealing of amorphous carbon (mixture of $sp^2$ and $sp^3$) to cause sufficient values of undercooling ($\sim 1000$ K) to form a new phase of carbon (Q-carbon) and diamond.

2.4. Thin Film Epitaxy

Recently, there has been a tremendous increase in the research related to thin films which are used in multifunctional electronic devices. In these thin films, defects and interfaces play important roles in determining their physical properties. The next-generation solid-state devices use defect engineering, chemical diffusion, and exchange coupling at the interfaces to generate novel functionalities. The integration of various materials with existing complementary metal oxide semiconductors (CMOS) also necessitates a detailed knowledge regarding the thin film epitaxial
characteristics. The lattice misfit in these systems may range from 1-25% or higher. The strains developed in the heterostructures are due to: (a) lattice misfit, (b) thermal misfit, and (c) microstructural strains arising from dopants and defects. The term epitaxy refers to the formation of single-crystalline thin film on a substrate such that the thin film has a fixed orientation relationship w.r.t the substrate. In those cases, where the substrate and film have different crystal symmetries, there can be more than one orientation relationship of the thin film with the substrate. There can be homoepitaxy and heteroepitaxy. In the case of homoepitaxy, the same material is grown as a thin film on its substrate. In some metal oxide semiconductors, the growth of Si thin film on Si substrates by using vapor phase route is an example of homoepitaxy. In heteroepitaxy, different materials are epitaxially deposited onto dissimilar substrates (TiN thin films grown on Si substrates by using pulsed laser deposition). In the case of heteroepitaxy, strains can be developed in the heterostructures due to different lattice constants and thermal expansion coefficients (of the thin film and the substrate). According to the isotropic elastic theory, the in-plane stress ($\sigma_0$) generated by the lattice mismatch strain ($\varepsilon$) can be calculated by using the equation (2.14):

$$\sigma_0 = 2G\varepsilon \left(1 + \vartheta\right) / \left(1 - \vartheta\right)$$

(2.14)

where, $G$ and $\vartheta$ denote shear modulus and Poisson’s ratio, respectively. The lattice mismatch strain can be calculated by using the equation (2.15):

$$\varepsilon = (a_f - a_s) / a_s$$

(2.15)

where, $a_f$ and $a_s$ indicate film and substrate lattice constants, respectively. In a broader context, thin film epitaxy can be subdivided into lattice matching epitaxy and domain matching epitaxy which are explained below.
2.4.1. Lattice Matching Epitaxy

In lattice matching epitaxy (LME), there occurs one to one matching of lattice parameters of the thin film and the substrate. In the case of LME, the lattice relaxation occurs as a result of dislocations generation at the free surface of the thin film when the thin film grows beyond a critical thickness. At this point, the dislocations are generated at the free surface, which propagate to the interface via the lattice. Therefore, lattice frictional stresses play important roles to relax the thin films grown utilizing the LME approach. The critical resolved shear stress ($\sigma_{crss}$) is given by the relation: $\sigma_{crss} = (\sigma_{XX} = \sigma_{YY}) \times \cos \varphi \times \cos \theta$, where $\varphi$ and $\theta$ denote the angle between the applied stress and dislocation plane and angle between the applied stress and plane normal, respectively. In those cases, where $\sigma_{crss} = 0$, dislocations are not generated in the thin films and therefore they are not relaxed. This turns the thin films into polycrystalline. It should also be noted that the obstacles to the glide of dislocations (or high frictional stresses) result in high density of threading dislocations which is detrimental to electronic devices. The LME can handle lattice misfits up to 7%. Therefore, domain matching epitaxy comes into play for higher misfit systems, which is explained in detail below.

2.4.2. Domain Matching Epitaxy

The epitaxial growth of thin films, where the lattice misfit exceeds 7-8%, can be explained by domain matching epitaxy (DME) paradigm proposed by Narayan et al.\textsuperscript{11,12} In this theory, integral matching of lattice planes is considered, which could be different in different orientations at the thin film-substrate interface. The DME paradigm uses the concept of strain relaxations within a couple of monolayers and the dislocations are confined near the thin film-substrate interface. The rest of the film grows free of defects and lattice strains. Therefore, larger misfit systems are
preferred in DME thin film growth. In DME, the lattice misfit is accommodated by matching of integral multiples of lattice planes. Therefore, one extra half plane corresponding to each domain is found in DME. The size of the domain can also vary in a systematic way to accommodate the lattice misfit in DME. In DME, the initial lattice misfit strain is extremely large which results in matching of $m$ planes of film with $n$ planes of substrate so that the residual strain ($\varepsilon_r$) can be calculated by using the equation (2.16):

$$\varepsilon_r = \left(\frac{md_f}{nd_s} - 1\right)$$

(2.16)

A perfect matching occurs when $\varepsilon_r = 0$. If $\varepsilon_r$ is finite, then two domains may alternate with certain frequency ($\propto$) to cause the compete strain relation thereby favoring an epitaxial growth of thin films. The lattice relaxation then follows the equation (2.17):

$$(m+\propto)d_f = (n+\propto)d_s$$

(2.17)

Using the concept of DME, high-quality epitaxial heterostructures of TiN/Si(100), GaN/Si (111), and ZnO and III-nitrides on sapphire (0001) have been grown by using pulsed laser deposition.\textsuperscript{12} In the present research, DME paradigm is used to analyze the epitaxial nature of diamond and c-BN formed on sapphire (0001) by using the ultrafast pulsed laser annealing (figure 2.3). This also proves that DME is a versatile tool and can be used for various thin film processing techniques.

Figure 2.3. Diamond and cBN epitaxy on c-sapphire (0001).
The epitaxial relations and DME via matching of the planes are given below:

Epitaxial Relations:

<111> Diamond or cBN // <0001> Sapphire

<110> Diamond or cBN // <\overline{2}110> Sapphire

<112> Diamond or cBN // <10\overline{1}0> Sapphire

Domain Matching Epitaxy via Matching of Planes:

a) DME of <111> Diamond on <0001> Sapphire
   In plane: 19 (2d_{110}) Diamond = 20 (d_{\overline{2}110}) Sapphire

b) DME of <111> cBN on <0001> Sapphire
   In plane: 15 (2d_{110}) cBN = 16 (d_{\overline{2}110}) Sapphire

2.5. Bardeen-Cooper-Schrieffer (BCS) and Non-BCS Superconductivity

After the discovery of superconductivity (zero-resistance condition) in Hg (below 4.2 K) by K. Onnes in 1911 there had been a continuous improvement in the microscopic theory of superconductivity until BCS theory was formulated in 1957. Before the discovery of the BCS theory, Meissner and Ochsenfeld discovered a perfect diamagnetism below $T_c$ in superconductors in 1933. The BCS theory relies on the formation of Cooper pairs where the attractive interaction dominates over the Coulombic repulsion. The Cooper pair is an electron-electron bound pair mediated by phonons, and therefore electron-phonon coupling plays an important role in BCS superconductivity. To form the Cooper pairs, the energy difference between the electrons should be less than the phonon energy ($\hbar\omega$). The electrons forming the Cooper pair have opposite spin and momentum (therefore Cooper pairs are bosons and not fermions) and lower energy than the normal state. The BCS theory explains the second-order phase transition at the critical temperature, variation of electronic specific heat capacity near $T_c$, Meissner effect, infinite conductivity, and the
dependence of \( T_c \) on isotopic mass. According to this theory, the pairing of electrons occurs extremely close to the Fermi level (\( E_F \)), and therefore density of states near \( E_F \) plays an important role in the superconducting characteristics. The evidence for the small energy gap at the Fermi level can be explained by the Bose-Einstein condensation theory which also explains the drastic change in conductivity below \( T_c \). The band gap (\( E_g \)) predicted by the BCS theory is given by the equation (2.18):

\[
E_g = 3.5k_B T_c
\]  

(2.18)

There occurs a reduction in the energy gap as the critical temperature is approached in a superconductor due to the collective nature of the charge carriers (or Cooper pairs). This explains both the phonon-mediated interaction and the isotope effect in superconductors. The two characteristic lengths in a superconductor are the London penetration depth and the coherence length. The London penetration depth is related to the density of the superconducting electrons, and it is defined as the depth (from the surface) inside the superconducting material where the magnetic field exponentially decays to zero. Therefore, the London penetration depth is related to the Meissner effect which states that the magnetic field inside a superconductor (below \( T_c \)) is zero. The coherence length is related (directly proportional) to the Fermi velocity and (indirectly proportional to the) energy gap of the superconducting material. The superconducting electron density does not change quickly and therefore there is a minimum length beyond which the change occurs. There are two types of superconductors, namely type-I and type-II. In a type-I superconductor, the critical field abruptly falls to zero and the material attain a normal state. The type-II superconductors have a perfect diamagnetic response up to a certain critical magnetic field (lower critical field). Beyond the lower critical field, an inhomogeneous (mixed or vortex) state occurs where magnetic flux is present inside the superconductor. When the magnetic field is
further increased, there occurs an increase in the density of magnetic flux inside the superconductor. Beyond the upper critical field the material attains a normal state. The BCS theory fails to explain the high-temperature superconductivity which is observed in cuprates (YBCO, BSCCO, HBCCO, etc.). The attractive interaction ($V_{eff}$) present between the two electrons in a Cooper pair is given by using the equation (2.19):

\[
V_{eff} = \frac{|g_{eff}|^2}{(k_B T)^2 - \omega_D^2}
\]  

(2.19)

where, $g_{eff}$ and $\omega_D$ indicate the effective electron-phonon coupling vertex (probability of an electron emitting a virtual phonon and another electron absorbing it) and Debye frequency, respectively. Therefore, at low temperatures, an attractive interaction is present ($V_{eff}$ is negative) but turns into repulsive beyond the Debye temperature. Therefore, the BCS theory fails to explain the high-temperature superconductivity in the cuprates. It should also be noted that the Debye temperature for carbon (light-weight and strongly-bonded) is extremely high and therefore is an ideal candidate for high-temperature BCS superconductors. The Debye temperature of diamond is 2240 K as compared to 450 K in YBCO and 250 K in BSCCO. The superconductivity in non-BCS superconductors can be caused by magnons (as compared to phonons in BCS superconductors). Therefore, the BCS theory indicates that higher $T_c$ can be achieved by using materials having higher Debye temperature and by increasing the electron-phonon coupling and electronic density of states near the Fermi energy level.
2.6. References


3. Experimental Techniques

The thin film deposition technique employed in this thesis work was Pulsed Laser Deposition (PLD). The PLD was followed by Pulsed Laser Annealing (PLA), where the thin films were melted into a super undercooled state and subsequently quenched to form amorphous Q-carbon phase. By varying the degree of undercooling, Q-carbon (for highest undercooling) and diamond (for low undercooling) were synthesized by PLA. The major steps followed for the thesis work are as follows: (a) substrate preparation, (b) deposition of thin films (by PLD), (c) conversion (melting and subsequent quenching by PLA), and (d) analysis of the as-deposited and after PLA thin films. Each of the listed steps is explained in detail in the following sections.

3.1. Substrate Preparation

Sapphire (0001) substrates were used for thin film deposition by using PLD in this thesis work. The substrates were thoroughly cleaned before they were mounted inside the PLD vacuum chamber. The major steps followed for substrate cleaning are mentioned below:

- Substrates were cleaned in acetone vapor maintained at 200ºC for 5 minutes. This process removes organic wastes and dust (or debris) formed on c-sapphire substrates.
- Substrates were then ultrasonically cleaned in methanol for 10 minutes to remove the polar acetone and fine dust particulates.
- Substrates were blow-dried by using high purity nitrogen which cleans the methanol.
- After cleaning, the substrates were immediately loaded on the sample stage in the PLD vacuum chamber.
3.2. Pulsed Laser Deposition

PLD is a highly non-equilibrium technique, which is followed for thin film deposition onto various substrates. This process is a physical vapor deposition technique where the kinetic energy of the ablated species is much greater than in other thermal evaporation techniques. In the PLD technique, the material which is deposited onto substrates is referred to as target and is mounted on target carrousel system. The high energy nanosecond laser beams are focused on targets and an energetic plasma (ablated species) is formed. The forward-directed nature of the plume renders the PLD technique to be highly non-equilibrium. The ablated materials move perpendicular to the target substrate and therefore the substrates are mounted in front of the target. The plume containing ablated species falls on the substrates which can be heated using W filament heaters (temperatures are controlled by using an external voltage source). Excimer lasers having wavelengths 193 and 248 nm are generally used for the PLD processes. Figure 3.1 shows the PLD deposition technique which uses 248 nm excimer laser source. The laser beam is focused using a focusing lens on the target. The material used in laser window is fused silica which has a large optical band gap. The incident laser beam ablates the target material, which creates a plume thereby forming thin films on the substrate. The laser ablation of materials from the target starts when the laser fluence exceeds a minimum threshold value. This threshold value is determined by the laser parameters (wavelength and pulse width) and properties of the target materials (thermal diffusivity, reflectivity, and absorption coefficient). Therefore, an effective laser-material coupling is important for pulsed laser ablation of the target materials thereby forming high quality thin films on various substrates. The plasma temperatures can exceed $10^4$ K. The laser ablation process comprises of the following steps:

- Evaporation of the target materials by laser-material interaction.
• Interaction of the nanosecond laser with the evaporated material (until the end of the laser pulse), which forms a high-temperature isothermally expanding plasma.

• After the termination of the laser pulse, there occurs an anisotropic three-dimensional adiabatic expansion (forward-directed) of the plume.

The PLD is a highly non-equilibrium technique and there occurs a stoichiometric transfer of material from the target to the thin film. Therefore, PLD is a highly sought-after technique used to deposit multi-element complex materials (YBCO, BFO, LSMO, etc.). In contrast to the thermal evaporation technique where the kinetic energy of the ablated species is ~ 100 meV, PLD has highly energetic plume containing 10-100 eV species. PLD also has an excellent control of the film thickness where 1 pulsed laser shot is approximately equal to 1 Å. The important parameters used for PLD are laser wavelength, laser width, repetition rate of laser, energy density, spot size of laser, distance between target and substrate, background gas pressure, and substrate temperature. In this study, Lambda LPX 210 KrF and ArF nanosecond excimer lasers were used for PLD deposition processes. The laser and substrate parameters are given in the table 3.1 below:

**Table 3.1.** Laser and substrate parameters.

<table>
<thead>
<tr>
<th>Name</th>
<th>KrF</th>
<th>ArF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>248 nm</td>
<td>193 nm</td>
</tr>
<tr>
<td>Pulse width</td>
<td>25 ns</td>
<td>20 ns</td>
</tr>
<tr>
<td>Laser spot size</td>
<td>2 mm × 3 mm</td>
<td>2 mm × 3 mm</td>
</tr>
<tr>
<td>Pulse frequency</td>
<td>10 Hz</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Energy density</td>
<td>3-3.5 Jcm⁻²</td>
<td>3-3.5 Jcm⁻²</td>
</tr>
<tr>
<td>Target-substrate distance</td>
<td>4 cm</td>
<td>4 cm</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>30-300°C</td>
<td>30-300°C</td>
</tr>
</tbody>
</table>
The base pressure in the PLD chamber was $\sim 10^{-6}$ Torr prior to thin film deposition. This pressure is attained by using a roughing (Tri Scroll pump) and turbo molecular pump. On the other hand, laser MBE chamber which was used for NV-diamonds and c-BN formation was maintained at ultra-high vacuum conditions ($\sim 10^{-9}$ Torr) by using dry pump, turbo molecular pump, cryo pump, and ion pump. RF plasma of $\text{N}_2^+$ was also used during the formation of NV-diamonds in the laser MBE system which is shown in figure 3.2.
3.3. Pulsed Laser Annealing

Pulsed laser annealing (PLA) is a liquid-phase annealing/processing technique. Nanosecond excimer lasers are commonly used for PLA. In this process, a melt state of a material is formed which is subsequently quenched at an ultrafast rate. In the melt, defects lose their identity and it is a first-order phase transformation. The diffusivities are extremely high (10^4-10^5 cm^2/sec) in this process. The pulsed laser annealing is accomplished by illuminating the thin film with laser of appropriate wavelength, energy density, and pulse duration. Most of the laser light is absorbed in a thin surface layer in a few hundreds to angstroms deep into the solid. This produces high
temperature and melting which help to anneal out damage and zone refines the substrate. Laser annealing is carried out in air as the surface layer cools so rapidly (few hundreds of nano seconds) that the introduction of impurities from the atmosphere is minimized. The highly localized laser annealing process assists in the formation of patterned features onto the substrate, which have profound implications on device processing. The annealing process involves melting of the crystal in the near surface region, dopant diffusion in the molten state, and subsequently liquid phase epitaxial growth from the underlying substrate. A unique one-dimensional contraction or expansion of the lattice in the implanted region in a direction perpendicular to the surface (out of plane) is produced by laser annealing which indirectly helps the dopants to zone refine to the surface for certain impurities. Continuous wave (CW) or pulsed type lasers are commonly used for the laser annealing. The mechanism of annealing differs on the type of the laser used. Redistribution of dopants by laser annealing cannot be explained by diffusion in solid, as the time of diffusion is too short. The diffusion coefficients in liquid counterparts are much higher than its solid phase and thereby give a reasonable understanding of the dopant profile after laser annealing. It has been observed that there are significant modifications in the implanted region of Si lattice as a result of laser annealing. There occurs a substitution of the dopant atoms in the Si lattice sites. Ion back scattering and ion channeling techniques help to determine this lattice substitution.\textsuperscript{1,2} The lattice contraction (after substitution of lower atomic radii elements) and expansion can be measured by X-ray diffraction and ion channeling techniques. The lattice always expands or contracts 1D in out-of-plane conditions. High dopant concentrations can also cause a measurable strain in the substrate lattice. The time associated with laser annealing is too small to cause the formation of misfit dislocations which tend to relieve the strain and destroys the one-dimensional change of lattice parameter. The ease of transportation of dopants to surface after laser annealing
is dependent on the low dopant’s segregation coefficient in the substrate. During the process of solidification, the concentration of the dopant in the liquid increases until it exceeds that in solid. Since the surface is the last region to be solidified the dopant “swims up” and stays there, thereby forming interesting solid-state electronic devices.\(^3\)

Calculation of the threshold energy is crucial for this study, as it will determine the minimum laser energy needed for melting carbon. The threshold energy \(E_{th}\) required for melting can be calculated using the equation (3.1):\(^4\)

\[
E_{th} = \frac{K_s T_m \zeta^{0.5}}{(1-R_l) D^{0.5}}
\]

\(K_s\) = thermal conductivity

\(T_m\) = melting point

\(\zeta\) = pulsed laser width

\(R_l\) = reflectivity of the liquid

\(D\) = thermal diffusivity

The maximum molten depth of the material as a function of laser energy density (J/cm\(^2\)) can also be calculated. Two different pulse widths corresponding to 25 ns and 50 ns are commonly analyzed for a comparative study. The thickness of the melted regions varies linearly with the pulse energy density. The slopes of the curves are related to the sensitivity of the melt depth to the pulse energy density. The \(x\)-intercept measures the minimum energy required by the melt to propagate into the substrate, commonly referred to as \(E_{th}\). The threshold energy increases with the increase in pulse width. This is due to the reason that less heat is utilized in melting (and more heat is being conducted away) as the pulse duration increases. Variation of pulse duration affects the maximum melt depths (increasing the pulse duration decreases melt depth). So, the solidification velocities
considerably change as we change the pulse duration. The position of melt front at different laser pulse duration for a fixed laser energy density can also be calculated. The analyses indicate that the surface starts to melt slowly due to a sudden change in reflectivity during the phase transition. As the laser pulse terminates, the melt front recedes back to the surface. The initial stages of solidification see a low velocity but quickly reach the maximum when the steady state condition is achieved. With the increase in pulse duration the onset of melting decreases with a decrease in solidification velocity. The maximum melt depth decreases with the increase in pulse duration. The time for peak melt depth also increases with increase in the laser duration.

The maximum melt depth ($\Delta x$) is calculated by using equation (3.2):

$$\Delta x = C_1 (E - E_{th})$$  \hspace{1cm} (3.2)

where, the value of $C_1$ is calculated by using the equation (3.3):

$$C_1 = (1 - R_l)/(C_v T_m + L)$$  \hspace{1cm} (3.3)

where, $C_v$ is volume heat capacity, and $L$ is latent heat of fusion.

The melt in velocity ($v_{in}$) is expressed by using the equation (3.4):

$$v_{in} = \Delta T K_1/L \Delta x$$  \hspace{1cm} (3.4)

where, $\Delta T$ is the temperature difference between maximum temperature and melting point.

Again $\Delta T$ is calculated by the equation (3.5):

$$\Delta T = \frac{L C_1^2}{\kappa \iota \xi} (E - E_{th})^2$$  \hspace{1cm} (3.5)

To simulate the laser-material interactions, simulation of laser interaction with materials (SLIM) program was used. This program utilizes the concepts mentioned above to understand the non-equilibrium effects of high energy nanosecond laser pulses on various materials. The SLIM programming employs an accurate implicit finite difference scheme with varying spatial and
temporal node dimensions. This helps us to determine the time-dependent optical and thermal properties of the laser irradiated materials. The SLIM program takes into consideration the temperature-dependent optical and thermal properties of the material, profile of laser pulse, and formation and subsequent propagation of melt interfaces after laser irradiation. Multilayered structures can also be simulated by using the SLIM program. The major steps involved in PLA are: (a) absorption and rapid surface heating, (b) evaporation, (c) melting, and (d) solidification. In the present case, melting and subsequent quenching of the undercooled molten state of carbon cause the formation of Q-carbon and diamond. Figure 3.3 indicates the steps of PLA where the formation of quenched phases occurs after melting and subsequent quenching process.

![Diagram showing PLA steps](image.png)

**Figure 3.3.** Different steps of pulsed laser annealing showing (a) starting material, (b) melting, and (c) solidification.

### 3.4. Raman Spectroscopy

Raman spectroscopy detects and quantifies vibrational motions also referred to as vibrational modes (which are characteristics of a molecule) in a way similar to the infrared spectroscopy. The observation of these vibrations is however distinctly different from infrared spectroscopy. A Raman spectrometer measures and quantifies the scattered light, whereas the infrared spectroscopy deals with the absorption of photons. This spectacular discovery was made by the eminent Indian
physicist, Sir Chandrasekhara Venkata Raman and Kariamanikkam Srinivasa Krishnan in the year 1928. Interestingly, halfway around the world, similar phenomena was also reported by Russian physicists, Grigory Landsberg and Leonid Mandelstam. This breakthrough discovery revolutionized materials characterization and C. V. Raman was awarded the Nobel Prize in Physics in the year 1930. The feeble Raman signals thwarted Raman spectroscopy for quite a long time until the discovery of laser sources (in 1960’s) and high-end detectors which helped to rejuvenate the applications of this versatile material characterization technique.

When a monochromatic radiation of frequency $\omega_1$ is incident on a material, there occurs scattering of the incident radiation (figure 3.4). When the frequency content of the scattered wave is analyzed it is found that in addition to $\omega_1$ frequency it also contains $\omega_1 \pm \omega_M$ frequencies. In molecular systems, $\omega_M$ frequencies are found to be associated with rotational, vibrational, and electronic levels. The polarization characteristics of the scattered radiation are also different from the incident wave. The scattering is found to occur in all the directions and the intensity and polarization of the scattered wave are dependent on the direction of observation. The Raleigh scattering is an elastic scattering where there is no change in the frequency (i.e. $\omega_M = 0$) of the scattered radiation. In the spectrum of scattered radiation, the new frequencies (wavenumber) are referred to as Raman lines and the corresponding vibrational modes as Raman-active modes. Raman bands for frequencies less than the incident frequency ($\omega_1 - \omega_M$) are termed as Stokes bands, whereas those having higher frequencies ($\omega_1 + \omega_M$) are termed as anti-Stokes bands. In our Raman discussion all the scatterings are corresponding to the Stokes scattering. It is well known that with the incidence of electromagnetic radiation on a Raman-active material there occurs an induced dipole moment ($\mu$) which is governed by the equation (3.6):

$$\mu = \alpha E$$  \hspace{1cm} (3.6)
where, $\alpha$ and $E$ denote polarizability and electric field of the incident monochromatic radiation, respectively. Considering the Raleigh, Stokes, and anti-Stokes scattering we can develop the equation (3.6) to equation (3.7) shown below:

$$\mu = \alpha_{q=0}E_0 \cos2\pi\omega_1 t + \frac{1}{2} \frac{\partial \alpha}{\partial q_{q=0}} q_0 E_0 \left[ \cos2\pi(\omega_1 - \omega_M) t + \cos2\pi(\omega_1 + \omega_M) t \right] (3.7)$$

In the above equation (3.7), the first term denotes the Raleigh scattering whereas the second and third terms indicate Stokes and anti-Stokes scattering, respectively. Therefore, the material will be Raman inactive when $\frac{\partial \alpha}{\partial q_{q=0}} = 0$ i.e. when the polarizability derivative at the equilibrium position is 0. The electronic Raman spectroscopy which is performed close to the Raleigh scattering line gives an indication of the acceptor states (and energy levels) present in a heavily doped material.

The Raman scattering can be explained by both classical and quantum concepts of physics. Let us consider a molecule without a permanent dipole moment. An oscillating external electric field (laser source) can induce a dipole moment, also referred to as the polarizability of the molecule. According to the Raleigh scattering, there occurs emission of light with an equal frequency to that of the incident light wave. In addition to that, the molecule also emits two frequencies of light that are characteristics to the molecule and are phase-shifted with respect to the incident light wave. These scatterings are referred to as Stokes Raman scattering (scattered light having a lower frequency) and Anti-Stokes Raman scattering (scattered light having a higher frequency). The quantum theory illustrates the need of “virtual states” in a light wave absorbing molecule along with the Eigen states. These “virtual states” lie in-between the electronic excitation states. Upon excitation by an incident photon, the electrons are excited to these states. Thereby there occurs an emission of photon of equal energy (Raleigh scattering), less energy (Stokes scattering), and higher energy (Anti-Stokes scattering). However, at this point of time it should be recollected that the number of photons scattered is innumerably small (one in $10^3$ or $10^4$ photons). So, Raman
spectrometers are equipped with band-pass and edge filters to eliminate the Raleigh scattering thereby enhancing the weak Raman signals. The Stokes scattering is more intense than its Anti Stokes counterpart, and is collected as the Raman signal. The intensity of Raman scattering is also dependent on the scattering cross-section of a molecule, which in turn depends on the molecule’s polarizability. Therefore, the intensity of Raman signals is quite different for different molecules.

![Energy level diagram showing Raleigh, Stokes, and anti-Stokes Raman scatterings.](image)

**Figure 3.4.** Energy level diagram showing Raleigh, Stokes, and anti-Stokes Raman scatterings.

For the present research work, a solid-state laser (laser excitation wavelength = 532 nm) was being used as the excitation source. The confocal Raman microscopy (WITec Alpha 300 R) was used for the thesis work. This is a non-destructive technique having a lateral resolution ~ 200 nm and spectral resolution ~ 0.1 relative wavenumber. The sample was mounted on a motorized stage to facilitate easy acquisition of Raman signals from various parts of the sample. The laser light is reflected back to the monochromator and interferometer in a perfect 180\(^\circ\) scattering geometry. A 600 mm diffraction grating was used to provide better resolution of the collected Raman spectrum. A standard Si sample was used to calibrate the laser line before the start of acquisition. Si has a strong characteristic peak at 520.6 cm\(^{-1}\) which helps to align the spectrometer. Several acquisitions
were done and averaged out before the final spectra were acquired. Peak fittings were also employed to determine the vibrational modes present in the sample and were correlated with other structural experiments.

**3.5. Electron Microscopy**

Richard Feynman’s notable lecture entitled as “There’s Plenty of Room at the Bottom” on December 29th, 1959 at Caltech was the starting point of nanotechnology. From that time onwards there has been tremendous progress in electron microscopy which uses electrons to image materials. Microscopes can be classified as optical, electron or ion, and scanning probe. Optical microscopes use visible light and transparent lenses to magnify and image various materials for medical and engineering purposes. Electron microscopes use a beam of charged particles (electrons) and electromagnetic lenses to focus the electrons on various samples. Scanning probe microscopes use a physical pointed probe which can scan over the sample to image the forces and interactions (with the tip). After the discovery of wave-and particle-like properties of electrons in the year 1920, the field of electron microscopy evolved rapidly. Ernst Ruska was awarded the Nobel Prize for Physics on the year 1931 owing to the discovery of transmission electron microscope. The two types of electron microscopy are discussed below.

**3.5.1. Scanning Electron Microscopy (SEM)**

A scanning electron microscope (SEM) utilizes an electron beam to scan a material’s surface. After the electrons are generated from an electron source, they pass through electromagnetic lenses and scan and stigmator coils before they strike the surface of the material. There are no lenses below the sample which is thick in this case. Ultra-high vacuum conditions are achieved in the SEM chamber by using roughing and turbomolecular pump. The focused fine spot in SEM can be as
small as 1 nm (in diameter). The beam is scanned in a rectangular fashion. The secondary electrons are used for imaging in the SEM technique. In the present research, FEI Verios 460L was used for performing SEM on various samples. In this SEM, Everhart-Thornley low-energy detector is used for high-resolution imaging. An electron accelerating potential of 30 keV and beam current 4 nA were used during the image acquisitions. The resolution (for secondary electrons) in SEM is ~ 0.6 nm. The working distance was maintained to be less than 4 mm. When the substrates were insulating, proper care was taken to electrically ground the samples to avoid electrical charging effects during image acquisitions.

3.5.2. Transmission Electron Microscopy (TEM)

The TEM uses high-speed electrons to image electron transparent materials. The wavelength of electrons (at 200 keV) is 2.51 pm and are used for the TEM imaging purpose. The TEM helps to acquire atomic scale details of materials and interfaces, various crystalline defects, and grain boundaries. Therefore, in the present study, TEM analyses were critical in determining misfit dislocations and twinning in various crystalline materials. To determine the long-range and short-range ordering, selected area electron diffractions (SAED) were carried out. The in-plane epitaxial relations were also calculated by using the SAED patterns. The amplitude and phase contrast modes can be used during TEM. The contrast arises in TEM due to the scattering of incident beam by the material. There also occurs a change in the amplitude of the electrons after it passes through the material. Two types of amplitude contrast are: mass-thickness and diffraction. For the case of amorphous materials, mass-thickness contrast is important as there occurs an incoherent elastic scattering of electrons. The diffraction contrast occurs due to the coherent elastic scattering of electrons by the material. Bright- and dark-field images were formed from the direct beam and diffracted beam, respectively. The nature of the dislocations can be identified from the bright- and
dark-field images. The high-resolution TEM images are formed by phase contrast of the electrons (change in phase before and after scattering from the material). Phase-contrast images utilize more than one electron beam. The objective astigmatism was minimized before acquiring the atomic-resolution TEM images. A conventional STEM-JEOL 2000 FX was used for acquiring BF, DF images, and SAED patterns. The electron source which was used in the 2000 FX microscope was LaB6. The microscope was operated at 200 kV. The point and lattice resolutions were 0.28 and 0.14 nm, respectively. The SAED patterns were acquired by using 10-40 nm apertures. The high-resolution TEM imaging was performed in JEOL 2010F microscope where EELS and SAED detector were also attached for parallel acquisition using Gatan microscopy suite software. This microscope is equipped with a field emission electron gun which generates a highly coherent electron beam. An aberration corrected STEM-FEI Titan 80-300 microscope was used for STEM imaging of thin cross-sectional TEM samples. The monochromator makes the energy resolution of the electron source to be as low as 0.2 eV which also allows atomic-resolution EELS. The superX energy dispersive spectrometer (which uses Si drift detector) was used to acquired EDX spectra of various samples. The TEM samples were prepared by using the focused ion beam (FIB) technique in FEI Quanta 3D FEG. In this technique, the samples were mounted on an eucentric tilt holder (at 52°) and Ga ions are used for the material sputtering purposes. The samples were thinned down to less than 100 nm for high-resolution TEM and EELS acquisitions. We have also used mechanical grinding, dimpling, and ion milling methods for preparing high-quality TEM samples.


EELS is a versatile analytical technique which is based on inelastic scattering of highly energetic electrons in thin TEM samples. There occurs a broad range of inelastic interactions of electrons with a material ranging from phonon interactions to ionization process. EELS can be used to map
the elemental composition, and physical and chemical properties of various electron insensitive materials. In the EELS technique, after the inelastic interaction of electrons with the atomic electrons (of the material), the electron beam loses its energy and is bent through a small angle (5-100 milliradians). Therefore, the energy distribution of all the inelastically scattered electrons gives information about the local environment of the atomic electrons, which can be correlated to physical and chemical properties of the material. In an EEL spectrum, the first most intense peak is called as the zero-loss peak which represents unscattered (transmitted) and elastically scattered electrons through the thin sample. The zero-loss peak is used to calibrate the energy scale and its width is related to the energy resolution of the system. The low-loss region in an EEL spectrum provides valuable information pertaining to the band structure, dielectric properties, surface plasmons, etc. At higher energy losses (core-loss region), the EEL spectrum shows characteristic ionization edges which illustrate various antibonding electronic states present in a material. These edges are formed when an inner shell electron absorbs enough energy from the electron beam to be excited into energy states above the Fermi level. The ionization edges are used for quantitative analysis of atomic % and determination of crystal structure (amorphous or crystalline) of a material. The EELS spectrometer consists of a magnetic prism and detector. The magnetic prism is used to create a magnetic field perpendicular to the traveling direction of the electrons. The magnetic prism is designed so that the electrons only travel a quarter of a circle and then is captured by the detector. The electrons which have lost energy due to the inelastic scattering, bend in a circular path having small radius. The EELS detector can measure distribution of energy-loss of electrons and therefore the name of technique is electron energy-loss spectroscopy. The probability \( P_k \) that an electron will be observed in the core-loss spectrum is directly proportional to the areal density of atoms \( N \) of that element and is given by the following equation (3.8):
\[ P_k = N \sigma_k = \frac{l_k}{l_t} \]  

(3.8)

where, \( \sigma_k \), \( l_k \), and \( l_t \) denote constant of proportionality, extracted edge count, and total number of counts in the EEL spectrum, respectively. Therefore, plural scattering plays an important role in EELS quantification. But in most of the cases when the sample thickness is low enough, we can consider the plural scattering to be negligible. In general, higher atomic number and thick samples have considerable plural scattering which should be accounted for during the EELS quantification routine. In many cases, it may not be always possible to acquire low-loss spectrum with each core-loss spectrum. In these cases, relative EELS quantification is always possible after a careful background correction. The atomic ratio of species A and B can be calculated by using the equation (3.9):

\[ \frac{N_A}{N_B} \approx \frac{\text{conc } A}{\text{conc } B} \approx \frac{l_A \sigma_B}{l_B \sigma_A} \]  

(3.9)

In the above equation (3.9), the zero-loss integral divides out and the concentration can be calculated considering the same width of the signal window for the elements. This cancels out the effect of plural scattering. In the present work, EELS connected to HRTEM JEOL 2010F and STEM-FEI Titan 80-300 were used to quantify the atomic% of elements present in the material. The characteristic antibonding states (for diamond and Q-carbon) were also determined by using the above instruments. The monochromator used in FEI Titan microscope makes the energy resolution in EELS to be 0.2 eV, whereas the (EELS) energy resolution is ~ 1 eV in JEOL 2010F.

### 3.7. Magnetic Measurements

The magnetic measurements were carried out in a superconducting quantum interference device (SQUID) MPMS3 instrument. The SQUID is a highly sensitive magnetometer which can precisely
measure extremely small magnetic moments (or magnetic field changes). It is based on Josephson junctions (figure 3.5) which were experimentally realized in 1963. In rf-SQUID, the superconducting ring is interrupted at one point whereas in dc-SQUID the superconducting ring is interrupted at two points (by an electrically insulating material). The thickness of the insulating material is enough to cause a quantum tunneling of Cooper pairs (below the superconducting transition temperature).

Figure 3.5. SQUID magnetometer showing the Josephson junction.

When there occurs a change in an external magnetic field, an electrical current is generated in the ring, which causes a change in the magnetic flux associated with the ring. The magnitude of the magnetic flux generated is a multiple of the magnetic flux quantum (2.07×10⁻¹⁵ Tm²). In dc-SQUID, two Josephson junctions are used. When the direct current flows in the ring, there occur a measurable electrical voltage. In SQUID device, a constant biasing current is maintained. Therefore, with a slight change in the magnetic flux, the measured voltages at the Josephson junctions change. The evaluation of voltage-flux curve allows to resolve extremely small magnetic fields (~10⁻¹⁸ T). The superconducting ring is Nb-based, therefore it needs a permanent cooling by
liquid He (since the critical temperature of Nb is ~ 9.5 K). The MPMS3 measurement system is an ultra-sensitive magnetometer having ~10^-8 emu sensitivity. Both the DC scan mode and VSM mode were used during the data acquisitions. The operating temperature range is from 1.8 K to 400 K, although we have used temperatures ranging from 5-300 K in our measurements. The temperature stability and field uniformity in MPMS3 are +/- 0.5% and 0.01% over 4 cm, respectively. We have performed detailed temperature-dependent magnetic moment and field and time-dependent magnetic moment measurements for various samples mounted parallel as well as perpendicular to the magnetic field in SQUID MPMS3 measurement unit.

3.8. Electrical Measurements

A PPMS MultiVu instrument was used to measure the electrical properties of thin films. This instrument utilizes a closed-cycle He refrigerator setup and highly sensitive temperature probes therefore enabling an accurate measurement of resistivity in thin films and bulk samples. In this research, four-probe resistivity technique was used to measure electrical resistivity of various samples. In the four-probe technique, two probes are used to apply a current and the other two probes are used to measure the voltage drop. The separation of current and voltage leads eliminates the lead and contact resistances in this technique. Therefore, accurate resistivity measurements can be performed at low temperatures and at different magnetic fields. For thin films, when the spacing between the probes are much greater than the film thickness (t), the current profile from the probes can be considered to be rings. The resistivity can therefore be calculated by using the equation (3.10):

\[ \rho = \frac{\pi t V}{(\ln 2) \times I} \quad (3.10) \]
where, \( V \) and \( I \) are the measured voltage drop and applied current, respectively. Indium pads were used to make electrical contacts with the films, and gold wires were attached to the Indium contacts for electrical measurements. The van der Pauw configuration was used for electrical measurements where we can find the values of resistances (\( R_A \) and \( R_B \)) by using two different channels on the PPMS sample puck. The sheet resistances (\( R_S \)) were calculated by using the equation (3.11):

\[
e^{-\pi R_A/R_S} + e^{-\pi R_B/R_S} = 1
\]  

(3.11)

For magnetic field-dependent resistivity measurements, utmost care should be taken to remove any trapped magnetic field in the coils before cooling down the sample. Since the magnetic field, current, and voltages are all mutually perpendicular to each other temperature-dependent Hall measurements were also carried out by using the PPMS setup. From the Hall equation (3.12):

\[
V_H = \frac{BI_{net}}{n_e}
\]  

(3.12)

the Hall voltages (\( V_H \)) can be calculated after a current is applied in the sample in a fixed magnetic field (\( B \)). The value of Hall constant (\( =1/ne \)) can also be found out from the slope of \( V_H \) vs \( I \) plots. Again, the charge carrier mobility (\( \mu \)) can be calculated by using the equation (3.13):

\[
\mu = \frac{\sigma}{ne}
\]  

(3.13)

We have also used the Ecopia HMS 3000 Hall measurement setup to measure concentration and Hall mobility of charge carriers in thin films at 300 K. This setup can only accommodate 0.5 and 1.0 T magnets. A 5-probe electrical measurement was carried out to determine the extraordinary Hall coefficient values in Q-carbon thin films. This was done to measure accurately the Hall voltages which should be perfectly perpendicular to the bias field. If the perpendicular component
is not calculated, the Hall voltage will include some resistive part and therefore the Hall voltages measurements will not be accurate (shown in figure 3.6(a)). Figure 3.6(b) shows the offset nulling by using the 5-probe electrical measurements. When the magnetic field is turned off, a potentiometer between the 4\textsuperscript{th} and 5\textsuperscript{th} lead was used to null the offset that was created due to sample resistance. We have also employed Keithley 2400 series sourcemeter and customized LabView programming to automate the measurement sequence for I-V diodes.

![Figure 3.6. (a) Four-wire and (d) offset nulling Five-wire Hall measurements.](image)

### 3.9. Electron Backscatter Diffraction (EBSD)

The electron backscatter diffraction technique helps us to identify grain orientations, local texture, and phase identifications of crystalline materials. The EBSD detector is generally mounted in a SEM chamber and is therefore an additional characterizing technique which is versatile in nature due to minimum sample preparation. The high-speed data acquisition on a submicron scale, high spatial resolution, and orientation correlations render the EBSD technique ideal for various materials. The first observation of crystal diffraction patterns (Kikuchi lines) in the backscatter mode was reported by Nishikawa and Kikuchi in 1928. In the current technology, EBSD patterns
are generated on a phosphor screen (mounted on the EBSD detector) by backscatter diffraction of stationary beam of high energy electrons emanating from a crystalline material which is mounted 70° to the electron gun. The characteristic feature of the Kikuchi pattern which is observed in EBSD is the regular arrangement of parallel bands. In SAED mode (in TEM) an array of diffraction spots is seen from a single-crystal material. It should also be noted that the intersection of Kikuchi lines forms prominent and distinct zone axis. Therefore, Kikuchi bands provide important information regarding the crystallinity and orientation of a material.

**Figure 3.7.** Schematics of EBSD arrangement.

In EBSD, there occurs a gnomonic projection of a crystal lattice on a flat phosphor detector (shown in figure 3.7). The center of the projection is the point of impingement of the primary electron beam which is the center of the EBSD pattern. Therefore, the center of the EBSD pattern (observed on the detector) is not always the center of the Kikuchi diffraction pattern that we observe on the EBSD detector. Figure 3.7 also shows the two diffracting cones from a particular plane which
gives rise to two Kikuchi lines. The width of the Kikuchi bands is also related to the interplanar spacing \(d_{hkl}\) by the equation (3.14):

\[
2d_{hkl} \sin \theta = n \lambda
\]  

(3.14)

where, \(\theta\), \(n\), and \(\lambda\) denote Bragg angle, order of reflection, and wavelength of the incident electron beam (which depends on the accelerating voltage in SEM), respectively. A decrease in the accelerating voltage causes an increase in the electron wavelength and therefore an increase in the width of the Kikuchi bands. Therefore, during the phase determination in EBSD, proper calibration of the accelerating voltages with the width of the Kikuchi bands should be performed. The indexing of the Kikuchi bands is the most important step for a successful interpretation of phase and crystalline orientation. The bands formed on the EBSD detector are sorted according to their intensities and widths. The indexing is based on the comparison between the measured interplanar angles (angles between the Kikuchi bands) and interplanar spacings (Kikuchi band widths) which are derived from the theoretical values. Computer programs are used to cross-correlate between the experimental and theoretical values. For a successful index solving, 3 to 4 families of \{hkl\} planes are considered. The large angular range of backscatter Kikuchi pattern in EBSD assists in correct indexing. Reference directions in the specimen space (e.g. normal and transverse directions) are indexed after the computer simulations. This helps us to determine the grain orientation described in \(hkl\)[uvw], Euler angles (\(\phi_1\), \(\Phi\), \(\phi_2\)), and rotation matrix (\(g\)). It should also be remembered that a correct background spectrum (showing no Kikuchi pattern) should be acquired prior to Kikuchi band analysis. The algorithm used to index planes in EBSD follows the method of “Class Indexing” based on refined accuracy which examines the permutation of four bands. It measures the coherence of the Kikuchi bands w.r.t standard crystal structures. Then the solutions are broken into smaller blocks which facilitate better analysis of the Kikuchi patterns.
This algorithm solves various issues regarding grain boundary resolution, distinguishing similar crystal structures (e.g. Pt and Ni), highest orientation precision, and pseudo symmetry. Dynamical simulations of the EBSD pattern were also carried out in the present research work. According to this model, the observed EBSD patterns are a superposition of diffraction patterns from electrons having a fixed energy. The observed intensity ($I_B$) of the Kikuchi bands can therefore be expressed mathematically by using the equation (3.15):

$$ I_B \approx \int_0^{E_p} dE \int_0^{t_{\text{max}}} dt \, D [n_B(\theta, \phi, \theta_{\text{in}}, \phi_{\text{in}}, E, t)] $$

(3.15)

where, $D$ denotes the diffraction process of electrons at energy $E$. The distribution of inelastically scattered electrons is given by $n_B(\theta, \phi, \theta_{\text{in}}, \phi_{\text{in}}, E, t)$ which is calculated by using the Monte Carlo simulations, where $t$, $\theta$, and $\theta_{\text{in}}$ denote sample depth, direction of the scattered and incident beam, respectively. The goodness of fit in a EBSD indexed pattern is found by the mean angular deviation (MAD) number. The solution with lowest MAD value is chosen to be the correct one. Therefore, MAD values close to 0.10° are chosen for identifying the correct phase and orientation of a material analyzed by EBSD technique. Therefore, EBSD Kikuchi patterns can also provide important information regarding twinning in crystal structures, which is discussed in detail on Chapter 10.

In the present work, NordlysNano EBSD detector mounted in FEI Quanta 3D FEG was used to acquire the EBSD patterns. The EBSD detector has a customized optics design facilitating a high throughput to the sensor. In addition, the sensor has high quantum efficiency to analyze samples (nano- and microstructured) at low beam currents. The EBSD has CCD detector and the processing times during data acquisition are not as fast as the MOSFET detector which is used in the EBSD detector mounted in the FEI Verios 460 L microscope. The AZtec software was used to analyze the EBSD patterns. The samples were tilted at an angle of 70° w.r.t the electron gun and an
accelerating voltage of 20 kV and 4 nA beam current were used during the EBSD Kikuchi pattern acquisitions.

3.10. X-Ray Diffraction (XRD)

X-ray diffraction is a non-destructive technique employed to determine the crystal structure, phase, crystallographic orientation (out-of-plane), and lattice parameter (from interplanar spacing) of a material. The X-rays from Cu metal target having a wavelength of 0.154 nm (Cu Kα radiation) are generally used for XRD. X-rays are produced when high-speed electrons collide with a metal target. In most of the cases, W filament acts as the source of the electrons (cathode) which strike onto water-cooled Cu anode. In this work, θ–2θ scans were performed by using the Rigaku D-MAX/A diffractometer with Cu-Kα radiation. The conditions for crystal diffractions are governed by the Bragg’s law (equation (3.14)). Sir William Henry Bragg and his son William Lawrence Bragg were awarded the Nobel prize in physics in 1915 for determining the crystal structures of NaCl, ZnS, and diamond. In the present research, θ-2θ scans were performed by using Rigaku D-MAX/A diffractometer. The instrument employs a two-circle diffractometer where the sample rotates along one axis (θ) and the detector around an independent axis (2θ). This geometry is adopted to facilitate the condition that the diffracted beam always lies in the plane containing the incident beam and the plane normal. The sample is only restricted to rotate along one axis, therefore XRD gives only out-of-plane orientation conditions. The in-plane epitaxial conditions can be obtained by using the φ scans. Since in the present work, crystalline diamonds are grown by using the PLA process, we have discussed in detail below about the diffracting planes observed in diamond. The structure factor (F) in diamond can be calculated by using the equation (3.16):

\[
F = \sum_j f_j e^{-2\pi i (h u_j + k v_j + l w_j)}
\]  

(3.16)
where, \( f_j \) indicates the atomic scattering factor. Considering the values of \((u_j, v_j, w_j)\) as \((0, 0, 0)\), \((\frac{1}{2}, \frac{1}{2}, 0)\), \((\frac{1}{2}, 0, \frac{1}{2})\), \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\), \((\frac{1}{4}, \frac{3}{4}, \frac{3}{4})\), \((\frac{3}{4}, \frac{1}{4}, \frac{3}{4})\), and \((\frac{3}{4}, \frac{3}{4}, \frac{1}{4})\) the structure factor in diamond can be calculated to be:

\[
F(h, k, l) = f \left[ 1 + e^{-\frac{i\pi}{2}(h+k+l)} \right] \left[ 1 + e^{-i\pi h} + e^{-i\pi k} + e^{-i\pi l} \right] \quad (3.17)
\]

Therefore, it can be seen from the equation (3.17) that the structure factor is zero when \(h, k, l\) are mixed and \(h+k+l=2n(n+1)\), where \(n\) is an integer. Therefore, in XRD, (200), (222), etc. peaks are not observed. However, it should be noted that in selected area electron diffraction, (200) ring can be observed due to the double electron diffraction from (1-11) and (11-1) planes.

3.11. Photoluminescence Spectroscopy (PL)

When a material is irradiated with low wavelength photons, the electrons are excited from the ground state to higher energy levels. There can be radiative recombinations of the excited electrons from the higher energy states to lower energy states. This emanates a photon of characteristic wavelength from the material which is detected by a highly sensitive spectrometer in the PL spectroscopy. Therefore, PL is a process in which a material absorbs photons and re-radiates photons having characteristic wavelength, and therefore is a versatile technique to identify various materials. Photoluminescence implies both fluorescence and phosphorescence. In the case of fluorescence, the electrons are excited from ground state to singlet state, whereas in the case of phosphorescence the electrons are excited to triplet state. The various types of spectral acquisitions are discussed below:
• Photoluminescence spectrum: A specific wavelength of light is used to illuminate the sample and the variation of PL intensity as a function of wavelength is acquired. This helps us to gather the information about radiative transitions in a material.

• Photoluminescence excitation spectrum: This spectrum contains valuable information about the energy transformation among various energy levels in a material. In this technique, intensity of specific luminescence wavelength as a function of the wavelength of the incident electromagnetic wave is recorded.

• Time-resolved photoluminescence spectroscopy: This technique is used to determine the decay times of optically active centers in diamond. The sampling of PL intensity decay is performed after the pump pulse of PL excitation for a very short time. However, it should also be noted that the short and intense laser pump cause various non-linear effects which should be accounted for during the decay life calculations. From the decay time measurements, we have calculated the quantum efficiency of various optoelectronic devices.

A Horiba Labram Aramis system utilizing a HeCd laser as the excitation source (325 nm) was used for the room-temperature PL measurements. In the experimental setup, the samples were illuminated from top and the PL signal was transferred through a photomultiplier tube (PMT) to the spectrometer. The spectral acquisitions were performed by using LabSpec software which is connected to the PL system. For the low-temperature PL acquisitions using 532 nm excitation, the samples were mounted in a cryogenic chamber and the PL signals were acquired via a monochromator and PMT. To perform the time-resolved PL measurements we have used a 415 nm 250 KHz 200 femtosecond laser pump and customized LabView programming to capture the decay characteristics.
3.12. Absorption Spectroscopy

There occurs a transmission, reflection, and absorption of light waves when they are incident on a material. The absorption of the electromagnetic wave occurs due to the transition of electrons from ground state to higher energy levels. Absorption coefficient ($\alpha$) of a material determines the change in intensity of the light beam per unit length when the light beam passes through the material. The final intensity of the light wave ($I(\lambda)$) emanating from the material can be expressed by the Beer-Lambert’s law (equation (3.18)):

$$I(\lambda) = I_o(\lambda)e^{-\alpha t}$$ (3.18)

![Image](image.png)

**Figure 3.8.** Electric-field dependent UV-vis spectroscopy.

The main principle of ultraviolet-visible absorption spectroscopy is governed by the above equation (3.19). The molecules having non-bonding electrons can absorb energy from the UV or visible light and the electrons can be excited to anti-bonding molecular orbitals. The molecules in which the electrons can be excited very easily can absorb longer wavelength of light. The
electronic transitions can be from $\sigma$, $\pi$, and $n$ states to $\pi^*$ and $\sigma^*$ states. The absorption coefficient of a material is also related to extinction coefficient which is the imaginary part of the index of refraction. Therefore, optical characteristics of a material can be obtained from UV-vis spectroscopy in transmission or reflection mode.

In the present research, a Hitachi U3031 UV-visible spectrometer was used for performing the absorption measurements. This spectrometer uses two continuous light sources (tungsten and deuterium lamps) to cover the entire UV-visible spectrum. The tungsten bulb covers the range from 320-1000 nm whereas deuterium covers 200-320 nm spectrum. The light from the sources is transmitted to reference and sample via a monochromator. The transmittance signal is captured in a detector which is a photomultiplier tube. The data was collected by using the Spectra suite software. Proper background (dark) corrections were carried out prior to the data acquisitions. For electrochromic measurements, the sample arrangement is shown in figure 3.8, where an electrical voltage was applied by using customized LabVIEW programming in a GPIB Keithley 2400 sourcemeter.


The TOF-SIMS is a highly surface sensitive technique where a pulsed and focused ion beam, and time of flight analyzer are employed to emanate positive and negative ions from a material. Therefore, SIMS can detect trace elements (in ppb) and can also provide detailed information about the molecular structures present on the surface of a material. The SIMS data can also be collected in a “static mode” to analyze the surface with less damage as well as a depth profile can also be used (in TOF-SIMS) for elemental analysis. In SIMS, both atomic and molecular ions are emitted from the outer layers of the material surfaces. The mass of the species is measured by using a time
of flight detector. The analysis cycle is often repeated at high frequency to generate a complete mass spectrum. The high-sensitivity, dynamic nature, and parallel detection of all ions render TOF-SIMS technique an ideal analytical tool to characterize complex materials. In the present study, depth profiling was performed on various samples. For the depth profiling, two beams operate in a dual beam mode. The first beam is used to sputter a crater onto the sample, whereas the second beam analyses the elemental composition of the sample. The sputter speed can be as high as 10 m/hr. with a depth resolution lower than 1 nm. Therefore, multi-component assembly can be easily analyzed by SIMS. The ion gun uses Cs⁺ ions for the sputtering and analysis technique. The spatial resolution is less than 300 nm and a 10 kV beam energy was used during the experiments. The pulse width of the source was less than 1 ns. The stage onto which the samples were mounted was motorized and an electron gun was used to reduce the charging from the insulating sapphire substrate. From the SIMS depth profile, we have also analyzed the diffusivity during the pulsed laser annealing process and a detailed explanation can be found in chapter 6.
3.14. References


4. Room-Temperature Ferromagnetism and Extraordinary Hall Effect in Nanostructured Q-Carbon: Implications for Potential Spintronic Devices

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4.1. Abstract

We report extraordinary Hall effect and room-temperature ferromagnetism in undoped Q-carbon, which is formed by nanosecond pulsed laser melting and subsequent quenching process. Through detailed structure-property correlations in Q-carbon thin films, we show the excess amount of unpaired electrons near the Fermi energy level, which give rise to interesting magnetic and electrical properties. The analysis of the extraordinary Hall effect in Q-carbon follows non-classical “side-jump” electronic scattering mechanism. The isothermal field-dependent magnetization plots confirm room-temperature ferromagnetism in Q-carbon with a finite
coercivity at 300 K and a Curie temperature of 570 K, obtained by the extrapolation of the fits to experimental data using modified Bloch’s law. High-resolution scanning electron microscopy and transmission electron microscopy clearly illustrate the formation of Q-carbon and its subsequent conversion to single crystalline diamond. Further, we have found n-type conductivity in Q-carbon in the entire temperature range from 10 - 300 K based on the extraordinary Hall coefficient versus magnetic field experiments. This discovery of interesting magnetic and electron transport properties of Q-carbon show that non-equilibrium synthesis technique using super undercooling process can be used to fabricate new materials with greatly enhanced physical properties and functionalities. The observed robust room-temperature ferromagnetism coupled with extraordinary Hall effect in Q-carbon will find potential applications in carbon-based spintronics.

4.2. Introduction

Carbon-based materials possess versatile physical and chemical properties. The outer 2s and 2p shells in a carbon atom can hybridize in three different ways to form sp, sp² and sp³ orbital wave functions. For the carbon materials comprising a mixture of sp² and sp³ bonding types, a dominant factor in determining their physical properties is the sp²/sp³ ratio. Graphite is considered to be one of the strongest diamagnetic materials among naturally occurring substances. This is due to the large orbital diamagnetism and small effective electronic mass in its band structure. The diamagnetic effect is also observed in graphene. Fullerenes (C₆₀) also exhibit diamagnetic and paramagnetic ring currents due to the existence of mobile (delocalized) \( \pi \) electrons. With a few exceptions, most of the carbon allotropes exhibit a diamagnetic susceptibility. Recently, an extremely interesting coexistence of superconducting and ferromagnetic states have been observed in hydrogenated boron-doped nanodiamond. The ferromagnetic properties of carbon-based materials arise primarily due to: (i) radicals which form chain-like structures and interact with each
other (long-range and short-range interactions),\textsuperscript{5,6} (ii) carbon mixtures comprising of the fractions of $sp^2$ and $sp^3$ hybridized states,\textsuperscript{7,8} (iii) carbon structures consisting of impurities, namely P, N, B,\textsuperscript{9-11} and (iv) irradiation of graphite and highly oriented pyrolytic graphite (HOPG).\textsuperscript{12,13} Yet surprisingly, theory predicts (assuming each carbon atom has a spin of one unpaired electron which contributes to ferromagnetic ordering) much higher values of $M_s$ (saturation magnetization) than those observed experimentally (only 0.1\% of the theoretical value is observed).\textsuperscript{14} Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) studies also suggest that topological defects, such as functional groups and point defects perturb the electronic properties of graphite thereby giving rise to its magnetic properties.\textsuperscript{15} In addition, the magnetic properties of pure and doped graphene can also be explained by itinerant ferromagnetism of dilute two-dimensional electron gas with the strong Coulomb interaction between electrons.\textsuperscript{16} At the edge states (and defect sites), there occur electron-electron interactions which cause magnetic polarization. The examination of the electron-electron interaction effects in the Hubbard model also reveals a possibility of spontaneous magnetic ordering in the nanometer-scale fragments of graphite.\textsuperscript{17} This also causes the formation of excitonic states which assist in the alignment of the unpaired electrons thereby giving rise to weak ferromagnetism in carbon-based materials.\textsuperscript{18} Ferromagnetism is also reported in N-doped polycrystalline diamond thin films due to the presence of $sp^3$-$sp^2$ electronic moieties.\textsuperscript{19} This reduces the orbital Coulomb repulsion thereby causing ferromagnetism.\textsuperscript{19} The synthesis of hybrid carbon-based photochromic and electrochromic molecules are also being vigorously pursued to fabricate multifunctional molecular materials.\textsuperscript{20}

In a search for bulk ferromagnetism in carbon, we have synthesized a novel amorphous phase of carbon by quenching the undercooled liquid carbon,\textsuperscript{21} which is distinctly different from other thermodynamically stable forms of carbon namely, graphite, diamond, liquid and vapor.\textsuperscript{22} The
synthesized phase, Q-carbon is ferromagnetic, electron-emissive, *harder* than diamond and can be transformed into single-crystal diamond at room temperature and ambient pressure.\textsuperscript{21,23} This phase is a new state of solid carbon with a higher mass density than amorphous carbon and comprises of a mixture of mostly four-fold $sp^3$ (75-85\%) and the rest three-fold $sp^2$ bonded carbon (with distinct entropy).\textsuperscript{23} The formation of Q-carbon is accomplished by nanosecond laser melting of amorphous carbon in a super undercooled state and subsequently quenching the molten carbon. The process of pulsed laser irradiation causes the electrons to be excited into the conduction band. These excited electrons transfer their energy quickly to phonons, leading to rapid heating and melting. The formation of Q-carbon depends on the laser energy density, physical properties of the as-deposited amorphous C film and the substrate. The molten state of carbon is metallic\textsuperscript{24} and thereby in the structure of Q-carbon, the C atoms can be densely packed. This packing causes an increase in the hardness, density and the electron concentration near the Fermi energy level in Q-carbon.

The process of super undercooling and subsequent quenching can transform the as-deposited amorphous carbon into Q-carbon, nanodiamond, microdiamond and/or large-area diamond. The thermal conductivities of as-deposited diamond-like carbon (DLC) or amorphous C thin films and the substrate (sapphire) play vital roles in the formation of Q-carbon. A high quenching rate leads to large solidification velocity thereby promoting the formation of densely packed amorphous Q-carbon structure. We have also demonstrated the formation of single-crystal diamond on lattice and planar matched substrates (Cu, sapphire) using the pulsed laser annealing technique.\textsuperscript{25-27} These transformations are dictated by the undercooling temperatures and quenching rates, according to the free-energy *versus* temperature diagram.\textsuperscript{23} The formation of supersaturated alloys of Si and Ge by using pulsed laser annealing technique have been extensively studied.\textsuperscript{28-30} The undercooling in Si and Ge was estimated to be 241 K and 336 K, respectively.\textsuperscript{31} In the case of amorphous C, the
undercooling values can be well over 1000 K. The undercooling phenomenon in carbon (graphite) was not followed with any vigor due to the understanding from the equilibrium phase diagram, according to which graphite converts into vapor above around 4000 K and at low pressures.\textsuperscript{22} Q-carbon has a high fraction of $sp^3$ hybridized electronic states and dangling bonds which contain delocalized electrons. The electronic structure of Q-carbon consists of overlapping orbitals of $sp^2$ and $sp^3$ electronic states and is expected to possess exciting physical, chemical and catalytic properties. Undoped Q-carbon is ferromagnetic, which upon doping turns paramagnetic. B-doped (25 at \%) Q-carbon exhibits high-temperature BCS superconductivity.\textsuperscript{32} Spintronic applications demand coupling of magnetic and transport properties in robust ferromagnets.\textsuperscript{33} Though there are several reports on magnetotransport in various materials,\textsuperscript{34,35} such studies are not available for carbon-based materials. Therefore, magnetotransport properties of carbon-based materials should be investigated to confirm that the charge carriers are indeed coupled to the magnetic spins, thereby giving rise to novel functionalities. An observance of extraordinary Hall effect in thin films also suggests that the charge carriers interact with the ferromagnetic coupling. The coexistence of room-temperature ferromagnetism and extraordinary Hall effect in thin films is extremely important because the ferromagnetically spin-polarized carriers can be controlled electronically thereby leading to ultrafast switching device applications in the field of multifunctional electronics.

In the present study, we have focused on structure-property correlations using various state-of-the-art measurements and characterization techniques to understand the ferromagnetism and extraordinary Hall Effect in Q-carbon. The structure and properties of Q-carbon are studied by employing secondary ion mass spectroscopy (SIMS), electron energy-loss spectroscopy (EELS), high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, X-ray diffraction, magnetic force microscopy (MFM) and field emission scanning electron microscopy
The formation of Q-carbon is also simulated by employing the simulation of laser interaction with materials (SLIM) software developed by Singh and Narayan.\textsuperscript{36} We have examined the ferromagnetic behavior of Q-carbon using the temperature-dependent magnetic susceptibility measurements in superconducting quantum interference device (SQUID). To study the non-classical electron scattering mechanism in Q-carbon, five-probe electrical measurements to measure Hall voltage were performed in the physical property measurement system (PPMS). With this study, we propose that the non-equilibrium undercooling assisted synthesis methods can be used to fabricate novel materials, which possess greatly enhanced physical properties.

4.3. Methods

Amorphous carbon thin films were deposited onto c-sapphire using pulsed laser deposition with a thickness ranging from 50-500 nm in the temperature range of 30-300 °C and 4.0×10\textsuperscript{-7} Torr base pressure. During the pulsed laser deposition, nanosecond laser pulses of KrF (laser wavelength=248 nm, pulse duration=25 ns) with an energy density of 2.5-3.0 Jcm\textsuperscript{-2} are used. Subsequently, these amorphous carbon films are irradiated with nanosecond ArF excimer laser (laser wavelength=193 nm, pulse duration=20 ns) pulses using laser energy density 0.6-1.0 Jcm\textsuperscript{-2}. The pulsed laser annealing technique melts the amorphous carbon thin film in a highly super undercooled state which can be quenched rapidly. The pulsed laser annealing process is completed within 200-250 ns. This leads to conversion of amorphous carbon films into Q-carbon and/or micro and nano-structures of the diamond. This conversion is dependent on the degree of undercooling, rate of quenching and solidification velocities during the pulsed laser annealing technique. Figure 4.1(a) depicts the schematic of the synthesis of amorphous Q-carbon using pulsed laser deposition followed by pulsed laser annealing. The characterization of the Q-carbon phase was carried out using Raman spectroscopy, SIMS, EELS, FESEM, HRTEM, SQUID magnetometry, PPMS,
MFM and XRD. X-ray diffraction ($\lambda=1.5406$ Å) combined with secondary ion mass spectroscopy (SIMS) techniques rule out the presence of ferromagnetic impurities in a large-area and ppm level in Q-carbon. The figure 4.1(d) illustrates the simulation of laser interaction with materials (SLIM) theoretical calculations which indicate a melt-front velocity of 20 m/sec, essential for the formation of Q-carbon. The structure of Q-carbon and its conversion to diamond have also been reported previously.\textsuperscript{23} Alfa300 R superior confocal Raman spectroscope with a lateral resolution less than 200 nm was employed to characterize the Raman-active vibrational modes in Q-carbon and diamond. Crystalline Si with its characteristic Raman peak at 520.6 cm\textsuperscript{-1} was used to calibrate Raman spectra. High-resolution SEM in emission mode with a sub-nanometer resolution was carried out using FEI Verios 460L SEM to characterize the as-deposited and the laser-irradiated films. Time-of-Flight Secondary Ion Mass Spectrometer (TOF-SIMS) with a lateral resolution of <300 nm was used to detect the presence of C in addition to Al and other trace impurities in the Q-carbon thin films. FEI Quanta 3D FEG with dual beam technology employing both electron and ion beam guns was used for preparing cross-sectional TEM samples. A low-energy-ion beam (5 kV, 10 pA) was used to clean up the FIB surface damage. Aberration-corrected STEM-FEI Titan 80-300 was used in conjunction with electron energy-loss spectroscopy (EELS with a resolution of 0.15 eV) to acquire EELS spectra of diamond and Q-carbon thin films. The electron probe current used in the experiment was 38±2 pA. The EELS data was acquired with a collection angle of 28 mrads. Quantum Design magnetic property measurement system (MPMS3) was used to measure magnetic properties of thin films. VSM and DC modes were used for measuring field-dependent magnetization. The magnetic measurements were made with samples mounted parallel to the magnetic field. We have measured the thickness of Q-carbon using the high-resolution cross-sectional transmission electron microscopy and are represented in the figure 2(c). The thickness is
calculated as 20 nm. The volume of the sample is therefore calculated as $3.2 \times 10^{-7}$ cm$^3$. Taking the density as 3.51 gm/cc, the normalized magnetization values were calculated. Five probe electrical measurements are performed on Q-carbon thin films using PPMS to probe the non-classical electronic scattering mechanism. The misalignment voltage was adjusted to less than 0.1 $\mu$V prior to data acquisition at each temperature. The sign of the Hall voltage ($V_H$) was calibrated using a standard Fe sample (positive $V_H$ at 300 K). Asylum Research MFP-3D Infinity AFM was employed for MFM imaging. MFM silicon probe with 50nm Co-Cr coated tip was used for the MFM scans. The MFM image was taken with a delta height of 50 nm and was flattened to zeroth order to improve its contrast. The samples were stabilized on the granite platform in the Asylum Research MFP-3D instrument for 24 hours prior to MFM measurements.

4.4. Results and discussion

Figure 4.1(b) depicts the Raman spectra from as-deposited DLC, Q-carbon and diamond on sapphire performed using 532 nm laser excitation. The Q-carbon is formed on the substrate after a single laser pulse of ArF laser (energy density: 0.6 Jcm$^{-2}$). The nucleation of nano and micro-diamonds is also achieved during the formation of Q-carbon which contains the seeds ($sp^3$ hybridized electronic states) of diamond nuclei. Subsequent pulsed laser annealing of Q-carbon can also lead to the formation of nano, micro, and large-area single crystal diamond.23 The Raman peak of the diamond grown from the Q-phase is centered at 1334 cm$^{-1}$. This mode corresponds to the vibration of the two-interpenetrating cubic sublattices present in the diamond.37 The inset of figure 4.1(b) represents the peak-fitted Raman spectra of Q-carbon. The Raman spectrum of Q-carbon can be deconvoluted to a diamond peak at 1329 cm$^{-1}$ with a broad peak around 1350 cm$^{-1}$, a small peak at 1140 cm$^{-1}$ which is associated with the strained $sp^2$ carbon at the interface and the graphitic peak at 1560 cm$^{-1}$. The peak fitting of the Q-carbon Raman spectra yields a 75-80% of
$sp^3$ hybridized electronic states. From preliminary electron diffraction experiments, we derive that Q-carbon is formed as result of random packing of carbon tetrahedra with packing efficiency of over 80% with $sp^3$ bonding within and $sp^2$ in between them. The blue shift of the diamond peak in the Q-carbon Raman spectrum is associated with the strains generated after the quenching process. The small peak at 1040 cm$^{-1}$ is due to the presence of $sp^2$ bonds on the surface of nanodiamonds which is present in the structure of Q-carbon. The increase in the FWHM of the diamond peak which is associated with Q-carbon can also be due to phonon confinement effects due to the presence of nanodiamonds in the Q-carbon structure.

Figure 4.1(c) represents the XRD spectrum of amorphous Q-carbon grown on c-sapphire. The diffraction peaks at 2θ=41.6$^0$ and 91.1$^0$ correspond to (0006) and (00012) sapphire. The absence of any other peaks in the logarithmic plot of XRD spectrum (up to 2θ=130$^0$) indicates that the Q-carbon thin films are pristine in nature. Figure 4.1(d) indicates the SIMS profile of Q-carbon. There are no impurity elements at ppm level in the Q-carbon thin films. Very recently we have also demonstrated homogeneous melting of B-doped carbon using the nanosecond pulsed laser annealing technique.$^{32,38,39}$ From boron distribution, the diffusivities were determined to be $\sim 10^{-4}$ cm$^2$/V/sec, which confirmed the melting of carbon. The pulsed laser annealing (PLA) process is an ultra-fast technique (completed in less than 250 ns) and thereby minimizing contamination of impurities from the atmosphere. The calculation of threshold energy is crucial for this study, as it determines the minimum laser energy required for melting amorphous carbon, which leads to the formation of Q-carbon. We have used the SLIM programming$^{36}$ to simulate the laser-solid interactions. The initial layered structure consists of amorphous carbon (75% $sp^3$)/sapphire. The threshold energy ($E_{th}$) required for melting few layers of amorphous carbon/sapphire is calculated as 0.4 Jcm$^{-2}$.$^{36}$ Figure 4.1(e) depicts the temperature vs time (in ns) plots for various energy
densities which are calculated using the SLIM program by employing a nanosecond laser ($\lambda=193$ nm, laser width=20 ns). As it is evident from the plots that melting of the as-deposited amorphous carbon layer occurs when energy densities above 0.4 Jcm$^{-2}$ are used. The red dotted line indicates the melting temperature ($T_m$) of carbon. The thickness of the melted region varies linearly with the pulse energy density. The surface starts to melt slowly due to the sudden change in reflectivity during the phase transition. As the laser pulse terminates, the melt front recedes back to the surface.

The initial stages of solidification see a low velocity but quickly reaches the maximum when the steady state condition is achieved. The melt front velocity is estimated to be 20 m/sec for 0.6 Jcm$^{-2}$, as shown in the inset of the figure 4.1(e). These calculations involve an extremely accurate finite difference method to calculate the melt depth and temperature profile in the laser annealed samples thereby providing valuable insights to the formation of Q-carbon.

Figures 4.2(a) and (b) represent high-resolution scanning electron microscopy images of Q-carbon and formation of diamond from Q-carbon, respectively. The super undercooled carbon is formed near the film-substrate interface. Subsequent quenching of this structure leads to the formation of a filamentary structure of Q-carbon. The formation of these cellular structures (figure 4.2(a)) indicates an interfacial instability at the solid-liquid interface. The formation of these cellular structures in Q-carbon can also be controlled by thermal conductivity through the variation of $sp^3$ fraction in the as-deposited amorphous carbon sample. The inset of figure 4.2(a) illustrates the formation of Q-carbon from the as-deposited amorphous C layer. The sharp interface (as shown by the black arrow) corresponds to a first order phase transformation (of amorphous Q-carbon to diamond transformation). The Q-carbon thus formed has about 75-80% $sp^3$ bonding and also contains nanodiamond-embedded in its structure. These nanodiamonds act as seeds or nucleating agents for subsequent nucleation of diamonds when the Q-carbon is irradiated with higher laser
energy densities (0.6-1.0 Jcm$^{-2}$). The formation of diamonds at the Q-carbon triple points is illustrated in figure 4.2(b). The inset of figure 4.2(b) clearly shows the formation of nano and micro-sized crystals of diamond from the filamentary structure of Q-carbon. The nanodiamonds and microdiamonds can be formed either by heterogeneous (on the sapphire) or by homogeneous (on the diamond) nucleation.\textsuperscript{21,23} Figures 4.2(c) and (d) show the high-resolution transmission electron microscopy images of Q-carbon grown on c-sapphire. It is evident from the figure 4.2(c) that Q-carbon has mostly amorphous structure with a few nanodiamonds embedded into it. The interplanar spacing of the nanodiamonds corresponds to the \{111\} lattice planes and is shown by black arrows in figure 4.2(c). In figure 4.2(d) we show the formation of crystal facets of diamond from Q-carbon. Recently, we have also reported the formation of nanoneedles, microneedles and large-area diamond from Q-carbon.\textsuperscript{21,23,41}

The details of bonding characteristics and electronic structure of Q-carbon were thoroughly investigated and compared with that of DLC and diamond. Figure 4.3(a) shows the high angle annular dark field (HAADF) image of Q-carbon on c-sapphire substrate. The associated Ronchigram for the Q-carbon and c-sapphire are also presented in figure 4.3(a), demonstrating the amorphous and crystalline nature of the two, respectively. Figure 4.3(b) shows the EELS spectra obtained from Q-carbon, the parent DLC and diamond, revealing the $sp^3 (\sigma^*)$ and $sp^2 (\pi^*)$ bonding characteristics. EEL spectra of Q-carbon and DLC consist of a sharp $\pi^*$ peak (onset at 284 eV) and a broad $\sigma^*$ peak (onset 290 eV). On the other hand, EEL spectrum for diamond shows only $\sigma^*$, as it purely consists of $sp^3$ hybridized carbon atoms. Using a fitting routine to the EELS, the $sp^3$ was estimated to be ~77%, which is in excellent agreement with the Raman spectroscopy results (75\% $sp^3$) from Q-carbon. In the first look, EEL spectra of Q-carbon and DLC appear very similar (characteristic of amorphous C). However, upon closer observation, we discover that there is a
significant difference between them. The $\pi^*$ peak is sharper and $\sigma^*$ peak is broader in Q-carbon as compared to the DLC. It is worth noting that the EELS results in Q-carbon were repeatable across different sets of samples. Though it is expected that the parent DLC (containing $\sim60\%$ $sp^3$ based on Raman spectroscopy) should exhibit a higher intensity $\pi^*$ peak in EELS as compared to Q-carbon ($\sim77\%$ $sp^3$), the results were totally inverse. A representative fitting routine performed on Q-carbon EELS spectrum is shown in Figure 4.3(c). This demonstrates the fitting of one Gaussian in $\pi^*$ and two in $\sigma^*$ region. The Gaussian fitted $\pi^*$ peaks for Q-carbon, parent DLC and diamond are shown in figure 4.3(d) which unambiguously points out the highly enhanced intensity of $\pi^*$ peak in Q-carbon. It is known that the long- and medium-range ordering of atoms in a material give rise to a sharper peak profile. This unexpected enhancement in $\pi^*$ intensity in Q-carbon is attributed to the presence of a large number of unpaired spin electron density associated with distinct electronic states near the Fermi energy level. The area under the $\pi^*$ peak, which is related to the increase in the unpaired spins electrons, is increased by 80% in Q-carbon as compared to DLC. We propose that the unpaired spin electrons arise due to the presence of dangling C bonds in Q-carbon which are formed through a highly non-equilibrium quenching process. This direct observation of the presence of a large number of unpaired spin electrons is envisaged to create unexpected magnetic and electronic behavior in Q-carbon, which is the primary objective of this study.

Figure 4.4(a) represents the field-dependent magnetization curves of Q-carbon performed at different temperatures (10, 100, 200 and 300 K). The magnetic curves (M-H) show room-temperature ferromagnetism in Q-carbon. There is a finite coercivity ($\sim11945$ A/m) of Q-carbon at 300 K. Controlled samples containing only diamond, diamondlike carbon and sapphire substrate show only diamagnetic behavior, which was subtracted in the represented magnetic plots. The
insets in figure 4.4(a) represent a finite coercivity ($H_c$) of ~15925 A/m at 10 K (upper inset) and diamagnetic behavior of the as-deposited amorphous carbon grown on c-sapphire substrates (lower inset). The origin of magnetism in Q-carbon can be due to the electronic mixing of $sp^2$ and $sp^3$ orbital states during its formation. Q-carbon is formed by quenching and super undercooling of liquid metallic carbon which consists of a large fraction of unpaired electrons. Some of these unpaired electrons remain in the Q-carbon structure, which lead to the observed ferromagnetism. In Q-carbon, the ferromagnetism is, therefore, intrinsic in nature without the presence of hydrogen or any other impurities.

Several hypotheses were advanced for this new kind of magnetism (in carbon) without the presence of magnetic ions, due to spin ordering effects with the low dimensionality and Dirac-like electron spectrum.\textsuperscript{44} Magnetism in $sp$ oxides like MgO or in carbon-based materials like graphite is not observed owing to the fact that Stoner criterion suggests less density of delocalized electrons.\textsuperscript{7} However, due to the presence of intrinsic defects, ferromagnetism can occur in these materials. Recently room temperature ferromagnetism in graphene, MgO and other oxides have been reported.\textsuperscript{45-47} So, the mechanism of ferromagnetism in $s$ and $p$ electrons in carbon, in contrast to $3d$ or $4f$ electrons (in traditional magnets), is quite significant and very interesting. At room temperature (300 K) as well as at low temperature (10 K), all the Q-carbon samples exhibit hysteresis loops in $M$-$H$ data indicating the presence of a long-range ferromagnetic ordering in this structure. The hysteresis loops open up at low fields and magnetization seems to approach a saturation value above 1500 Oe. The $H_c$ of all samples increases with decreasing temperature. This indicates an increase in the number of active magnetic pinning centers at lower temperatures. In order to further explore the ferromagnetism in Q-carbon, we have also estimated the Curie temperature by extrapolation of the steepest portion of the square of the high field magnetization
versus temperature (M² vs T) plots and are discussed below. Figure 4.4(b) shows a phase contrast MFM image of Q-carbon along with diamond and DLC at 300 K. The phase detection mode measures shift in the phase of cantilever oscillation in MFM imaging to minimize the optical interference effects during data acquisition. The change in the phase is caused by magnetic interactions of the tip with the sample surface. The change in phase (Δθ) is represented by the following equation (4.1):

\[ \Delta \theta \approx \frac{Q}{k} F \tag{4.1} \]

where, \( Q \), \( k \) and \( F \) denote quality factor, stiffness (of the cantilever) and the vertical force on the cantilever. With the increase in the vertical force on the cantilever, there occurs an increase in the contrast of the phase image acquired in MFM. In general, attractive interactions cause a negative phase shift (dark image contrast) and repulsive interactions cause a positive phase shift (bright image contrast). As it is evident from the AFM (figure 4.4(c)), that there occurs a shrinkage of ~40 nm when the Q-carbon forms. As it is evident from the MFM image in figure 4.4(b) that Q-carbon has an attractive interaction with the magnetic tip as compared to DLC or diamond. This difference in the phase contrast indicates a ferromagnetic nature of Q-carbon as compared to the rest of the film. The absence of any anti-symmetric contrast in the MFM image rules out the possibility of any topographic features (short-range interactions) related artifacts in the magnetic response. The magnetic force microscopy measurements clearly demonstrate that Q-carbon is highly magnetic, and the interface region between diamond or DLC and Q-carbon exhibit magnetic contrast at 300 K, while diamond crystallites and DLC are found to be diamagnetic in nature.

Figure 4.5(a) shows the linear extrapolation of the M² vs T plot. Curie temperature of the Q-carbon sample is calculated as 570 K, in close agreement with the previously reported value.23 We have used the “Law of Approach (LA)” to determine the temperature-dependent magneto-crystalline
anisotropy constant $K(T)$ and temperature-dependent saturation magnetization $M_s(T)$, which is discussed later in this section. The magnetization of a material can be represented by the following equation (4.2): 

$$M = M_s \left(1 - \frac{8K^2}{105\mu_0^2M_s^2H^2}\right) + cH$$

where $M$ is the magnetization, $H$ is the applied magnetic field, $M_s$ is the saturation magnetization, $\mu_0$ (4\pi in CGS; $4\pi \times 10^{-7}$ in SI) is the magnetic permeability of free space, $K$ is the magnetic anisotropy constant, and $c$ is the linear constant term. The contribution of the linear term $cH$ is small compared to the first term at large magnetic fields. The term $B$ in the inset of figure 4.5(a) equals to $8K^2/105\mu_0^2$. The temperature dependence of $K(T)$ and $M_s(T)$ are extracted by fitting the values of magnetization corresponding to the high magnetic field part of the curve i.e. from the saturated portion of the magnetization curve to equation (4.2).

For the fitting process, only magnetization data above 700 kA/m are used. The fit to equation (4.2) is shown in the inset of figure 4.5(a). As represented in figure 4.5(b), the value of magnetic anisotropy constant decreases with increasing temperature. The values of $K$ are calculated as $4.8 \times 10^2$ J/m$^3$ and $3.5 \times 10^2$ J/m$^3$ at 10 K and 300 K, respectively. The magnetic anisotropy constant plays an important role in determining the relaxation behavior in magnetic materials. The anisotropy energy restricts the rotation of magnetic moments away from the easy magnetization axis. Therefore, the thermal energy at higher temperatures assists in reducing the value of $K$ in the Q-carbon structure. The non-linear dependence of magnetic anisotropy with temperature in Q-carbon can be due to the presence of an electronic mixture of $sp^2-sp^3$ hybridized states. From the established theories on magnetic anisotropy as proposed by Van Vleck and Zener, the value of correlation exponent in Q-carbon is calculated as 1. This qualifies Q-carbon to be an uniaxial ferromagnet. The solid curve in figure 4.5(b) is the fit to the equation (4.3).
\[ K(T) = K(0) \left[ 1 - \left( \frac{T}{T_c} \right)^n \right] \] (4.3)

where \( K(0) \) denotes the magnetic anisotropy at 0 K. The values of \( K(0) \) and \( n \) are calculated as 0.49×10³ J/m³ and 2.045, respectively. The value of the exponent \( (n) \) is also verified by the modified Bloch’s law in Q-carbon where the Bloch exponent is calculated to be 2.039 and is discussed below in detail. The \( H_c(\sqrt{T}) \) dependence in Q-carbon (as shown in the inset of figure 4.5(b)) depicts the ensemble of oriented uniaxial ferromagnetic domains ⁵²-⁵⁴ (in Q-carbon) magnetized by an external magnetic field. The low-temperature and high-temperature regions signify the blocking and interaction effects, respectively. ⁵⁴ The blocking temperature \( (T_B) \) is calculated to be 270 K from the intersection point \( (\sqrt{T_B}) \) of the two regions. The fact that \( H_c(\sqrt{T}) \) dependence has two linear regions, indicates the presence of ferromagnetic interparticle interaction in the ensemble. This interaction leads to the formation of a homogeneous ferromagnetism ⁵⁴ in Q-carbon. Additional magnetic measurements namely NMR (nuclear magnetic resonance), FMR (ferromagnetic resonance) and \( \mu \)SR (muon spin resonance) spectroscopy are an exhaustive study in itself and will be performed (and reported) in near future to determine the homogeneous nature of ferromagnetism in Q-carbon.

The temperature dependence of the saturation magnetization for the case of a continuous distribution of spin-wave states can be well fitted to the Bloch’s theory and is represented by the equation (4.4): ⁵¹,⁵⁵

\[ M_s(T) = M_s(0) \left[ 1 - b \left( \frac{T}{T_c} \right)^n \right] \] (4.4)

where \( M_s(0) \) is the magnetization of the ground state at \( T = 0 \) K, \( b \) is Bloch’s constant, \( n \) is the Bloch exponent and \( T_c \) is the Curie temperature. As shown in Figure 4.5(c), the temperature-dependent saturation magnetization \( M_s(T) \) obtained by fitting to equation (4.4), decreases with
increasing temperature. The values of saturation magnetization for undoped Q-carbon are calculated as 70 kA/m and 51 kA/m at 10 and 300 K, respectively. The calculated parameter \( \alpha = b / (T_c)^n \) is \( \sim 10^{-6} \) K\(^n\). The low values of \( \alpha \) indicate an increase in the spin wave stiffness coefficient, thereby increasing the spin wave excitation energy required to switch the spin states in Q-carbon. The value of Bloch exponent varies slightly from 2.039 to 2.042 in the Q-carbon samples. The Bloch’s law suggests that the decrease in the saturation magnetization with increasing temperature is due to spin-wave excitations and can be described by a power law in \( T \).

However, the magnitude of \( M_s \) in the Q-carbon structure may depend on the solidification rates. The Bloch constant is inversely proportional to \( D^n \), where \( D \) is the coefficient of spin-wave stiffness. The excitation energy \( E_k \) of spin wave in the limit of small wave vectors (\( k \rightarrow 0 \)) is expressed by the following equation (4.5):\(^{56}\)

\[
E_k = D k^2
\]  
Equation (4.5)

The finite size of the particles leads to a discrete set of energy values corresponding to a discrete spectrum of the spin-wave modes. In case of a cubic particle with side \( d \), the spin wave energies can be roughly estimated using the equation (4.6):\(^{56}\)

\[
E_k = D \left( \frac{n\pi}{d} \right)^2
\]  
Equation (4.6)

where \( n \) is an integer. An increase in the value of \( b \) represents a decrease in the spin wave stiffness constant and thereby less spin wave excitation energy, \( E_k \) is required to demagnetize ferromagnetic materials at temperatures well below the transition temperature by the process of excitation of long-wavelength spin waves. It can also be inferred from the equation (4.6) that a decrease in lattice parameter increases the spin wave excitation energy. Q-carbon is formed after melting and subsequent quenching of liquid carbon. This leads to a \( \sim 5\% \) decrease in the C-C bond length in the Q-carbon structure as compared to diamond\(^{19}\) which can affect the values of \( E_k \).
Generally, superparamagnetism is observed in the case of miniature-sized ferromagnetic or ferrimagnetic nanoparticles. In these materials, the magnetization randomly flips direction with an increase in thermal energy. The magnetization curves of Q-carbon can be explained on the basis of the theory of superparamagnetic relaxation, assuming that the atomic magnetic moments inside the clusters are parallel. The Bloch exponent is a structure independent parameter but is dependent on the magnetic domain size. The Bloch constant depends on the effective coordination number, $z_{\text{eff}}$ in the ferromagnetic material. The effective coordination number depends critically on the structure of the outermost shells in the cluster (the cluster closure) as well as on the cluster size. Smaller $b$ values correspond to "closed" magnetic clusters. According to the Linderoth et al, magnetization may not follow the Bloch’s $T^{3/2}$ law in all ferromagnetic materials. The temperature-dependent saturation magnetization curve in Q-carbon can be fitted (as shown in figure 4.5(c)) using the modified Bloch’s law where the value of the Bloch exponent ($n$) is equal to 2.04 and a pre-factor of $3.02 \times 10^{-6} $ K$^{-2.04}$. Therefore, the temperature-dependent saturation magnetization behavior in Q-carbon can be ascribed to the finite size effects in the spin-wave spectrum. The finite size might also affect electronic properties, resulting in exchange energy constants that vary with position and site-dependent magnetic moments in Q-carbon thin films. The change in magnetization with the temperature raised to the calculated mean of Bloch exponent for all the Q-carbon samples follow a linear trend. This linear dependence also corresponds to the pristine nature of samples and instills confidence about the magnetization data acquisition and the analysis technique.

From the M-H isotherms at various temperatures between 10 to 300 K, it is evident that the magnetic moment for all the temperatures remain parallel to the H-axis. Generally, above the Curie temperature, the isotherms will become straight lines passing through the origin. Since, the Curie
temperature of the Q-carbon samples are much above 300 K, no such trend was observed in the M-H isotherms. The linearity is also not observed in the Arrott plots (M^2 vs H/M). The value of T_c (from Arrott plots) is calculated as 630 K. This value is ~60 K (11%) higher than that calculated from Bloch’s Law. This difference is due to the fact that Arrott plot is based on Weiss molecular field theory of the ferromagnetism, and therefore can only be elegantly applied to ferromagnetic materials having low Curie temperature. The discrepancy of ~11% is due to presence of critical fluctuations which are present in the mean-field calculations (whereas absent in the spin waves calculation: Bloch’s law). The high-temperature magnetization experiments (T » T_c) are being pursued and the same will be reported at a later date. The magnetization measurements at higher temperatures through the critical region (in the vicinity of T_c) and up to 1000 K (paramagnetic region), is a study in itself and would certainly facilitate better estimation of T_c in Q-carbon.

Figures 4.6(a), (b), (c) and (d) represent the extraordinary Hall effect configuration and measurements in Q-carbon. These measurements provide a better understanding of the ferromagnetic state and elucidate the dominant scattering process in this new and exotic phase of carbon. The phenomenological expression for the Hall resistivity of magnetic metals and their dilute alloys can expressed by the equation (4.7)

\[ \rho_H = R_0 B + \mu_0 R_s M, \]  

where \( R_0 \) is the ordinary Hall coefficient = \( 1/ne \) for a single electron or hole band but involves mobilities as well for two-band or multi-band metals, \( R_s \) is the extraordinary or the anomalous Hall coefficient, \( B \) is the magnetic field, and \( M \) is the magnetization. In equation (4.7), the first term represents the ordinary Hall effect and it results from the Lorentz force acting on the moving charge carriers under the influence of an external magnetic field while the second term represents the
extraordinary or the anomalous Hall effect which originates from the spin-orbit interaction in a ferromagnet.

There exist several models in the literature about the origin of the EHE. In some models the conduction electrons are assumed to be magnetic and the scattering centres are non-magnetic while in other models it is just the opposite. But, in all the cases the spin-orbit coupling between the conduction electrons and the scattering centres have been considered as the basic mechanism causing the EHE. It is a characteristic property of a ferromagnetic material and is proportional to the magnetization of the sample. The origin of the extraordinary Hall coefficient, $R_s$ has been understood in terms of the left-right asymmetry in the differential scattering cross-section of the conduction electrons leading to the anomalous Hall effect. Usually $R_s$ is much larger than $R_o$ and it has a strong dependence on the temperature as well as on the impurity concentration. For a ferromagnetic material, both theoretically and experimentally, $R_s$ is found to have a power law relation with the longitudinal Ohmic resistivity, $\rho$ and is given by: $R_s = a\rho + b\rho^2$, where $\rho$ is the bulk resistivity and $a$ and $b$ are constants which are the characteristics of the material itself. The linear term in $\rho$ is attributed to the Smit asymmetric scattering or the skew scattering of the charged carriers, derivable from the classical Boltzmann equation while the quadratic term in $\rho$ is attributed to the side-jump mechanism proposed by Berger. This is purely a quantum mechanical effect. Both the scattering phenomena mentioned above have their origin in the spin-orbit interaction present in a ferromagnet. The skew scattering shows up for pure materials at low temperatures. On the other hand, the side-jump scattering is dominant for impure and disordered materials or at high temperatures. This non-classical transport is most commonly seen in Fe-Cr and other concentrated alloys. Figure 4.6(b) depicts the variation of Hall resistivity with magnetic field at various temperatures (from 10 to 300 K). It shows an initial steep rise of the Hall resistivity at low fields.
followed by a small negatively sloped characteristics at high fields that exhibit nearly saturation behavior as observed in a ferromagnetic material. As it is evident from the figure 4.6(b) that there is a minimal change in the slope of Hall resistivity at high fields in the Q-carbon structure. This is due to a minimal change in the conductivities of the electron and hole bands.\(^{61}\) The negative slopes of the \(\rho_H \text{ vs } B\) plots indicate an \textit{n-type} conductivity in Q-carbon in the entire temperature range of 10 to 300 K. The decrease of Hall resistivity with an increase in the applied magnetic field in Q-carbon can be due to the quenching of the long wavelength magnons. In figure 4.6(c) we have plotted the change in \(R_0\) with temperature (with error bars) in Q-carbon. \(R_0\) shows an overall increasing trend with the increase in temperature. The negative values of \(R_0\) are due to the fact that the electron band is the dominant conduction channel than the hole band in Q-carbon. There is also a minimal change in the conductivity over a wide range of temperature (10 to 300 K). There is a considerable change in the values of the intercept in figure 4.6(b). \(R_H\) can be extracted by dividing the intercepts by \(\mu_0 M_S\). \(M_S\) is calculated from the modified Bloch’s law equation (4.4) in Q-carbon. The low field region of the Hall resistivity at 300 K is shown as the inset in figure 4.6(c). It is clearly observed that there occurs an onset of saturation at \(\sim 1000\) Oe (0.1 T), which is consistent with the M-H hysteresis loop (at 300 K) in Q-carbon. In figure 4.6(d) we have plotted \(-\ln(R_S) \text{ vs } -\ln(\rho)\). The calculated slope \((n)\) of the linear fit in figure 4.6(d) is 1.95. This value of \(n\) is very close to the prediction of quantum transport theory where \(R_S \propto \rho^2\).\(^{63}\) The “side-jump” mechanism exists in Q-carbon due to the presence of scattering centers which distort the wave function and create a local current density. However, in the case of disordered dilute alloys and Q-carbon the scattering centers are located far from each other thereby the outgoing scattered waveforms lack a definite phase relationship.
The structure-property correlations of Q-carbon lead to a better understanding of the interesting magnetic and electron transport properties. The formation of Q-carbon is dependent on the laser parameters and physical properties of the substrate, which control the solidification velocity. The solidification velocity ($v$) is directly related to the undercooling by the equation (4.8):

$$v = \frac{D_{\infty} f}{\lambda f_D} \left(1 - e^{\Delta G / kT} \right)$$

(4.8)

where, $D_{\infty}, f, \lambda, f_D, \Delta G, k$ and $T$ denote diffusivity of the amorphous carbon, fraction of the available sites, atomic jump distance, geometrical factor associated with diffusion (~1), chemical free energy barrier for amorphous carbon to Q-carbon phase transformation, Boltzmann constant and temperature, respectively. Again $\Delta G = (T_m - T_u) \Delta S$, where $T_u$ and $\Delta S$ denote the undercooling temperature and the change in entropy, respectively. Detailed calculations of the variation of undercooling temperatures with the $sp^3$ fraction in the as-deposited C layer will be reported elsewhere. An increase in the value of $T_u$ decreases the value of chemical free energy barrier for amorphous to Q-carbon phase transformation. This increases the velocity of the melt front. Therefore, the values of undercooling are a determining factor for the production of Q-carbon from the carbon melt. The thermal conductivity of the as-deposited amorphous carbon film and the substrate also play important roles in the formation of the new phase of carbon. With the increase in the pulse duration, the onset of melting decreases with a decrease in the solidification velocity. The maximum depth of melt also decreases with the increase in the duration of the laser pulse. There is also an increase in the time of peak melt depth with increasing laser pulse width. Calculations also show that the melt depth increases with the increase in substrate (sapphire) temperature. In all of the above-mentioned calculations, the substrate temperature was considered as 300 K. The relatively low plasma frequency of amorphous carbon leads to a better material-laser coupling when 193 nm excimer laser is used. As it is evident from the temperature profile in
the figure 4.1(d), the onset of melting occurs at ~ 5 ns after the laser is incident on the amorphous C structure. A flatter temperature profile with time is essential for a homogeneous growth of Q-carbon structure. The high values of solidification velocity cause a sufficient undercooling to form amorphous Q-carbon on c-sapphire. It should be noted that a larger undercooling is needed to form Q-carbon as compared to diamond.\textsuperscript{23} Since Q-carbon is formed by the quenching of molten carbon, there are dangling bonds which contain unpaired electrons. This in turn, leads to ferromagnetism and extraordinary Hall effect in Q-carbon. As evident from the Raman spectrum, the shift in the diamond peak ($E_{2g}$) in Q-carbon is due to the presence of hydrostatic pressure. Up to pressures of 40 GPa, the Raman shift of the diamond peak can be calculated using the following equation (4.9):

$$\omega(P) = \omega_0 + a_1 P + a_2 P^2$$

where, $\omega_0$, $a_1$ and $a_2$ are $1333.0$ cm$^{-1}$, $2.83$ cm$^{-1}$ GPa$^{-1}$ and $-3.65\times10^{-3}$ cm$^{-1}$GPa$^{-2}$, respectively.\textsuperscript{37} The hydrostatic pressure calculated using the above equation (4.9) in Q-carbon is -1.36 GPa (compressive). This indicates a decrease in the C-C $\sigma$ bond length in Q-carbon. However, the decrease in C-C bond length is primarily derived from the quenching of molten state. The decrease in the bond length is associated with an increase in hardness and density of the electronic states which may lead to room-temperature ferromagnetism and extraordinary Hall effect in Q-carbon. The asymmetry near the $\pi^*$ peak in Q-carbon indicates excitonic distortion due to its semimetallic structure. This indicates a strong Coulomb interaction. Similar kind of “quasi-metallic“ nature have also been reported in $C_{60}$\textsuperscript{66} which leads to interesting physical and chemical properties. An increase in the intensity and FWHM of the $\pi^*$ peak in Q-carbon as compared to the as-deposited DLC or diamond (as it is evident from the figure 4.3(c)), indicate an increase in the electronic density of the dangling bonds (present near the Fermi level). This increase leads to ferromagnetism and non-classical extraordinary Hall Effect mechanism in Q-carbon. When spin
imbalances are created only by an external applied magnetic field, the material assumes a paramagnetic state. In the case of Q-carbon, there is a high density of electronic states \( N(E) \) near the Fermi level and strong Coulomb interaction (excitonic distortion). This induces an exchange interaction which causes spin imbalance thereby leading to ferromagnetic ordering in accordance with the Stoner criterion (equation (4.10)) for ferromagnetism which states that:

\[
I_{ex} \cdot N(E) > 1
\]  

(4.10)

where \( I_{ex} \) and \( N(E) \) denote exchange integral and electronic density of states at Fermi energy level, respectively. The exchange integral in Q-carbon is calculated using the equation (4.11):\(^{67}\)

\[
I_{ex} = \frac{3k\theta}{2zS(S+1)}
\]  

(4.11)

where \( k, \theta, z \) and \( S \) denote the Boltzmann constant, Curie temperature, coordination number and spin quantum number, respectively. The exchange integral in Q-carbon is calculated as \( 6.10 \times 10^{-15} \) erg which is \( \sim 13\% \) to that in Fe \( (4.85 \times 10^{-14} \) erg). These exchange forces are primarily dependent on the interatomic distances and not on the crystalline structure of a material.\(^{54}\) The exchange integral value in Q-carbon suggests that the exchange energy is minimum when the electron spins are parallel to each other. This magnetic alignment coupled with an increase in the electronic density of states near the Fermi energy level give rise to room-temperature ferromagnetism and extraordinary Hall effect in the amorphous Q-carbon structure.

**4.5. Conclusion**

The field-dependent magnetization plots of Q-carbon confirm a finite coercivity and a saturation magnetization in the temperature range of 10 - 300 K. The origin of intrinsic ferromagnetism in Q-carbon is due to the electronic mixing of \( sp^2 \) and \( sp^3 \) orbitals during its formation. Some of the unpaired electrons remain in the Q-carbon structure which renders it to be ferromagnetic in nature.
This is the first direct evidence for bulk intrinsic ferromagnetism in carbon without the presence of hydrogen or any other magnetic impurities. In our carefully conducted experiments, amorphous carbon (as-deposited DLC) with 50% \( sp^2 \) and 50% \( sp^3 \) is found to be diamagnetic. This amorphous carbon turns magnetic only when it is melted in a super undercooled state and quenched to form Q-carbon. The high density of states near the Fermi level in Q-carbon (as compared to DLC) is illustrated by EELS. Usually, \( \pi^* \) peak intensity of carbon K-edge increases with increasing \( sp^2 \) fraction. Interestingly, \( \pi^* \) peak intensity in Q-carbon is drastically enhanced as compared to parent DLC, in spite of having much lower \( sp^2 \) content (20% \textit{vs} 40% in DLC). The area under the \( \pi^* \) peak can be directly correlated to the density of electronic states near the Fermi level, which is clearly higher in Q-carbon as compared to the DLC and diamond, which are diamagnetic in nature. The temperature-dependent magnetic anisotropy constant calculations in Q-carbon indicate a non-linear dependence with an exponent value of 2.03 which is attributed to the presence of an electronic mixture of \( sp^2-sp^3 \) hybridized states. The temperature-dependent saturation magnetization curve in Q-carbon follows the modified Bloch’s law with the Bloch exponent equal to 2.04, pre-factor of \( 3.02 \times 10^{-6} \text{ K}^{-2.04} \) and a Curie temperature of 570 K. The negative values of the ordinary Hall coefficient in the temperature range 10 to 300 K indicate that the electron band is more conducting than the hole band in Q-carbon. An exponent value of 1.95±0.05 has been extracted from the extraordinary Hall Effect calculations in Q-carbon, suggests that the electron scattering in Q-carbon follows a non-classical “side-jump mechanism”. This electronic scattering mechanism exists in Q-carbon due to the presence of non-conducting centers which distort the wave function and create a local current density. There is an increase in the intensity and FWHM of the \( \pi^* \) peak in Q-carbon (as it is evident from the EEL spectrum) as compared to the as-deposited DLC or diamond. This indicates an increase in the electronic density of the dangling
bonds (present near the Fermi level) leading to exciting magnetic and electrical properties in Q-carbon. The coexistence of room-temperature ferromagnetism and extraordinary Hall effect in Q-carbon thin films suggests that the ferromagnetically spin-polarized carriers can indeed be probed and controlled electronically. Our results clearly show that Q-carbon thin films can be used in spintronics based and various other room-temperature magnetoelectronic applications. We envisage that this discovery of room temperature ferromagnetism and extraordinary Hall effect in Q-carbon will certainly stimulate further research in carbon-based materials.

4.6. Acknowledgements

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4.7. Figures:

Figure 4.1. (a) Schematic of the synthesis of amorphous Q-carbon using pulsed laser deposition followed by pulsed laser annealing technique; (b) Raman spectroscopy of as-deposited amorphous C thin film, Q-carbon, and diamond formed from Q-carbon after PLA; (c) XRD of Q-carbon on c-sapphire; (d) SIMS profile of Q-carbon; and (e) SLIM profiles at various laser energy densities. The red dotted region in (a) shows random DCL (sp³) tetrahedra with sp² bonding at the interfaces in Q-carbon. The inset in (b) shows the peak fitted Raman spectrum of Q-carbon indicating a 75% sp³. The inset in (e) shows the melt-front velocity (20 m/sec) when 0.6 Jcm⁻² laser energy density is used.
Figure 4.2. (a) High-resolution SEM images showing the formation of Q-carbon with the inset indicating (by the black arrow) a first-order phase transformation during the formation of Q-carbon; (b) SEM image indicating formation of single-crystal diamonds at the Q-carbon triple points with the inset showing the formation of nanodiamonds and microdiamonds from Q-carbon; (c) HRTEM image of Q-carbon showing the nucleation of nanodiamonds (NDs); and (d) HRTEM image indicating (by black arrows) the formation of diamond facets. The scale bar in the insets of (a) and (b) are 500 and 200 nm, respectively.
Figure 4.3. (a) HAADF image of Q-carbon on c-sapphire along with the Ronchigram pattern confirming amorphous and crystalline nature of Q-carbon and c-sapphire, respectively; (b) EELS spectra of Q-carbon, as-deposited DLC and diamond; (c) Representative fitting routine performed on Q-carbon EELS spectrum; and (d) the fitted $\pi^*$ peaks indicating an increase in the density of the electronic states in Q-carbon as compared to DLC and diamond.
Figure 4.4. (a) M-H plots of Q-carbon at various temperatures with the insets indicating finite coercivity at 10 K and diamagnetic property of the as-deposited amorphous carbon thin film; (b) MFM image showing distinct magnetic phases of Q-carbon and the rest of the film; and (c) AFM of Q-carbon along with DLC.
Figure 4.5. (a) Temperature-dependent square of magnetic moment with the linear extrapolation indicating a Curie temperature of 568 K with the inset showing the “law of approach“ fitting at 10 K; (b) temperature-dependent magnetic anisotropy with the inset showing $H_c(\sqrt{T})$ dependence; and (c) modified Bloch’s law indicating a Bloch exponent of 2.03 with the inset showing $T_c \sim 570$ K.
Figure 4.6. (a) Five-probe electrical connection (with nulling of offset voltage) for extraordinary Hall effect measurements; (b) Hall resistivity vs magnetic induction plots in Q-carbon at various temperatures; (c) temperature-dependent ordinary Hall coefficient indicating that the electron band is more conducting than the hole band in Q-carbon; and (d) linear fit of $-\ln(R_s)$ vs $-\ln(\rho)$ plot with a slope of -1.95 indicating a “side-jump” non-classical electronic scattering mechanism in Q-carbon.
4.8. References


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5. Electrochromic Effect in Q-Carbon

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Keywords: Q-carbon, electrochromic materials, Raman spectroscopy, electron energy-loss spectroscopy.

5.1. Abstract

Here, we report the electrochromic effect in undoped Q-carbon. This phase of carbon, Q-carbon, is formed by pulsed laser melting of amorphous carbon and subsequent ultrafast quenching process. The excess amount of unpaired electrons near the Fermi energy level in Q-carbon causes a 48% increase in the optical absorption at 265 nm with an applied electric field of 10 V. The Kelvin probe force microscopy (KPFM) also indicates that the Fermi level of Q-carbon is situated ~40 meV higher than that in the neighboring diamond-like carbon region. It is also observed that, with an increase in the tip voltage from 0 to 10 V in KPFM, there occurs an increase in the image phase contrast thereby indicating an increase in the concentration of electrons. This causes an increase in optical absorbance with the application of an electric field in Q-carbon. The direct and indirect optical band gaps in Q-carbon are calculated to be 3.82 and 2.93 eV, respectively using the Tauc analysis. High-resolution scanning electron microscopy, transmission electron
microscopy and selected area electron diffraction pattern depict the formation and amorphous nature of Q-carbon. Raman and electron energy-loss spectroscopy of Q-carbon reveal over 75% \( sp^3 \)-bonded carbon (rest \( sp^2 \)) and excess electrons near the Fermi level. This discovery of electrochromic effect in Q-carbon shows that highly non-equilibrium synthesis can be elegantly used to fabricate smart windows with immense energy-saving applications.

5.2. Introduction

Electrochromic materials modulate their optical properties under the influence of an external electric field. Therefore, electrochromic materials can be integrated with optoelectronic devices, leading to a tremendous saving of energy.\(^1\) The commercial applications of electrochromic materials include smart windows, antiglare car mirrors, devices for frozen-food monitoring, fabrics, and optical information and storage.\(^2,3\) The optical changes in these materials are effected either by an electron-transfer (redox) process or an electrochemical potential change. Electrochromic devices where the electrochromic materials are solid in all the redox states\(^4\) have optical memory (i.e. no further charge injection is required to maintain the electrochromic state), thereby increasing the versatility of the optoelectronic devices.\(^3\) Thin films of WO\(_3\), having the oxidation state W\(^{VII}\), are colorless which turns deep blue (electrochromic) with the formation of W\(^V\) oxidation state (by electron injection process).\(^5\) Therefore, the electron transfer process facilitates a change in the optical properties thereby giving rise to electrochromism (or electrocoloration).\(^6\) During the charge cycling process, ion trapping occurs in electrochromic devices which causes degradation of its optical efficiency.\(^7\) Recently, electrochromic action is also demonstrated in multilayer graphene showing 55% change in optical transmittance in the visible and infrared region under the application of 5 V.\(^8\) The formation of ozone holes in stratosphere prevents the blocking of harmful UV radiation (UVB and UVC) from reaching the
Earth’s surface. Blocking UV radiation is of utmost importance as exposure to UV radiation causes severe irreparable skin burns. Therefore, there is a continued effort for synthesizing superior and robust electrochromic devices which can be electrically controlled in the UV region.

Recently, there has been a renewed interest in electrochromism in carbon-based materials. Carbon-based materials can possess versatile chemical and physical properties due to the electronic hybridization of their outermost 2s and 2p electrons, thereby leading to the formation of sp, sp$^2$ and sp$^3$ hybridized electronic states. Interestingly, tuning of the sp$^2$/sp$^3$ ratio in carbon-based materials gives rise to novel functionalities. In a search for unique physical and chemical properties of carbon, we have synthesized a new phase of amorphous carbon, Q-carbon, by ultrafast quenching of superundercooled molten carbon. This phase of carbon has a distinct entropy, thermodynamically stable, ferromagnetic, harder than diamond, and highly electron-emissive in nature. Upon doping with boron, Q-carbon shows high-temperature superconductivity (BCS, s-wave) with record superconducting transition temperature. The structure of Q-carbon consists of a non-periodic arrangement of tetrahedrally-bonded carbon (sp$^3$) with sp$^2$ at the interfaces. The fraction of sp$^3$ bonding ranges from 75-85 % and the rest is sp$^2$. The formation of Q-carbon is accomplished by pulsed laser annealing of diamond-like carbon (formed by pulsed laser deposition of a glassy carbon target) by using a nanosecond Excimer laser. During the process of pulsed laser annealing, there occurs an avalanche of electrons to the conduction band and a quick transfer of the electronic energy to phonons (thereby leading to the formation of molten carbon). With subsequent quenching of the molten carbon (metallic) in a superundercooled state, it leads to the formation of the densely packed amorphous Q-carbon structure. The quenching rates (solidification and regrowth velocities) determine the formation of Q-carbon (solidification velocities exceeding 10 m/sec) and/or single-crystal diamond (solidification velocities ~ 5
m/sec). The quenching rates are governed by thermal conductivities of diamond-like carbon (as-deposited DLC) and the substrate (sapphire). We have also reported the formation of nano, micro and large-area single crystal diamond using the pulsed laser annealing technique. Similar strategies are adopted for conversion of h-BN into Q-BN and/or c-BN structures, which has tremendous applications in solid-state multifunctional electronic devices. In the present study, we show the electrochromic action in Q-carbon thin films without the use of an electrolyte. The electrochromic action is confined to the UV region without causing an appreciable change in the visible region of the solar spectra. Q-carbon electrochromic devices can effectively block the harmful and energetic UVC radiation (wavelength = 100-280 nm), which can reach the Earth’s surface due to the formation of ozone holes. The conjunction of Q-carbon based electrochromic devices with conventional electrochromic devices, which work best in the visible and IR region, will lead to the fabrication of superior smart windows. Therefore, we envisage that the use of Q-carbon in electrochromic devices will assist in the fabrication of UV-blocking smart windows, optoelectronic devices, and enrich the physics of electrochromism in carbon-based materials.

For the present research, amorphous carbon thin films were deposited onto high-quality double-side polished c-sapphire (optical band gap = 8.7 eV) using pulsed laser deposition in the temperature range of 30-300°C and 4.0×10⁻⁷ Torr base pressure. Since the UV-vis measurements were performed in the transmission geometry, double-side polished sapphire substrates were used.

5.3. Results and discussion

Figure 5.1 depicts the high-resolution TEM, SAED, high-resolution SEM, Raman spectroscopy and core-loss EEL spectra of Q-carbon. As it is evident from the figure 5.1(a), that there exist nanodiamonds (100% sp³) in Q-carbon (marked by circles). The fast Fourier transformation (FFT) of the nanodiamonds and the rest area are shown as lower left and upper right insets, respectively.
The FFT of nanodiamond regions and the rest area show crystalline diamond structure and amorphous region, respectively. Since Q-carbon is formed after the quenching process of molten carbon in a superundercooled state, it adheres strongly to the sapphire substrate. The formation of Q-carbon is strongly dependent on the thermal conductivities of the substrate and the as-deposited amorphous carbon thin film. Selected area electron diffraction (SAED) pattern of Q-carbon (figure 5.1(b)) depicts its amorphous nature and the presence of distinct (111) and (022) diffraction rings. Diffused but distinct Bragg reflections from the two planes indicate the preservation of the tetrahedrally bonded $sp^3$-C in the Q-carbon structure. The high-resolution SEM (in figure 5.1(c)) shows highly electron-emissive Q-carbon structure formed after the ultrafast quenching of molten carbon. The SEM also indicates the formation of large-area Q-carbon along with the unconverted (low electron-emissive) DLC structure. Figure 5.1(d) indicates room-temperature unpolarized Raman and EEL spectra (lower inset) of Q-carbon. The Raman spectrum of the as-deposited amorphous carbon on sapphire shows the presence of peaks centered at ~1340 ($sp^3$ fraction) and ~1560 cm$^{-1}$ ($sp^2$ fraction). As it is evident from the Raman spectrum of Q-carbon that there is a distinct Raman active peak centered at 1329 cm$^{-1}$. This peak arises due to the nucleation of nanodiamonds in the Q-carbon structure and is also seen in the HRTEM image. An increased FWHM of the diamond peak in Q-carbon is due to phonon confinement effects (arising due to the presence of nanodiamonds in the Q-carbon structure). The Raman spectra of Q-carbon and as-deposited amorphous carbon clearly indicate an increase in the $sp^3$ fraction in Q-carbon (as compared to as-deposited amorphous carbon). To calculate the $sp^3$ fraction in Q-carbon, peak-fitting was performed and is shown as the upper right inset in figure 5.1(d). The Raman spectrum of Q-carbon can be deconvoluted to three peaks centered at 1140, 1329 and 1560 cm$^{-1}$. The first two Raman active peaks arise due to the presence of $sp^3$ entities$^{19}$ and the third peak is due to $sp^2$
entity. The diamond peak is broader and is shifted to lower wavenumber (1329 cm\(^{-1}\) in Q-carbon from 1332 cm\(^{-1}\) in microdiamond) due to small crystallite size of \(sp^3\) entities (phonon confinement) and residual stress\(^{20}\) in Q-carbon thin films. These stresses are generated due to ultrafast melting and subsequent quenching process. The isotropic biaxial stress (\(\sigma_{\text{diamond}}\)) can also be calculated from the peak shift using the following equation: 
\[
\sigma_{\text{diamond}} = -0.49(\omega_{\text{diamond}} - \omega_0) \text{ GPa/cm}^1.
\]

The residual stress calculated from the peak shift is ~1.5 GPa in the Q-carbon thin films. The peak fitting of the Q-carbon Raman spectrum yields 75% \(sp^3\) and rest \(sp^2\) hybridized electronic states. Similar \(sp^3\)% (76%) is calculated after peak-fitting of the EEL spectrum of Q-carbon (shown as the lower inset in figure 5.1(d)). The room-temperature core-loss EEL spectrum of Q-carbon reveals the \(sp^3\) (\(\sigma^*\)) and \(sp^2\) (\(\pi^*\)) bonding characteristics. The antibonding electronic states are centered at 285 eV (\(\pi^*\)) and 293 eV (\(\sigma^*\)). The EEL spectrum of Q-carbon is considerably different from that of glassy carbon and diamond\(^{22}\). The \(\pi^*\) peak is sharper and \(\sigma^*\) peak is broader in Q-carbon as compared to the glassy C. In contrast to the characteristic fine post-edge structures in the EELS of diamond showing distinct EELS peak at 292, 297, 305, and 326 eV, Q-carbon shows broad peaks ~300 eV. The ELNES (electron energy loss near edge spectroscopy) region of diamond and Q-carbon is also shown (shaded region) in the lower inset of figure 5.1(d). The dip at 302 eV in the diamond ELNES corresponds to the second absolute band gap (II\text{nd}) of diamond\(^{23}\). The broadening of the antibonding states associated with the \(\sigma^*\) bond in Q-carbon is a local electronic effect arising due to interaction of similar electronic \(sp^3\) states oriented at different direction (amorphous structure). This is also an indication of a disordered arrangement of the tetrahedrally bonded C atoms (\(sp^3\)-bonded C) in Q-carbon. The long-range periodic structure of crystalline diamond gives rise to modulation to the density-of-states\(^{24,25}\) and is evident from the \(\sigma^*\) region in EELS. The schematic diagram of the bonding and antibonding electronic states is
shown as an inset in figure 5.1(d). The Fermi energy level is situated between the $\pi$ and $\pi^*$ electronic states. The enhancement of $\pi^*$ intensity indicates a higher density of unpaired electron cloud near Fermi energy level in Q-carbon as compared to glassy C.\textsuperscript{22}

As discussed above, there is a high density of unpaired electrons in Q-carbon. This is due to the reason that Q-carbon is formed after quenching of the metallic liquid melt of carbon. Figure 5.2(a) indicates the UV-visible spectroscopy of Q-carbon at zero volt (0 V) and under the application of external electric fields. As it is evident from the plots that there is a considerable increase in absorbance in Q-carbon with the application of an electric field. The maximum optical absorbance in Q-carbon is centered at 265 nm. Applying a voltage assists in a change of the nature of the electronically charged states in the Q-carbon structure. Since Q-carbon has a negative electron potential \textit{w.r.t.} the surrounding DLC matrix, application of an external electric field changes the electron concentration in Q-carbon thereby changing its absorbance. This case is similar to the standard electrochromic films, where the absorbance is controlled by the transport of ions and is also referred to as the “rocking chair” process in lithium battery technology.\textsuperscript{26} A similar nature of electronic switching between the $\pi/\sigma$ orbital states has been observed in Trinuclear Cyanines (TNCs), a carbon-based material.\textsuperscript{27} This intramolecular switching gives rise to a pronounced electrochromic effect in TNCs.\textsuperscript{27} Figure 5.2(b) indicates an increase in $\Delta$ absorbance with the application of the external electric field. The absorbance at 0 V is considered as the baseline in the above-mentioned calculations. The inset shows the % of absorption enhancement in the Q-carbon structure with the application of an external electric field. An enhancement of $\sim$48% is observed at $\sim$265 nm in Q-carbon with the application of an external electric field of 10 V. To further understand the optical properties of Q-carbon, Tauc analysis was performed and is shown in figure 5.2(c). The Tauc approach was derived using the parabolic band representation of localized energy
states for amorphous materials and can, therefore, be employed to calculate various optical transitions in Q-carbon. The optical direct and indirect band gaps of Q-carbon were extracted using the following Tauc equation (5.1):

$$\alpha = \frac{B(h\theta - E_g)^n}{h\theta}$$

(5.1)

where $h\theta$ is the energy of the incident photon, $\alpha$ is the absorption coefficient, $E_g$ is the optical band gap, $B$ is a material dependent constant, and $n$ is the exponent whose values depend on the nature of the transitions ($n = 1/2$ for direct allowed transitions, $n = 3/2$ for direct forbidden transitions, $n = 2$ for indirect allowed transitions, and $n = 3$ for indirect forbidden transitions). As it is evident from the Tauc plots, that the intercept of the straight line on the $h\theta$ axis corresponds to the optical band gap of Q-carbon. The direct and indirect optical band gaps in Q-carbon are calculated to be 3.82 and 2.93 eV, respectively. The bandgap widening in nanostructured Q-carbon can be due to the quantum confinement effect. This occurs due to the quantum localization of energy which is partially balanced by the Coulomb repulsion and electron correlation. Considering the band gap of diamond and graphite as 5.47 and -0.04 eV, respectively the optical band gap of 75% $sp^3$ (and rest 25% $sp^2$) Q-carbon phase can be calculated to be 4.09 eV, which is very close to the value of the direct band gap calculated using the Tauc plot. It is also important to note that the absorption spectra of Q-carbon may contain small contributions from subgap absorption tails (due to defect states and intraband transitions) and nonlinear effects (plasmonic scattering), which will affect the Tauc analysis. In the case of allowed direct and indirect transitions, the momentum matrix element characterizing the transition is non-zero. Therefore, the transitions are possible if sufficient energy is given to the electrons in the valence band. On the other hand, the momentum matrix element is zero in the case of forbidden direct and indirect transitions occurring at 2.95 and 2.96 eV, respectively in Q-carbon.
Figure 5.3(a) represents the contact potential difference (CPD)-KPFM image of Q-carbon along with the neighboring DLC structure. It is evident from the figure 5.3(a) that Q-carbon is at a negative surface potential (≈40 meV) as compared to the DLC. This leads to electron emissive properties in Q-carbon. The electron-emissive nature in Q-carbon helps to distinguish itself (glows) from DLC when it is imaged in the immersion mode in FESEM (where secondary electrons are taken into consideration). The CPD is defined by the equation (5.2):

\[ \text{CPD} = \frac{(\Phi_{\text{sample}} - \Phi_{\text{tip}})}{e} \] (5.2)

where, \( \Phi_{\text{tip}} \), \( \Phi_{\text{sample}} \), and \( e \) denote workfunction of the KPFM tip and the sample and electronic charge, respectively. Therefore, a negative CPD indicates lower workfunction of the sample as compared to the tip. The KPFM surface potential results indicate that the Fermi level of Q-carbon is situated ≈40 meV higher than that of the neighboring DLC. Figures 5.3(b) and (c) indicate KPFM phase images with 0 and 10 V applied tip bias voltage (\( V_{\text{tip}} \)), respectively. The applied tip voltage is related to CPD by the following equation (5.3):

\[ V_{\text{tip}} = (V_{\text{DC}} - V_{\text{CPD}}) + V_{\text{AC}} \sin(\omega t) \] (5.3)

where, \( V_{\text{DC}} \) and \( V_{\text{AC}} \) denote the backing voltage typically controlled by the bias feedback loop and sinusoidal voltage modulation at the excitation frequency (\( \omega \)), respectively. With an increase in the tip bias, \( V_{\text{CPD}} \) increases. Therefore, an increase in the tip voltage from 0 to 10 V increases the phase contrast in the KPFM phase image as is evident in the figures 5.3(b) and (c). With the increase in the applied voltage in the sample, there is an increased concentration of the electrons in the Q-carbon structure. This causes an increase in the optical absorbance with the applied electric field. As it is evident from the schematic drawing of the band structure of Q-carbon in figure 3(d), that there exists a direct band gap of 3.82 eV and an indirect band gap of 2.93 eV. There is also ≈ 40 meV energy difference between the Fermi level in Q-carbon and DLC.
(surrounding the Q-carbon). The Fermi level in Q-carbon is situated close to the conduction band (as Q-carbon is \( n \)-type in nature).\(^{22}\) The energy level of the conduction band (CB) in Q-carbon and DLC are taken at -1.6 eV (from the vacuum level). Considering the band gap of Q-carbon and DLC as 3.8 and 5.4 eV, respectively, the position of the valence band (VB) is calculated to be at -5.4 eV (in Q-carbon) and -7.0 eV (in DLC). Therefore, with the application of an electric field, there occurs a change in the energy level of the electrodes (Indium). This causes a change in the effective optical band of the Q-carbon device thereby exhibiting an electrochromic behavior.

### 5.4. Summary

In summary, we have shown that undoped Q-carbon is electrochromic in nature. Q-carbon is formed by pulsed laser melting of amorphous carbon and subsequent quenching process. Raman and electron energy loss spectroscopy of Q-carbon reveals 75% \( sp^3 \)-bonded carbon (and rest \( sp^2 \)). The excess amount of unpaired electrons near the Fermi energy level in Q-carbon causes a 48% increase in the optical absorption at 265 nm with an applied electric field of 10 V. The direct and indirect optical band gaps in Q-carbon are calculated to be 3.82 and 2.93 eV, respectively from the Tauc analysis. Electron microscopy and SAED patterns illustrate the formation (of large-area) and amorphous nature of Q-carbon. The KPFM results indicate that the Fermi level of Q-carbon is situated ~40 meV higher (or closer to the vacuum level) than that in the neighboring diamond-like carbon region. It is also observed that there is an increase in the KPFM phase contrast with the increase in the tip voltage from 0 to 10 V. This shows an increase in the concentration of electrons which ultimately causes an increase in optical absorbance (with the application of an electric field in Q-carbon). This discovery of electrochromic effect in Q-carbon proves that highly non-equilibrium synthesis and novel carbon-based materials can be used to fabricate smart electronics having energy-saving applications.
5.5. Figures:

**Figure 5.1.** (a) HRTEM of Q-carbon showing the nanodiamonds (ND) and the fast Fourier transformation (FFT) of the nanodiamonds and the rest area are shown as lower left and upper right insets, respectively; (b) Selected area electron diffraction (SAED) pattern of amorphous Q-carbon showing the (111) and (022) diffraction rings; (c) FESEM of Q-carbon; and (d) Raman spectrum of Q-carbon along with the insets showing core-loss EELS (of Q-carbon and diamond), fitted Raman spectrum of Q-carbon showing 75% \( sp^3 \)-bonded carbon and schematic of bonding and antibonding orbitals.
Figure 5.2. (a) UV-vis plots of Q-carbon under the application of an external electric field; (b) Δ Absorbance vs wavelength plots indicating a maximum change of optical absorbance at 265 nm with the inset showing absorption enhancement up to 48% at 265 nm; and (c) Various optical transitions in Q-carbon.
Figure 5.3. (a) KPFM image indicating a ~40 meV difference in the work function between Q-carbon and the rest of the film; (b) and (c) indicate KPFM phase contrast image at 0 V and 10 V tip bias, respectively; and (d) Schematic of energy band diagram in electrochromic Q-carbon.
5.6. References

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6. A Novel High-Temperature Carbon-Based Superconductor: B-Doped Q-Carbon

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6.1. Abstract

Following a brief report on high-temperature superconductivity in B-doped Q-carbon (ACS NANO, DOI: 10.1021/acsnano.7b01294), we present detailed structure-property correlations to understand the origin of superconductivity in strongly bonded lightweight materials and methods to further enhance the superconducting transition temperature ($T_c$). Nanosecond melting of carbon in a super undercooled state and rapid quenching result in strongly bonded unique phase of B-doped Q-carbon. The temperature-dependent resistivity and magnetic susceptibility measurements demonstrate a type II superconductivity in this material with a transition temperature of 36.0±0.5 K and upper critical field of 5.4 T at ~0 K. It has also been shown that in B-doped Q-carbon, the upper critical magnetic field ($H_{c2}(T)$) follows $H_{c2}(0) [1-(T/T_c)^{2.1}]$ temperature dependence and is consistent with the Bardeen-Cooper-Schrieffer formalism. In the present study, B-doped Q-carbon
thin films are formed on sapphire substrates by employing pulsed laser annealing using a nanosecond excimer laser. This process involves the rapid quenching of highly undercooled melt of homogenously mixed B and C. Through the structure-property correlation measurements in B-doped Q-carbon, we estimate a higher electronic density of states near the Fermi level. Higher density of states near the Fermi-level along with higher Debye temperature and phonon frequency are responsible for enhanced $T_c$. As a result of rapid melting and quenching, we can achieve 17.0±1.0 or higher atomic % of B in the electrically active sites of Q-carbon which leads to the formation of shallow electronic states near the valence band maximum. From the critical current density versus field moments, the value of critical current density ($J_c$ (2T)) in B-doped Q-carbon at 21 K is calculated as $4.3\times10^7$ Acm$^{-2}$, which indicates that this novel material can be used for the persistent mode of operation in MRI and NMR applications. This discovery of high-temperature superconductivity in B-doped amorphous Q-carbon shows that non-equilibrium synthesis technique using super undercooling process can be used to fabricate materials with greatly enhanced physical properties.

6.2. Introduction

The versatility in the arrangements of C atoms to form various allotropes and phases has led to the discovery of several new structures with unique properties. One of them is the evolution of superconductivity in the carbon-based materials. In principle, high-temperature superconductivity can be achieved in the structures with strongly-bonded light C atoms due to the large Debye frequency. However, the lack of strong electron-phonon coupling and electronic density of states near the Fermi level in the pure C structures limits to achieving higher superconducting transition temperatures ($T_c$). The superconductivity has been observed in carbon-based materials, e.g. graphite intercalated superconductors ($T_c \sim 15 \text{ K}$),$^1$ single-walled carbon nanotubes ($T_c \sim 15 \text{ K}$),$^2$
alkali doped fullerenes ($T_c \sim 40$ K), $^3$ B-doped diamond ($T_c \sim 11$ K), $^4$ etc. Superconductivity in the bulk B-doped diamond is limited to 11 K, where it is caused by a strong electron-phonon mediated pairing of the charge carriers, well established by the Bardeen–Cooper–Schrieffer formalism.$^5,^6$

Superconductivity in B-doped diamond is the most studied subject due to its broad applications in electronics.$^7,^8$ It is shown experimentally that $T_c$ ranging from 4 K to 11 K is achieved in B-doped diamond with increasing boron concentration in substitutional lattice sites of diamond.$^4,^7,^9$ According to theoretical predictions, without considering the electronic compensating defects, $T_c$ in B-doped diamond can be increased up to 55 K with $\sim 20$ atomic % B.$^{10}$ Increasing the concentration of B dopant ($n > 10^{20}$ cm$^{-3}$) decreases the activation energy and it exhibits a metal-like behavior.$^9$ Achievement of such higher concentrations by equilibrium Chemical Vapor Deposition (CVD) methods is a major challenge. Therefore, non-equilibrium methods based upon energetics of plasma and lasers, are needed to attain concentration beyond the thermodynamic solubility limits. However, theoretical studies also indicate that the B atoms, beyond the solubility limits generate strains and form dimers in the B-doped diamond.$^{11}$ This pairing leads to the symmetric and anti-symmetric combinations of bound states of B, which do not contribute to the density of states at the Fermi level, and adversely affect the value of $T_c$.$^{11}$ This remains a major challenge in improving the superconducting properties of B-doped diamonds, grown by CVD based techniques.$^4,^{12,13}$ The CVD process is close to an equilibrium synthesis method and it restricts the B-doping in substitutional sites above the thermodynamic solubility limits, which is about 2.0 at% in diamond.

Non-equilibrium processes, such as pulsed laser deposition, pulsed laser annealing, plasma enhanced CVD and ion implantation, allow dopant concentration exceeding the thermodynamic solubility limits. The doping by non-equilibrium laser quenching is a primary focus of the present
work. It has also been established that the amorphous/disordered counterparts of the crystalline phases exhibit higher $T_c$. Recently, the reports indicate experimentally measured superconductivity in amorphous Bi ($T_c=6$ K) which is significantly higher than that in crystalline Bi ($T_c=53$ mK).\textsuperscript{14} This is due to the increased number of electronic density of states near the Fermi level and strong electron-phonon coupling in amorphous Bi.\textsuperscript{15} It is also been suggested that the mobility of the Cooper pairs in amorphous structure is not hindered by the transition from semi-metallic to metallic behavior of Bi during the amorphization process.\textsuperscript{15} Based on these experimental studies and theoretical predictions, we embarked upon the creation of a new class of strongly bonded carbon-based amorphous materials where dopant concentration can be exceeded beyond thermodynamic limits.

Recently, we have reported the formation of a novel phase of carbon (Q-carbon) by melting of carbon layers in a super undercooled state by using pulsed laser annealing and subsequent quenching of molten carbon layers.\textsuperscript{16-18} Q-carbon is formed after nanosecond laser melting and subsequent quenching of amorphous carbon thin film deposited on c-sapphire. This phase is a new state of carbon which comprises a mixture of mostly four-fold $sp^3$ (75-85\%) and the rest three-fold $sp^2$ bonded carbon (with distinct entropy).\textsuperscript{16-18} Upon pulsed laser irradiation, electrons are excited into the conduction band and these excited electrons transfer their energy quickly (within about a picosecond) into phonons, leading to rapid heating and melting. Depending on the laser energy density, physical properties of the amorphous film and the substrate, a process of super undercooling and quenching takes place which leads to the formation of metastable state of amorphous Q-carbon structure possessing unique properties.\textsuperscript{16} High $T_c$ in strongly-bonded lightweight materials can be achieved if doping is high enough to sustain a moderate electron-phonon coupling. Q-carbon consists of a phase mixture of $sp^3$ (>80\%) and $sp^2$ bonded C atoms and
exhibits interesting properties, such as low electron affinity in electric field, room temperature ferromagnetism, etc.\textsuperscript{17} Undoped Q-carbon shows room-temperature ferromagnetism with Curie temperature above 570 K. Upon doping with B, Q-carbon turns diamagnetic and exhibits high-temperature superconductivity with $T_c \geq 36$ K. We have employed the nanosecond pulsed laser annealing on the B/amorphous C multilayer structures to synthesize B-doped Q-carbon. The structure, properties and distribution of B atoms in Q-carbon are characterized by various nanoscopic and microscopic spectroscopic techniques, such as Secondary ion mass spectroscopy (SIMS), electron energy-loss spectroscopy (EELS), energy dispersive spectroscopy (EDS) in a scanning transmission electron microscope (STEM), Raman spectroscopy, Scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). We examine the superconductivity behavior of B-doped Q-carbon using the resistance versus temperature and the temperature-dependent magnetic susceptibility measurements in PPMS and superconducting quantum interference device (SQUID), respectively. We reported initial results\textsuperscript{19} on the discovery of high-temperature superconductivity in B-doped Q-carbon. In this paper, we present details of laser-solid interaction modeling and melting, experimental procedures, critical current versus temperature, temperature versus field and possibilities of higher $T_c > 37$ K with increasing boron concentration. Finally, we discuss the origin and nature of superconductivity in B-doped Q-carbon. With this study, we expect that the non-equilibrium undercooling assisted synthesis methods can be used to fabricate highly doped materials, which have greatly enhanced superconducting properties.

6.3. Experimental

Alternating layers of boron and amorphous carbon thin films are deposited onto c-sapphire using pulsed laser deposition (PLD) with a total thickness ranging from 100-500 nm in the temperature
range of 300-570 K and 1.0E-07 torr operating pressure (base pressure). This operating pressure was achieved in less than three hours by employing an (oil-free) scroll pump in conjunction with a turbo molecular pump. The PLD can be made highly nonequilibrium forward-directed process by controlling the laser spot size. For the PLD process, KrF excimer laser (laser wavelength=248 nm, pulse duration=25 ns) was used. The pulsed laser beam is rastered through the glassy carbon and B (sector) targets mounted on the same target holder during the growth process. The laser energy density used during the deposition process ranges from 3.0-3.5 Jcm⁻². Before the start of thin film deposition, the targets are pre-ablated to eliminate surface contaminants. Subsequently, these B-doped amorphous carbon thin films are irradiated with nanosecond ArF excimer laser (laser wavelength=193 nm, pulse duration=20 ns) using laser energy density 0.6-1.0 Jcm⁻². The pulsed laser annealing technique melts the B-doped carbon film in a highly super undercooled state, and followed by quenching to complete the whole process within 200-250 ns. This leads to conversion of amorphous carbon films into B-doped quenched carbon structure where B concentration can exceed the thermodynamic solubility limit. The characterization of the B-doped Q-carbon phase was carried out using Raman spectroscopy, XPS, SIMS, EELS, FESEM, and SQUID magnetometry. Alfa300 R superior confocal Raman spectroscope with a lateral resolution less than 200 nm was employed to characterize the Raman-active vibrational modes. Crystalline Si was used to calibrate the Raman spectra, which has its characteristic Raman peak at 520.6 cm⁻¹. High-resolution SEM with sub-nanometer resolution was carried out using FEI Verios 460L SEM to characterize the as-deposited and the laser-irradiated films. The B atoms are incorporated into Q-carbon during rapid liquid-phase growth and solute trapping, where dopant concentrations can exceed far beyond the thermodynamic solubility limits. High-resolution SEM measurements were carried out using the field emission mode in FEI Verios 460L SEM. Time-of-Flight
Secondary Ion Mass Spectrometer (TOF-SIMS) with a lateral resolution of <300 nm was used to detect the presence of C, O, B, Al and other trace impurity elements in the B-doped Q-carbon thin films. XPS with X-ray energy 10-14kV for Al/Mg and Al/Ag sources employing superior analyzer (PHOIBOS 150) having <1eV resolution were used for the collection of XPS data. FEI Quanta 3D FEG with dual beam technology employing both electron and ion beam guns was used for preparing cross-sectional TEM samples. A low energy ion beam (5 kV, 10 pA) was used to cleanup the FIB surface damage. Aberration-corrected STEM-FEI Titan 80-300 was used in conjunction with electron energy-loss spectroscopy (EELS with a resolution of 0.15 eV) to acquire HAADF images and EELS spectra of B-doped Q-carbon thin films. The electron probe current used in the experiment was 38±2 pA. The EELS data was acquired with a collection angle of 28 mrads. Quantum design magnetic property measurement system (MPMS3) was used to measure magnetic properties of thin films. VSM and DC modes were used for measuring field- and temperature-dependent magnetization. The magnetic measurements were made with samples mounted parallel to the magnetic field. The SQUID magnetometer can detect magnetic field with ~10⁻⁸ emu sensitivity and has a working temperature range: 1.8-400 K. The temperature stability is ±0.5 % and the magnetic field uniformity is 0.01% over 4 cm (sample length). The magnetic field strength of as high as 7 Tesla (with a field charging resolution of 0.33 Oe) was used to perform the field dependent measurements in B-doped Q-carbon samples. Temperature-dependent resistivity measurements were carried out in the physical property measurement system (PPMS) at zero magnetic field.

6.4. Results and discussion

Figures 6.1(a) and (b) represent TOF-SIMS of as-deposited B&C and B-doped Q-carbon thin films, respectively. As it is evident from the figure 6.1(a) that there are alternating layers of B and
amorphous carbon in the as-deposited thin films. The as-deposited layered thin films are engineered to have a top amorphous carbon layer. This results in an enhanced laser coupling due to low reflectivity and high absorption of amorphous carbon as compared to metallic B at 193 nm. An effective coupling is required during the pulsed laser annealing (PLA) process\textsuperscript{20,21} to cause melting and subsequent quenching to form B-doped amorphous Q-carbon structures. The C and B concentration profiles in the as-deposited sample exhibit periodic variation. However, after the pulsed laser annealing B and C concentration profiles are uniform, as shown in figure 6.1(b). The high-energy laser photons cause an avalanche of electrons in the conduction band which interact with phonons, thereby melting amorphous carbon and B composite layers. The high concentration of free electrons caused by laser excitation leads to a non-equilibrium phase transition with a considerable modification of the interatomic bonding. The energy is transferred from the excited electrons to phonons thereby causing a homogeneous melting of the laser annealed region. During this melting process, the B dopants diffuse into molten Q-carbon to form a homogeneous mixture. The PLA process is completed in less than 200-250 ns, the details of which are explained in the last section (laser-solid interaction and melting mechanism). Using the two-dimensional diffusion equation \[ X=2(D^*t)^{0.5} \], the diffusivity coefficient (D) is calculated as \( \sim 2E-04 \text{ cm}^2/\text{sec} \). This high value of diffusivity is consistent with diffusion of B in liquid carbon during the PLA process. The high diffusivity in the liquid phase helps the formation of homogeneous B-doped Q-carbon, with B concentrations exceeding thermodynamic solubility limits of 2.0 at % in diamond. Higher B concentration is crucial for superconductivity in this material. The results from SIMS spectra also indicate that the as-deposited and PLA samples do not contain any impurities within a resolution of a few ppm.
Figure 6.2(a) depicts unpolarized Raman spectroscopy of as-deposited B-C, B-doped Q-carbon, and HFCVD grown B-doped diamond (formed from B-doped Q-carbon) using 532 nm as the excitation source. There is a considerable increase in the \( sp^3 \) fraction in PLA B-doped Q-carbon (85\%) as compared to as-deposited B-C sample. The inset in figure 6.2(a) shows the fitted cumulative curve in B-doped Q-carbon from which the \( sp^3 \) fraction can be extracted. In the range of 900-2000 cm\(^{-1}\), the spectrum can be deconvoluted into three Raman-active vibrational modes centered at 1105 cm\(^{-1}\), 1322 cm\(^{-1}\), and 1567 cm\(^{-1}\). The peak centered at 1105 cm\(^{-1}\) corresponds to the \( sp^2 \) dangling bonds on the surface of nanodiamonds. The unsaturated \( sp^2 \) bonds are predominantly seen in nanodiamonds as compared to microdiamonds or large area single crystal diamonds. The second and third peaks correspond to the presence of nanodiamonds and graphitic entities (G peak), respectively. The undoped phase of Q-carbon which is formed by nanosecond laser irradiation and subsequent quenching process, contains 75-85\% \( sp^3 \) bonding. The \( sp^3 \) fractions calculated in B-doped Q-carbon superconducting thin films after curve fitting varies from 83-86\%. The low intensity of the G peak is indicative of less graphitization in B-doped Q-carbon samples. The HFCVD prepared B-doped diamond by using B-doped Q-carbon as a template has a sharp diamond peak centered at 1331 cm\(^{-1}\) and a graphitic hump at 1557 cm\(^{-1}\). B-doped Q-carbon thin films have nuclei of B-doped diamond which grow during the HFCVD process. This leads to the formation of B-doped diamond at lower temperatures and time as compared to previously reported CVD synthesized B-doped diamond. Due to the presence of quantum mechanical interference between the zone-center Raman active optical phonon and the continuum of electronic states created by B atoms, there occurs an asymmetry and red-shift of the diamond peak in the B-doped Q-carbon thin films. In the case of B-doped polycrystalline diamond samples, there are vibrational modes between 475-1225 cm\(^{-1}\) which are due to maxima in the phonon density of
states (PDOS). These peaks in B-doped diamond thin films suggest distortion and the presence of defects in the diamond lattice. Reports also indicate that these peaks originate from local vibrational modes of B pairs present in the interstitial sites. High-resolution Raman spectroscopy of B-doped Q-carbon thin films shows the absence of these peaks, suggesting B doping in electrically active sites of Q-carbon. The vibrational mode centered at ~ 500 cm\(^{-1}\) in B-doped diamond suggests the presence of B pairs in the interstitial sites of the diamond. This causes a distortion of the hole-hole interaction at lower temperatures, thereby reducing \(T_c\) in B-doped diamond to 25.0±0.5 K from 36.0±0.5 K in B-doped Q-carbon. The electronic Raman spectra of B-doped Q-carbon, as-deposited B-C, B-doped diamond (by HFCVD), and c-sapphire substrate are shown in figure 6.2(b). The results show a distinct shallow acceptor energy level at 33.3 meV in B-doped amorphous Q-carbon, as compared to previously reported value of 37.0 meV in heavily B-doped crystalline diamond. As it is evident from the figure 6.2(b) that there are no electronic Raman transitions from 150-400 cm\(^{-1}\) in c-sapphire (substrate) and as-deposited B-C thin films. In the B-doped diamond thin films, there are various electronic transitions at 31.2 meV, 35.3 meV, and 41.6 meV. The first transition at 31.2 meV corresponds to 1s to 3s electronic transition, whereas the other two correspond to 1s to 4s transition. It has already been reported that at low B concentrations (<1E18 cm\(^{-3}\)) the electronic transitions pertaining to only 1s(p\(_{3/2}\)) → 1s(p\(_{1/2}\)) occur. This transition is seen in extremely low-concentration B-doped diamond samples at ~ 16 cm\(^{-1}\). Lyman series electronic transitions corresponding to 1s to ns transitions are predominantly seen in heavily B-doped diamond samples. There also occurs spin-orbit splitting (formation of p\(_{3/2}\) and p\(_{1/2}\)) of the acceptor states whose value linearly increases with the increase in principal quantum number. The value of spin-orbit splitting in B-doped Q-carbon is found to be ~ 7 meV as compared to ~ 6 meV in B-doped diamond and ~6.3 meV in HFCVD B-doped diamond. This coupling
causes a considerable overlap of the electronic acceptor states thereby increasing the density of the electronic density of states near the Fermi energy level. The schematic of electronic transitions and the energy levels are shown in figure 6.2(c). The presence of a shallow acceptor state at ~37 meV and ~6 meV spin-orbit splitting of the valence band in B-doped diamond cause superconductivity in B-doped diamond. This acceptor state is associated with the formation of metallic B-C nanosheets.\textsuperscript{24} In B-doped Q-carbon, the formation of a shallow acceptor energy level at ~33 meV results from the enhanced B concentration, and it is situated near the valence band maximum. The spin-orbit splitting associated with this energy level is ~7 meV. This causes an increase in the density of the electronic acceptor states near the Fermi level, which leads to high $T_c$ superconductivity in B-doped Q-carbon. As compared to the previously reported value of the shallow acceptor state at ~ 37 meV in B-doped diamond ($T_c = 5$ K), the HFCVD B-doped samples show the presence of an acceptor state at 35.3 meV, situated close to the valence band maximum. The B-doping in Q-carbon introduces a phonon softening of the diamond-related zero-optical phonon peak (from 1332 cm$^{-1}$ in diamond to 1322 cm$^{-1}$ in B-doped Q-carbon). A similar downshift is observed in the case of B-doped diamond thin films which is related to electron-phonon coupling thereby leading to superconductivity.\textsuperscript{26,27} The softening of phonon modes and the creation of new vibrational modes also cause an increase in the $T_c$ of the HFCVD prepared B-doped diamond prepared using B-doped Q-carbon as the template. There is no evidence of the formation of crystalline B-C phases. B-doped carbon nanotubes ($T_c$=12 K) have characteristic radial breathing mode (RBM) at ~ 200 cm$^{-1}$, which denotes the out-of-plane phonon vibrational mode. The pressure induced $T_c$ as observed in these materials are directly related to an increase in the phonon frequency of RBM.\textsuperscript{28,29} BC$_3$ and BC$_5$ phases have distinct Raman-active vibrational modes centered at ~500 and 1200 cm$^{-1}$. In addition to that, these B-C phases are crystalline in nature and have XRD peak
at \(2\theta \approx 10^0.3^0\). The XRD of B-doped Q-carbon contains no diffraction peaks corresponding to B-C crystalline phases, and there are no Raman peaks at 200 and 500 cm\(^{-1}\).

The X-ray diffraction spectrum of B-doped Q-carbon is shown in figure 6.3(a). The diffraction peak at 42.23\(^0\) (2\(\theta\)) corresponds to (0006) of the c-sapphire substrate. There are no other peaks in the x-ray scan, thereby indicating that the synthesized B-doped Q-carbon samples are pristine in nature. The spectrum also indicates that the B-doped Q-carbon is amorphous. Figure 6.3(b) depicts the XPS survey scans of as-deposited and B-doped Q-carbon thin films. The inset in figure 6.3(b) shows the high-resolution XPS scan of the PLA sample in the binding energy range 186-198 eV. There is a clear increase in C/O ratio after laser annealing. This is an indication of laser annealing assisted reduction process, where the oxygen-rich functional group carbon-based material is ablated off from the surface of the thin film. The absence of impurity peaks in the survey scan shows that the as-deposited as well as laser-annealed samples are largely impurity-free. Deconvolution of the high-resolution XPS scan in the range 188-196 eV gives rise to two peaks. The two peaks are centered at 188.5 eV and 192.0 eV and are attributed to B1s and B-O electronic state, respectively.\(^{31}\) It has been reported that the strength of the peak centered at 192.0 eV increases with oxidation (formation of B\(^{3+}\)).\(^{31}\) This peak in the PLA sample suggests the presence of B-O electronic states near the surface. Since PLA is a laser-assisted reduction process, there is a decrease in the volume fraction of oxygen present in the few surface layers. So, the amount of B-O present in the PLA samples is too low to perturb the superconducting properties of the B-doped Q-carbon structure.

Figures 6.4(a) and (b) depict the high-resolution FESEM images of a B-doped Q-carbon sample. The inset of figure 6.4(a) shows the dense structure of B-doped Q-carbon which is formed after melting and subsequent quenching of C and B mixed molten layer. The filamentary structure is
formed due to interfacial instability during the super undercooling process by nanosecond ArF laser.\(^\text{17}\) Formation of nano- and micro-diamonds is observed occasionally at the triple junctions and is shown in figure 6.4(b). The B-doped Q-carbon structures are having a negative electron affinity and it glows under the application of a stage bias. Previous reports on Q-carbon (using Kelvin probe force microscopy) also indicate a negative electron potential with respect to diamond-like carbon.\(^\text{17}\) The filamentary structures of the B-doped Q-carbon are disconnected, as shown by white arrows in the inset of figure 6.4(b). Homogeneous and heterogeneous nucleation of diamonds can occur from Q-carbon thereby forming diamonds having \(<110>\) and \(<111>\) out of plane orientation, respectively.\(^\text{17}\) Figure 6.4(c) shows the FESEM image of B-doped diamond formed using HFCVD technique where the B-doped Q-carbon acts as a template. As evident from the figure 6.4(c) that the diamond crystallites are preferentially oriented along \(<111>\) indicating heterogeneous nucleation of diamond from Q-carbon on (0001) sapphire substrate. The resulting B-doped diamond structures have \(T_c\) of 25.0\(\pm\)0.5 K, which is \(~14\) K higher than the B-doped diamond samples prepared by plasma enhanced chemical vapor deposition (PECVD) technique.\(^\text{4}\) The detailed structural and property correlations of HFCVD prepared B-doped diamond from B-doped Q-carbon will be discussed elsewhere.\(^\text{32}\)

Figure 6.5(a) shows the cross-sectional high-angle-annular dark field (HAADF) image of the B-doped Q-carbon on the c-sapphire substrate. The elemental maps of B and C [Figure 6.5(b,c)], obtained by electron energy-loss spectroscopy (EELS), clearly demonstrate the homogeneous distribution of B in Q-carbon throughout the analyzed region (in-boxed region in figure 6.5(a)), which is consistent with SIMS results (figure 6.1). A representative EELS spectrum is presented in Figure 6.5(d), showing the K-edges of B and C. The spectrum contains the characteristic \(\pi^*\) and \(\sigma^*\) peaks associated with K-edge of B and C, showing the presence of B and C bonded in both \(sp^3\)
and \( sp^2 \) hybridized state. The EELS quantification estimates the average B concentration to be 17.0±1.0 at% in the Q-carbon. The HRTEM, HAADF and CBED results show Q-carbon structure to be amorphous, which is consistent with X-ray diffraction. Our EDS elemental mappings show that B is homogeneously distributed in the amorphous carbon. We have also collected the HAADF image of B-doped Q-carbon and performed X-ray EDS elemental mapping of B, Al, and C, whose concentrations are consistent with EELS data. The homogeneous dispersion of B atoms as a result of laser melting and quenching is crucial for high-temperature superconductivity in B-doped Q-carbon thin films. No evidence for B clusters is found in the EDS maps, suggesting that the melting of B and C layer occurs during pulsed laser melting. The calculated \( sp^3 \) fraction from C edges by EELS quantification is in agreement with the measured values by Raman spectroscopy. The \( sp^3 \) fraction of B as calculated from the K-edge of B in EELS is 0.6. The B in its \( sp^3 \) electronic state resembles the substitutional B atom in the diamond lattice. On the other hand, a fraction of the \( sp^2 \) B electronic states are in the interstitial B states which act as shallow electron donors (free \( \pi \) electrons) thereby perturbing the superconducting properties of B-doped Q-carbon. There is an excellent correlation between the \( sp^3 \) fraction in B with \( T_c \) and electron-phonon coupling parameter as discussed below.

The magnetization vs temperature plot in zero field cooled (ZFC) and field cooled (FC) conditions are performed at 60 Oe applied magnetic fields for Q-carbon doped with 17.0±1.0 at% boron and is shown in figure 6.6(a). From these measurements, the \( T_c \) for B-doped Q-carbon was estimated to be 36.0±0.5 K. The \( T_c \) for crystalline diamond doped prepared from B-doped Q-carbon using HFCVD was found to be 25.0±0.5 K. As it is quite evident from the plots, the value of magnetic moment increases as a function of the magnetic field. The bifurcation with the application of magnetic field occurs at \( T_c \) (36.0±0.5 K). This is as result of trapping of magnetic fluxes in a
superconducting material below $T_c$ after the application of an external magnetic field. Our results on B-doped Q-carbon and diamond follow the characteristics of superconductivity in bismuth, where $T_c$ for amorphous bismuth is 6.8 K, compared to 53 mK for bismuth single crystal. This trend in bismuth has been correlated with enhanced electron-phonon coupling and higher density of states at the Fermi level in amorphous Bi compared to single-crystal Bi. There is a large difference in the magnetic moment between the ZFC and FC curves indicating the presence of large flux pinning forces in the material. This leads to trapping of magnetic flux in the FC condition. The transition temperature is shifted to lower values after application of the magnetic field, suggesting inhomogeneous superconductivity in the B-doped Q-carbon thin films. Figure 6.6(b) illustrates the magnetic moment versus applied magnetic field plots at different temperatures (below $T_c$) in B-doped Q-carbon thin film. This is also referred to as the “butterfly hysteresis” at different temperatures (below $T_c$). The value of $H_{c1}(T)$ and $H_{c2}(T)$ were calculated from the hysteresis loops. The magnetic field value for the highest point in the negative magnetic moment (4th quadrant) in the hysteresis loop corresponds to $H_{c1}(T)$. The value of $H_{c2}(T)$ was determined as the field from which $M(H)$ deviated first from the background (X axis). The $H_{c2}(T)$ is found to vary at a faster rate than predicted by the Werthamer-Helfand-Hohenberg (WHH) model. According to the WHH model, the value of $H_{c2}(0)$ is calculated using equation (6.1):

$$H_{c2}(0) = -0.69\left(\frac{dH_{c2}}{dT}\right)T_c$$

(6.1)

where $dH_{c2}/dT$ denotes the slope at $T_c$. Solving this equation yields the value of $H_{c2}(0)$ as 6.9 T, which is also shown in figure 6.6(c). In B-doped Q-carbon thin films, the value of $H_{c2}(0)$ as calculated from the intersection of the extrapolated trend curve with the Y axis is 5.4 T. The Ginzburg-Landau coherence length ($\xi_L$) can be calculated using the equation (6.2):

$$\xi_L = \left[\frac{\Phi_0}{2\pi H_{c2}(0)}\right]^{0.5}$$

(6.2)
Using the value of $H_{c2}(0)$ as 5.4 T, $\varepsilon_L$ is calculated as 79.3 Å. The value of penetration depth ($\lambda_d$) can also be calculated using the equation (6.3):

$$H_{c1}(0) = (\Phi_0/4\pi\lambda_d^2)\ln(\lambda_d/\varepsilon_L)$$ (6.3)

The value of $\lambda_d$ is calculated as 82.8 Å. The Ginzburg-Landau parameter ($k$) is calculated to be 1.04 (>1/2^0.5) thereby showing that B-doped Q-carbon is a type II superconductor. The zero-temperature energy gap ($\Delta(0)$) in B-doped Q-carbon is calculated as 5.5 meV using the equation: $\Delta(0) = 1.8 k_B T_c$. The value of the exponent (n) is calculated using the power law (equation (6.4)):¹¹

$$\frac{H_{c2}(T)}{H_{c2}(0)} = 1 - \left(\frac{T}{T_c}\right)^n$$ (6.4)

From the $H_{c2}(T)$ data fitting, the value of n is derived to be 2.1 for the case of $H_{c2}(T)$, which is consistent with the BCS formalism. There is a downward curvature ~0 K in the case of $H_{c1}(T)$, which can be explained by the increased contribution from $H_{c1}\sigma(T)$ as compared to $H_{c1}\pi(T)$.³⁷

From the viewpoint of practical applications, the critical current density of a superconductor as a function of temperature and field are the most important parameters. The critical current density ($J_c$) is calculated using the Bean’s formula (equation (6.5)) and is shown in figure 6.6(d):

$$J_c = \left[\frac{20\Delta M}{t w^2 (l - \frac{w}{2})}\right]$$ (6.5)

where $\Delta M$ is the difference in magnetization values (+M and -M) at a particular magnetic field, and $t$, $w$, and $l$ are the thickness, width, and length of the sample. The value of $J_c$ (0 Oe) at 2 K is calculated as 2.7E9 A/cm² which is quite large as compared to B-doped diamond. The large value of $J_c$(00e) in B-doped Q-carbon is due to its small dimension. A large value of $J_c$ (0 Oe) is also indicative of flux-melting in this material. The inset in figure 6.6(d) indicates a logarithmic plot of $J_c$ versus magnetic field. The dark dotted line indicates the value of $J_c$ (1 T) at 2, 6, 16 and 21 K. The value of $J_c$ (1 T) at 21 K is found to be 1.6E8 A/cm². As it is evident from the figure 6.6(d)
that there is a sharp decrease of $J_c$ with an increase in the magnetic field. There occurs a transition from the superconducting state to the normal state in a type-II superconductor above the upper critical field. The ability to transmit the critical current (with no heat loss) in a superconductor can cease much below the upper critical field. The corresponding magnetic field is termed as the irreversibility field ($H^\ast$~2.5 T), whose value is approximately half to that of $H_{c2}$ (~5.4 T). Above $H^\ast$, the Lorentz force which is created on the magnetic vortices causes depinning and thereby drastically reduces the critical current density. An increase in the value of $H^\ast$ is possible by introducing pinning centers in the matrix of a superconductor which in turn adversely affects the value of maximum critical current density. The high value of the $J_c$ (0 Oe) can also be predicted from the sharp fall in the magnetic moment at $T_c$ in the zero-field cooled condition (figure 6.6(a)). The high critical current density of B-doped Q-carbon (at low magnetic fields) makes it an ideal candidate for low field NMR inserts.

The temperature dependence of the critical field (at 0 Oe) can be fitted with $J_c (T) = J_c (0) [1- (T/T_c)]$. The value of $J_c (0)$ is extracted as 2.5E9 A/cm$^2$. At 4.2 K the value of $J_c (0)$ is calculated as ~10$^7$ A/mm$^2$ which is much higher than found in Nb-Ti, Nb$_3$Sn and YBCO superconductors (<10$^5$ A/mm$^2$). The energy per unit volume ($\Delta G_{ns}$) of the superconducting state relative to the normal state can be represented using the equation: $\Delta G_{ns} = -0.5 \mu_0 H_c^2$, where $\mu_0$ and $H_c$ denote magnetic permeability (in vacuum) and upper critical field (at ~0 K), respectively. The values of $H_c$ in Nb$_3$Sn and B-doped Q-carbon are 27.0 T and 5.4 T, respectively. So, $\Delta G_{ns}$ (of B-doped Q-carbon) = 0.04 $\times$ $\Delta G_{ns}$ (of Nb$_3$Sn). The high values of $J_c$ in B-doped Q-carbon is due to the fact that the energy required to exclude the magnetic field is extremely low in the case of B-doped Q-carbon (0.04 $\times$ energy required for Nb$_3$Sn superconductors). A weaker dependence of $J_c$ at higher fields is also observed in B-doped Q-carbon. This can be due to the presence of a large number of
weakly-coupled superconducting regions. The larger values of $J_c$ at lower temperatures are due to the presence of pinned states. Q-carbon may also contain diamond and DLC inclusions due to inhomogeneous melting, which can enhance flux pinning. Therefore, larger current density is required to move the pinned vortices. At larger magnetic field this phenomenon is negligible due to the presence of an external magnetic field which assists the movement of the pinned states. It is well known that in a pure annealed superconductor the values of $J_c$ are low due to the presence of flux lattice lines (FLL), which dissipate the energy and the superconductor eventually turns “normal”. The refinement of the superconducting grain size introduces pinning centers in a superconductor. This cause an increase in the value of $J_c$.

Figure 6.7 depicts the temperature dependence of critical current density in B-doped Q-carbon at ~0 Oe. It is clearly evident that $J_c$ decreases with an increase in temperature. Interestingly, it is seen that there is a crossover from the Ambegaokar-Baratoff (AB) model to Ginzburg-Landau (GB) model at ~ 15 K in B-doped Q-carbon. According to the AB temperature dependence, the critical current density is proportional to $(1-T/T_c)$, whereas GL predicts as $(1-T/T_c)^{1.5}$. As it is evident from the figure 6.7 that the solid curve (AB) fits better (than the dotted curve) at lower temperatures (≤15 K) whereas at higher temperatures (>15 K) up to $T_c$ the dotted curve (GL) fits better (than the solid curve). The AB temperature dependence at low temperatures is due to the presence of weak Josephson coupling and is observed in granular superconductors. Above 15 K up to $T_c$, GL dependence is observed in B-doped Q-carbon due to the presence of current-induced gap suppression effect. It has also been argued that an increase in the coherence length can also increase the crossover temperature in high-temperature superconductors. The crossover point also indicates an equality of the Josephson coupling energy and the superconducting condensation
energy, which is \(~15\) K in the case of B-doped Q-carbon. The ratio of Josephson coupling energy to the superconducting condensation energy (\(\varepsilon_0\)) can be calculated using the equation (6.6):\(^{41}\)

\[
\varepsilon_0 = \frac{1}{0.882 \left(1 - \frac{T_x}{T_c}\right)}
\]  

(6.6)

where \(T_x\) denotes the crossover temperature. Using the value of \(T_x\) as \(15\) K the dimensionless quantity \(\varepsilon_0\) is calculated as \(0.7\). This indicates a moderate Josephson-coupling in B-doped Q-carbon which causes the crossover between the AB and GL theory. The ratio \(\varepsilon_0\) is also inversely proportional to the electronic density of states near the Fermi level (\(N(0)\)).\(^{41}\) The value of \(\varepsilon_0\) is less than \(1\) thereby indicating an increase in the density of states near the Fermi level. This increase in \(N(0)\) is also envisaged to produce a moderate electron-phonon coupling in the B-doped Q-carbon structure. The current-induced gap suppression above \(~15\) K (in B-doped Q-carbon) indicates the formation of a core of radius \(\varepsilon_L(T)\) in its vortex state. With a decrease in temperature, there occurs a shrinkage of the core which causes the crossover to the AB theory (critical current density \(versus\) temperature dependence). The depairing current density \((j_0)\) in B-doped Q-carbon can be estimated as \(1.6\times10^9\) A/cm\(^2\) by using 

\[
\dot{j}_0 = \frac{\Phi_0}{\sqrt{3\pi \lambda^2 \xi}},
\]

where \(\Phi_0\), \(\lambda\) and \(\xi\) represent the flux quantum, penetration depth and coherence length, respectively. This indicates that we have achieved \(~15\%) of the depairing current (at \(~0\) Oe) in B-doped Q-carbon. A further enhancement in \(J_c\) can be envisaged by increasing the B concentration and pinning centers.

The coherence length, \(\varepsilon_L\) is calculated as \(79.3\) Å in B-doped Q-carbon samples. This coherence length can be compared to the size of the superconducting regions. So, the reduced size of superconducting regions in B-doped Q-carbon causes an increase in the value of \(J_c\). The \(T_c\) for phonon-mediated superconductivity can be calculated using the McMillan formula (equation (6.7)):\(^{23}\)
where, \(<\omega>_{\text{log}}\) is the logarithmic average of phonon frequencies, \(\mu^*\) is the screened Coulomb pseudopotential, and \(\lambda\) is the measure of average electron-phonon coupling. Using the value of \(<\omega>_{\text{log}}\), \(\mu^*\) and \(T_c\) as 67.4 meV, 0.1, and 36.4 K, respectively, the calculated value of \(\lambda\) is 0.8, which is consistent with theoretical calculations of Moussa and Cohen for B-doped diamond. The value of \(\lambda\) is indicative of moderate electron-phonon coupling in B-doped Q-carbon. This can be explained by the relation between \(\lambda\), the density of states at the Fermi energy \((N(0))\), mass \((M)\), average square of electron-phonon matrix element \((<I^2>)\), and the characteristic phonon frequency averaged over the phonon spectrum \((<\omega^2>)\). The average electron-phonon coupling parameter is related to the above variables by the following equation (6.8):

\[
\lambda = \frac{\langle N(0) < I^2 > \rangle}{\langle M < \omega^2 > \rangle}
\]  

Hall Effect measurements indicate a composite carrier concentration of \(\sim 10^{22}\) cm\(^{-3}\) in B-doped Q-carbon samples. This indicates a substantial value of \(N(0)\) in these films. The atomic mass is also quite low. But the moderate value of \(\lambda\) in B-doped Q-carbon is due to the presence of strong covalent bonds (stronger than diamond) thereby dramatically increasing the value of \(<\omega^2>\). In the B-doped Q-carbon thin films, all the valence states are of \(\sigma\) electronic states with stronger electron-phonon coupling as compared to B-doped diamond. The presence of substitutional disorder can quench \(T_c\) in B-doped diamond by opening a gap in the valence states. The value of \(T_c\) rises monotonically by increasing the B concentration (in the substitutional sites) in diamond. To date, the highest value of \(T_c\) achieved in diamond-5\%B thin film synthesized using PECVD technique is 11 K. At higher B concentrations, B-doped diamond enters into the dirty type II superconductor regime where scattering of Bloch states by impurities does not play an important role. The substitutional disorder states are not formed during the ultrafast pulsed laser annealing.
of Q-carbon. This gives rise to high $T_c$ in B-doped Q-carbon structure. The substitutional B in B-doped Q-carbon acts as shallow acceptor in the valence band. This gives rise to the formation of holes which strongly couple with phonons thereby giving rise to high $T_c$ superconductivity. There exists highly inhomogeneous nature of electron-phonon coupling in the disordered matrix. In the highly disordered B-doped Q-carbon structures, high value of $T_c$ may also result from the magnetic flux percolation through regions possessing above average electron-phonon coupling value. Due to the presence of $\sigma$ and $\pi$ electronic states in B-doped Q-carbon, there could exist two distinct superconducting gaps. It has been shown that the critical magnetic fields can be analyzed according to a theoretical model. In this model, the $\sigma$ and $\pi$ electronic states are separated by a Josephson contact (interband coupling). At lower temperatures the contribution from the $\pi$ electronic states are predominant, and this gives rise to an upward curvature in the doped thin films (having a significant $\pi$ fraction). This can be explained by an increased electronic scattering in the $\pi$ band of the doped superconductor. As evident from the inset of figure 6.6(c), the $H_{c1}$ follows a downward curvature at lower temperatures. This is indicative of predominant $\sigma$ band contribution as compared to $\pi$ band scattering. This is also consistent from the $H_{c2}$ plot. B-doped Q-carbon thin films have a superconducting property due to the presence of shallow acceptor electronic states associated with B. Deconvolution of the $H_{c1}$ curve gives rise to two peaks centered at 3.2 K and 16.4 K belonging to $H_{c1}(\sigma)$ and $H_{c1}(\pi)$, respectively. The $H_{c1}(\sigma)$ fraction calculated from the fitting program is 0.63. This is in excellent agreement with the B $\sigma$ electronic state fraction (0.62) calculated from the B K edge in EELS. The quantification routine in the EELS spectra takes into account of the electronic density of states which cause critical magnetic field in magnetic materials. Detailed theoretical modeling of the superconductivity in B-doped Q-carbon and diamond is under progress and will be reported elsewhere.\textsuperscript{32}
In amorphous B-doped Q-carbon where B doping exceeds the retrograde solubility limits (2.0 at % in diamond), a massive number of carriers in the form of positive holes are formed. These massive number of carriers create strong interaction with the hard phonons. Density functional theory (DFT) calculations indicate that at lower B concentrations (less than 5 at %), there occurs phonon mediated hole scattering to high energy optical phonon modes, thereby causing superconductivity in B-doped diamond. Acoustic modes provide a negligible contribution to superconductivity. The phonon states of B atoms play a vital role in the coupling to optical modes. Increased B concentration (in the substitutional sites) therefore causes an increase in the electron-phonon coupling strength leading to an increase in the $T_c$. A detailed theoretical study suggests that the density of electronic states near the Fermi energy level are predominantly characterized by the electronic states in substitutional B atom. Therefore, it can be assessed that an increase in $T_c$ is directly related to an increase in the electronic density of states near the Fermi level. Theoretical studies predict that in the superhard material, BC$_5$ with 16.7 at % of B, the electronic density of states near the Fermi energy level is 2.1 times higher than that in 2% B-doped diamond. This provides a direct evidence of increase in the number of charge carriers induced by B doping. From the phonon density of states and energy calculations in BC$_5$, it has been found that higher energy modes (115-160 meV) correspond to C-C vibrations, whereas the lower energy modes (<100 meV) are due to vibrations pertaining to B and its neighboring C atoms. There is also a direct evidence of increase in the intensity of the phonon density of states corresponding to lower energy with an increase in B doping. This is due to better coupling of low energy modes in highly doped samples. Therefore, superconductivity in B-doped carbon samples is attributed to vibrations associated with B atoms and its neighboring electronic concentration. In the superhard materials, with large values of elastic constant and strong chemical bonds, there are high-energy phonons.
and increased electronic charge densities.\textsuperscript{44} These properties can cause superconductivity in the superhard materials if they possess moderate to large electron-phonon coupling constants.

Figure 6.8(a) shows the magnetic moment versus temperature plots of c-sapphire substrate used in this work. Zero-field-cooled (ZFC) and field-cooled (FC) curves indicate the pristine nature of the substrate. The background substrate corrections were done by using the magnetic plots of the substrate under identical conditions. Figure 6.8(b) shows temperature-dependent magnetic moment curves of crystalline diamond doped with 17.0±1.0 at% boron. The ZFC and FC (at 100 Oe) curves indicate a transition temperature ($T_c$) of 25.0±0.5 K in the B-doped diamond samples. This transition temperature is higher than the previously experimentally reported value of $T_c$ in B-doped diamond. Figure 6.8(c) illustrates temperature-dependent magnetic moment plots at various applied magnetic fields in B-doped Q-carbon thin films. As it is quite evident from the plots, the value of magnetic moment increases as a function of the magnetic field. The bifurcation with the application of magnetic field occurs at $T_c$ (36.0±0.5 K). This occurs as result of trapping of magnetic fluxes in a superconducting material below $T_c$ after the application of an external magnetic field.

The temperature-dependent (normalized) resistivity measurements of B-doped Q-carbon thin films are shown in figure 6.9(a). It shows a clear evidence of the onset of superconducting transition below ~38 K. The zero-resistivity ($T_{c \text{ off}}$) condition is observed at 35.5 K. The sharper superconducting transition in B-doped Q-carbon indicates the presence of a high-quality superconducting phase. The inset in figure 6.9(a) shows the temperature derivative plot to depict the maximum resistivity drop at 37.8 K (shown by *). The figure 6.9(b) shows the enlarged view of the superconducting transition of B-doped Q-carbon. The transition width ($\Delta T$) is calculated to be 1.5 K. This transition width is comparable to that of high-temperature oxide superconductors.
but much wider than observed in single-crystal metallic superconductors (~10^-4 K). The transition width in a zero magnetic field condition is also dependent on the crystalline nature of a sample, with the single-crystal sample having a more narrow transition than their polycrystalline counterparts. An increase in the transition width in B-doped Q-carbon demonstrates its amorphous nature. The conditions of field and temperature necessary for the establishment of superconductivity in an amorphous sample will vary from one region of the sample to another in correspondence with the local value of the mean free path. This may also lead to magnetic field percolation through the regions of large electron-phonon coupling, thereby causing high-temperature superconductivity in B-doped Q-carbon.

Figure 6.10(a) shows the variation of electron-phonon coupling parameter with $T_c$ in B-doped Q-carbon using the McMillan equation. As evident from the plot that the $T_c$ dependence on the electron-phonon coupling parameter is not strong at low values of $\lambda$ (<0.40). When the values of $\lambda$ are in the moderate-coupling regime (greater than 0.45), $T_c$ increases rapidly. This is a characteristic feature of a superconducting material and it is due to the exponential relation between $T_c$ and $\lambda$. A value of electron-phonon coupling of 0.2 is calculated in 2.0 at % B-doped diamond which has $T_c$ of 4 K. The value of the electron-phonon coupling in B-doped amorphous Q-carbon is calculated as ~ 4 times as that in B-doped diamond. This suggests stronger electron-phonon coupling in B-doped Q-carbon as compared to B-doped crystalline diamond, thereby leading to high-temperature superconductivity in B-doped Q-carbon. The EELS quantification in B-doped Q-carbon provides a valuable insight into the origin of superconductivity in this novel material prepared by ultrafast melting and subsequent quenching process. Electronic states corresponding to the $\sigma$ bonding are present in both C and B in B-doped Q-carbon. After using the EELS quantification routine, the $\sigma$ fractions calculated for C and B are 0.8 and 0.6, respectively.
As discussed earlier, the B at % present in B-doped Q-carbon is 17.0±1.0 %. Therefore, the fraction of B contributing to the $sp^3$ bonding (σ electronic state) is 0.1 (10.5 at %). It is envisaged that the B electrons present in the σ electronic states play an important role in the superconductivity in B-doped Q-carbon. These electronic states act as shallow acceptor and are situated close to the Fermi level. When B-doped Q-carbon is cooled below ~36 K, hole Cooper pairs are formed. These Cooper pairs are mediated by the phonons and cause high-temperature superconductivity in B-doped diamond. On the other hand, B atoms present in the π electronic states have delocalized electrons (donor states) and can thwart the formation of hole Cooper pairs. This will lead to a reduction in $T_c$ in B-doped Q-carbon. Figure 6.10(b) shows the density functional theory (DFT) calculation of electron-phonon coupling and $T_c$ in B-doped diamond and their dependence on B at %. In these calculations, the substitutional disorder arising from the B doping is not considered. In other words, these calculations pertain to B-doped σ electronic states only. As it is evident from the plots in figure 6.10(b), a 10.5 at % of B sample (doped in the $sp^3$ hybridized electronic sites) gives rise to a value of 0.8 for the electron-phonon coupling parameter. This translates to a $T_c$ value of ~38 K. In the present case, 10.5 at % B-doped in the $sp^3$ electronic sites of Q-carbon results in a $T_c$ value of 36.0±0.5 K and $\lambda$ as 0.8. This is in excellent agreement with the DFT calculated values in B-doped diamond (without considering substitutional disorder). Thus, the high-temperature superconductivity in B-doped Q-carbon is due to the B doping in the $sp^3$ electronic sites of Q-carbon. B doping in $sp^3$ bonded carbon causes the formation of positively charged holes (p-type) which plays an important role in the superconducting behavior of B-doped Q-carbon. The highest value of $T_c$ (superconducting critical temperature) which was achieved in B-doped diamond was ~11 K. Increasing the B concentration in B-doped diamond causes the formation of substitutional disorder and B-interstitials (n-type). These factors quench the $T_c$ in
highly B-doped diamond. B-doped Q-carbon is formed by nanosecond melting and subsequent rapid quenching of the super undercooled state. This facilitates increased concentration (exceeding the retrograde solubility limit) of B in C. The structure of B-doped Q-carbon comprises of 85% \(sp^3\) and the rest \(sp^2\). The presence of \(sp^2\) bonded C in B-doped Q-carbon plays an important role in reducing the formation of B dimers and interstitials, which causes a reduction in \(T_c\).

Calculation of the threshold energy is crucial for this study, as it will determine the minimum laser energy required for melting amorphous carbon/B thereby leading to the formation of B-doped Q-carbon structures. We have employed the SLIM (simulation of laser interaction with materials) programming\(^{51}\) to simulate the laser-solid interactions. These calculations involve an extremely accurate finite difference method to calculate the melt depth and temperature profile in the laser annealed samples. The initial layered structure consists of amorphous carbon/B/sapphire. The threshold energy \((E_{th})\) required for melting few layers of amorphous carbon/B thin film can be calculated using the equation (6.9): \(^{51}\)

\[
E_{th} = \frac{K_s T_m \zeta^{0.5}}{(1-R_l)D^{0.5}}
\]

\(K_s\) = thermal conductivity of amorphous carbon (=0.3×\(T^{-0.53}\) W cm\(^{-1}\)K\(^{-1}\))

\(T_m\) = difference between the substrate temperature of c-sapphire and melting temperature of amorphous carbon (=3523 K).

\(\zeta\) = pulsed laser width (=20 ns).

\(R_l\) = reflectivity of the amorphous carbon at 193 nm (=0.1).

\(D\) = diffusivity of amorphous carbon at room temperature (=2 cm\(^2\) sec\(^{-1}\)).

The thickness of the melted region varies linearly with the pulse energy density. The surface starts to melt slowly due to the sudden change in reflectivity during the phase transition. As the laser pulse terminates, the melt front recedes back to the surface. The initial stages of solidification see
a low velocity but quickly reach the maximum when the steady state condition is achieved. With the increase in pulse duration the onset of melting decreases with a decrease in solidification velocity. The maximum depth of melt also decreases with the increase in pulse duration. There is an increase in the time of peak melt depth with increasing laser pulse width.

The maximum melt depth ($\Delta x$) is calculated by equation (6.10):

$$\Delta x = C_1 (E - E_{th})$$

(6.10)

where,

$$C_1 = (1 - R_l)/(C_v T_m + L)$$

(6.11)

In the equation (6.11), $C_v$ is the volume heat capacity of amorphous carbon at its melting point (=2.1 J cm$^{-3}$ K$^{-1}$), and $L$ is latent heat of fusion of amorphous carbon (= 19775 J cm$^{-3}$).

The melt in velocity ($v_{in}$) is calculated using equation (6.12):

$$v_{in} = \Delta T K_1/L\Delta x$$

(6.12)

where, $\Delta T$ is the temperature difference between maximum temperature and melting point of amorphous carbon.

Again, $\Delta T$ is calculated using the equation (6.13):

$$\Delta T = \frac{L C_1^2}{\kappa l \xi} (E - E_{th})^2$$

(6.13)

It was also calculated that the melt depth increases with the increase in substrate temperature. In all the above-mentioned calculations the substrate temperature was considered as 300 K. The relatively low plasma frequency of amorphous carbon helps for better material-laser coupling when 193 nm excimer laser is used. With the incidence of laser densities having energies more than the melting point of carbon, melting occurs of the carbon/B layers. This homogeneous metallic melt triggers the liquid phase diffusion process, where the dopant concentrations exceed
the retrograde thermodynamic solubility limits. As it is evident from the temperature profile in the figure 6.11, the onset of melting occurs at ~ 20 ns after the laser is incident on the layered structure. The dotted line denotes the melting point of C. The melting point of B is ~ 2349 K. As evident from the temperature profile, B and C form a homogeneous melt when laser energy densities greater than 0.6 J/cm² are employed for the PLA process. A flatter temperature profile with time is essential for a better formation of a homogeneous melt. As seen in the figure 6.11, there is a large overshoot of temperature when laser energy density of 0.8 J/cm² is used, and this annealing condition should be avoided. Insufficient laser energy densities (lower than 0.4 J/cm²) do not cause melting of carbon and thus are not effective in the PLA technique. The homogeneous melt cools down with high solidification velocities (30-40 m/sec). This causes sufficient undercooking to form B-doped amorphous Q-carbon. It should be noted that large and small undercooling causes formation of Q-carbon and diamond, respectively.17

The mechanism of annealing depends critically on laser and substrate parameters. Redistribution of dopants by laser annealing cannot be explained by diffusion in solid, as the diffusion time is ultrafast in nature. The diffusion coefficients in liquid counterparts are much higher than its solid phase and cause shallow and sharp dopant profile after laser annealing.21 It has been seen that there are significant modifications taking place in the implanted region of Si lattice as a result of laser annealing. There occurs a substitution of the dopant atoms in Si lattice sites. Ion backscattering and ion channeling techniques help to determine this lattice substitution in crystalline solids.21 The lattice contraction (after substitution of lower atomic radii elements) and expansion can be measured by X-ray diffraction and ion channeling techniques. The lattice always expands or contracts 1D in out of plane conditions. High dopant concentrations can also cause a measurable strain in the substrate lattice. The time associated with laser annealing is too small, less than a
microsecond (critical time for dislocation nucleation) to cause the formation of misfit dislocations which tend to relieve the strain and destroy the one-dimensional change of lattice parameter.\textsuperscript{21} In this case, there occurs the formation of B-doped amorphous Q-carbon after the PLA process which involves melting and subsequent quenching from the super undercooled state. During the melting, B and C diffuse rapidly into liquid with diffusivity $\sim 10^{-4}$ cm$^2$/sec, and produce homogeneous molten state. Upon quenching of the super undercooled state, this B-doped Q-carbon phase is created with B concentrations exceeding thermodynamic solubility limits \textit{via} solute trapping. This gives rise to the formation of shallow acceptor electronic states and moderate electron-phonon coupling in B-doped Q-carbon which causes the high-temperature superconductivity in this material.

\textbf{6.5. Conclusion}

A type II superconductivity in B-doped Q-carbon with a $T_c$ of 36.0±0.5 K and upper critical field of 5.4 T at \textasciitilde 0 K is achieved. This novel phase is formed as a result of nanosecond laser melting of boron and carbon layers in a super undercooled state and rapid quenching subsequently. This process of rapid nanosecond melting and quenching has been modeled to obtain detailed temperature distribution, melting and quenching kinetics. This process can enhance the dopant concentrations beyond the thermodynamic solubility limits, \textit{via} solute trapping, which can be incorporated into substitutional sites without affecting their energy levels and ionization efficiencies. The dopants can be substituted in the electrically active sites thereby giving rise to interesting magnetic and electrical properties. It has been observed both experimentally (TOF-SIMS, HAADF, and EELS) and theoretically (SLIM Modeling) that the melting of C and B layers occurs during the PLA technique. The liquid phase diffusivity of B in C causes an increase in the atomic concentration of B in C beyond the retrograde solubility limits to 17.0±1.0 at % in Q-carbon
as compared to the thermodynamic solubility limit of 2.0 at % in diamond. This increase in B at % in B-doped Q-carbon plays an important role in high-temperature superconductivity. It has been shown that in B-doped Q-carbon, the upper critical magnetic field $H_{c2}(T)$ follows $H_{c2}(0) [1-(T/T_c)^{2.1}]$ temperature dependence and is consistent with the BCS formalism. The moderate electron-phonon values of 0.8 and high electronic density of states near the Fermi energy level result in high-temperature superconductivity in B-doped Q-carbon. EELS and Raman spectroscopy of B-doped Q-carbon illustrate the structure, bonding, and $sp^3$ fraction in this novel material which ultimately leads to high-temperature superconductivity. The EELS quantification of the $sp^3$ fraction in B reveals that 10.5 at % of B is doped in the $sp^3$ electronic states of Q-carbon. According to the DFT calculations in B-doped diamond \cite{10} (without considering the substitutional disorder electronic states), $T_c$ and $\lambda$ values are calculated as ~37 K and 0.8, respectively. This is in excellent agreement with the corresponding values measured in B-doped Q-carbon, where the substitutional disorder is minimized as a result of amorphous structure. This suggests that the high-temperature superconductivity in B-doped Q-carbon is due to the B doping in the $sp^3$ electronic sites of Q-carbon. The electronic Raman spectra of B-doped Q-carbon reveal an acceptor energy level at ~33 meV with the spin-orbit splitting energy value of ~7 meV. This energy state corresponds to ~37 meV and ~6 meV (spin-orbital splitting) found in the B-doped diamond. The presence of this electronic state near the valence band maximum indicates an increase in the density of shallow acceptor electronic states near the Fermi energy level. Therefore, the moderate electron-phonon values and high electronic density of states near the Fermi energy level result in high-temperature superconductivity in B-doped Q-carbon. The EELS quantification estimates the average 17.0±1.0 at% B in the B-doped Q-carbon, which is crucial for the high-temperature $T_c$ in this material. The critical current density dependence with temperature and field in B-doped Q-
carbon indicate that this novel material can be used for MRI and NMR applications. The critical current densities with field show considerably large values (4.3×10^7 Acm^-2 at 21 K and 2 T) than typical oxide superconductors (BSCCO: 1.2×10^5 Acm^-2 at 4.2 K), which is an important consideration for practical applications.\textsuperscript{38} We have obtained \( T_c > 57 \) K with increasing B concentration to 27% atomic, the details of these results will be reported shortly. This discovery of high-temperature superconductivity in B-doped Q-carbon will stimulate further research in strongly-bonded carbon-based materials in the search for near room temperature superconductivity.
6.6. Figures:

![SIMS profiles of (a) as-deposited boron and carbon layers with the inset showing a schematic of the alternating layers of amorphous carbon and boron deposited on c-sapphire using pulsed laser deposition technique; and (b) pulsed laser annealed (B-doped Q-carbon) thin films with the inset showing a schematic of B-doped amorphous Q-carbon formed on c-sapphire.](image)

**Figure 6.1.** SIMS profiles of (a) as-deposited boron and carbon layers with the inset showing a schematic of the alternating layers of amorphous carbon and boron deposited on c-sapphire using pulsed laser deposition technique; and (b) pulsed laser annealed (B-doped Q-carbon) thin films with the inset showing a schematic of B-doped amorphous Q-carbon formed on c-sapphire.
Figure 6.2. (a) Raman spectroscopy of B-doped Q-carbon, B-doped diamond, and as-deposited B-C thin films with the inset showing 84.3% $sp^3$ in B-doped Q-carbon; (b) electronic Raman spectra of B-doped Q-carbon, B-doped diamond, as-deposited B-C, and c-sapphire substrate; and (c) the energy-level schematic diagram of B acceptor states in B-doped Q carbon (green band: 33.3 meV) and B-doped diamond (31.2, 35.3, and 41.6 meV). The sapphire peak in figure (b) is indicated by *.
Figure 6.3. (a) XRD scan of B-doped Q-carbon; and (b) XPS survey scan of B-C and B-doped Q-carbon thin films. The inset in figure (b) illustrates high-resolution XPS scan showing the presence of B-O and B-1s peaks.
Figure 6.4. (a) and (b) High-resolution FESEM images showing filamentary structures of B-doped Q-carbon with the insets in (a) and (b) showing dense and (some) disconnected filamentary structures of B-doped Q-carbon (indicated by white arrows) formed due to interfacial instability, respectively; and (c) FESEM image of B-doped diamond formed using B-doped Q-carbon as a template.
Figure 6.5. (a) Cross-sectional high-angle annular dark field (HAADF) image of the formed B-doped Q-carbon on the c-sapphire substrate; (b) B-EELS mapping; (c) C-EELS mapping; (d) EELS spectrum revealing characteristic K edges of B and C with estimated 17.0±1.0 at% of B in amorphous Q-carbon; (e) fitted EELS spectrum revealing the B K edge having 62 sp³ %; and (f) fitted EELS spectrum revealing the C K edge having 80 sp³ %. The scale bars shown in figures (b) and (c) correspond to 10 nm.
Figure 6.6. (a) Magnetic moment vs temperature plots of B-doped Q-carbon thin film showing $T_c = 36.0 \pm 0.5$ K; (b) depicts M-H loops at a constant temperature below $T_c$; (c) Upper critical field and lower critical field in B-doped Q-carbon thin films along with the WHH curve and the inset depicting deconvolution of the lower critical field to $H_{c1}^{(\alpha)}$ and $H_{c1}^{(\pi)}$ peaks in B-doped Q-carbon thin films; and (d) shows critical current density versus applied magnetic field at various temperatures below $T_c$ with the inset showing $J_c$ (1 T) at various temperatures. The error bars (5%) are shown in figure (c).
Figure 6.7. The temperature dependence of critical current density in B-doped Q-carbon. There occurs a crossover between the AB and GL model at ~15 K.
Figure 6.8. Magnetic moment vs Temperature plots of (a) sapphire substrate; (b) HFCVD grown B-doped diamond using B-doped Q-carbon as the template; and (c) B-doped Q-carbon at different applied magnetic fields.
Figure 6.9. (a) Temperature-dependent (normalized) resistivity measurements of B-doped Q-carbon thin films showing the onset temperature of superconducting transition temperature at 37.8 K and zero-resistivity condition at 35.5 K with the inset showing the temperature derivative measurements to depict the maximum resistivity drop at 37.8 K (shown by *); and (b) the enlarged view of the superconducting transition showing the transition width ($\Delta T_c$) to be 1.5 K. The transition width is calculated using the equation: $\Delta T_c = T_{90\%} - T_{10\%}$. 

$T_c \text{ on} = 37.8 \text{ K}$

$T_c \text{ off} = 35.5 \text{ K}$

$\Delta T_c = 1.5 \text{ K}$
Figure 6.10. (a) Variation of $T_c$ with $\lambda$ for B-doped Q-carbon; and (b) variation of $T_c$ and $\lambda$ with at% B in B-doped diamond\textsuperscript{10} (the blue dotted line corresponds to 10.5 B at% in B-doped diamond).
Figure 6.11. Temperature versus time profile after PLA using different laser energy densities and simulated using SLIM programming. The dotted red line corresponds to the melting point of carbon. The inset represents a schematic diagram of the initial arrangement of C and B layers and the nanosecond laser used for the simulation purpose. A melt depth of ~ 500 nm with solidification velocities 30-40 m/sec was calculated using the simulation program.
6.7. References


7. Magnetic relaxation and three-dimensional critical fluctuations in B-doped Q-Carbon -
A high-temperature superconductor

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7.1. Abstract

Dimensional fluctuations and magnetic relaxations in high-temperature superconductors are key considerations for practical applications in high-speed electronic devices. We report the creep of trapped magnetic flux and three-dimensional critical fluctuations near the superconducting transition temperature \((T_c = 36\) K) in B-doped amorphous Q-carbon. The superconducting phase in B-doped Q-carbon is formed by nanosecond pulsed laser melting in a super undercooled state followed by subsequent quenching. Time-dependent magnetic moment measurements in the B-doped Q-carbon follows Anderson-Kim logarithmic decay model with the calculated value of pinning potential to be 0.75 eV at 1 T near \(T_c\). There is also a strong evidence of three-dimensional (3D) critical fluctuations near \(T_c\) in B-doped Q-carbon. The crossover from 2D to 3D critical fluctuations is seen at \(T/T_c = 1.01\) as compared to \(T/T_c = 1.11\) in other conventional Bardeen-Cooper-Schrieffer (BCS) high-temperature superconductors. These critical fluctuations indicate moderate to strong electron-phonon coupling in B-doped Q-carbon. The isomagnetic temperature-
dependent resistivity measurements reveal a broadening of superconducting transition width with increasing magnetic field. The upper critical field \( (H_{c2}(0)) \) is calculated to be 5.6 T using the power law. Finally, the superconducting region is determined in B-doped Q-carbon, as the three vertices of the superconducting region are calculated as \( T_c = 36.0 \text{ K}, J_c = 2.9 \times 10^9 \text{ A/cm}^2 \) and \( H_{c2} = 5.6 \text{ T} \). The temperature-dependent magnetic moment and resistivity measurements also validate B-doped Q-carbon as a BCS type-II superconductor. B concentration in Q-carbon can be increased up to 50 at\% by nanosecond laser melting and quenching technique, thus providing an ideal platform for near room-temperature superconductivity.

### 7.2. Introduction

Carbon atoms readily form various allotropes and phases based on its electron configuration. The electronic mixing of \( sp, sp^2 \) and \( sp^3 \) hybridized states in carbon can lead to a development of several new structures possessing exciting physical and chemical properties.\(^1\),\(^2\) In theory, superconductivity in carbon can be achieved owing to its light mass and large Debye frequency, which are the prerequisites for high-temperature superconductivity. However, a weak electron-phonon coupling and low electronic density of states near the Fermi energy level thwart high-temperature superconducting transition in carbon-based materials. Dresselhaus and her coworkers showed (both theoretically and experimentally) that doping (small atoms) in carbon can cause an enhancement of the electron-phonon coupling strength thereby increasing the superconducting transition temperature.\(^3\)\(^-\)\(^5\) This concept has led to the evolution of superconductivity in electronically modified carbon-based materials: B-doped diamond \( (T_c=11 \text{ K}) \),\(^6\) alkali-doped fullerene \( (T_c =33 \text{ K}) \),\(^7\) graphene \( (T_c = 4 \text{ K}) \),\(^8\) polycyclic hydrocarbons \( (T_c =30 \text{ K}) \),\(^9\) graphite intercalated materials \( (T_c =11.5 \text{ K}) \),\(^10\) single-walled carbon nanotubes \( (T_c =15 \text{ K}) \),\(^11\) double-walled carbon nanotubes \( (T_c =7 \text{ K}) \),\(^5\) etc. In a nutshell, the superconductivity in carbon-based
superconducting materials is caused by a strong electron-phonon mediated pairing of the charge carriers and it follows the well-established BCS formalism. BCS superconductors can also be interfaced with topological insulators to create Majorana Fermions for quantum computing, sensing and communication. Three important parameters governing the practical applications of a superconductor are: (a) critical current density, (b) upper critical magnetic field, and (c) superconducting transition temperature. There is a loss of the zero-resistance state with an increase in temperature, current or field above a critical limit. Therefore, an increase in the critical current density and upper critical field without reducing $T_c$ in carbon-based materials will have a profound impact on practical applications, including frictionless motors, high-efficiency power transmission cables, magnetic resonance imaging (MRI), superconducting magnetic energy storage (SMES), electromagnetic pumps and generators, magnetic levitation, etc. The critical fluctuations and magnetic relaxations in high-temperature superconductor also play a vital role in the above-mentioned applications.

Superconductivity in B-doped diamond is quite interesting owing to the fact that $T_c$ can be increased from 4 K to 11 K with increasing boron concentration. Theoretical calculations by Cohen and coworkers have predicted $T_c$ in B-doped bulk diamond as high as 80 K with increasing B concentration. However, the increase in the boron concentrations (above ~6 at%) atomic disorder (and compensating defect) in B-doped diamond structure occurs which thwarts $T_c$. It is observed experimentally that an increase in the B dopant concentration ($n > 10^{20}$ cm$^{-3}$) decreases the activation energy and it exhibits a metal-like behavior. Attaining such high concentrations (beyond thermodynamic solubility limits ~2 at%) by equilibrium Chemical Vapor Deposition (CVD) techniques poses a major challenge. The non-equilibrium technique, plasma enhanced CVD (PECVD) was used to increase the B at% up to 6%, after which it started to form B-dimers.
The formation of B-dimers leads to the symmetric and anti-symmetric combinations of bound states of boron thereby reducing the value of $T_c$.\textsuperscript{17} We are able to overcome the above-mentioned challenges of B-doping by using non-equilibrium laser-assisted melt quenching technique. We have reported the formation of Q-carbon (quenched-carbon) by nanosecond pulsed laser melting of amorphous carbon in a super undercooled state and subsequent quenching of the molten carbon layers.\textsuperscript{18-21} The molten carbon in the super undercooled state has metallic bonding, which promotes close-packing of carbon atoms, and upon quenching $sp^3$ tetrahedra are formed. The $sp^3$ bonded carbon tetrahedra are randomly distributed, creating amorphous Q-carbon. Most of these tetrahedral can have $sp^3$ bonded B atoms. The carbon in the interfacial region between the tetrahedral is $sp^2$ bonded and B in this region is also $sp^2$ bonded. Similar conversion of h-BN to c-BN and Q-BN is also observed using the pulsed laser annealing (PLA) technique.\textsuperscript{22} The Q-carbon consists of a phase mixture of $sp^3$ (>80%) and rest $sp^2$ bonded carbon atoms and it can exist in Q1, Q2, and Q3 polyamorphic states.\textsuperscript{18,23} This novel material exhibits interesting properties, such as low electron affinity in electric field, room temperature ferromagnetism in undoped state, significantly enhanced hardness than diamond etc.\textsuperscript{18,21,24}

In the present study, we employ the PLA technique on the B/amorphous C multilayer structures to synthesize B-doped Q-carbon, where we can exceed B doping beyond thermodynamic solubility limits (17.0±1.0 at% and higher) by adjusting the relative thickness of B/C composite layers. This leads to a high-temperature superconductivity ($T_c = 36$ K) in B-doped Q-carbon. Recently, Sakai et al. have theoretically predicted $T_c = 37$ K in B-doped Q-carbon at 14 at% B-doping and confirmed our experimental results, including the enhancement in the density of states near the Fermi level.\textsuperscript{25} We examine the BCS superconductivity in B-doped Q-carbon using temperature and field dependent magnetic and electrical measurements. According to the BCS formalism,
Cooper pairs are formed below $T_c$, which move in zero-resistive paths in superconducting materials. This leads to a zero-resistance conduction in superconducting materials which have potential applications ranging from frictionless motors and high-efficiency power transmission cables to superconducting qubits. The superconducting creep measurements (time-dependent magnetic moment) are performed in a superconducting quantum interference device. Critical fluctuation measurements are performed in physical property measurement system. The electronic structure, vibrational modes and morphology of B-doped Q-carbon are characterized by electron energy-loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM), Raman spectroscopy and scanning electron microscopy (SEM). Finally, we discuss the origin and nature of superconductivity in B-doped Q-carbon using the BCS formalism.

7.3. Experimental

Pulsed laser deposition (PLD) technique is used to deposit alternating layers of boron and amorphous carbon thin films onto c-sapphire with a thickness ranging from 100-500 nm in the temperature range of 30-300°C and 1.0×10⁻⁶ Torr operating pressure. During the deposition process the pulsed laser beam (KrF excimer laser having laser wavelength=248 nm, pulse duration=25 ns and energy density=3.0 Jcm⁻²) is rastered through the carbon and boron (sector) targets. Both the targets are mounted on the same target holder during the PLD process. Subsequently, these B-doped amorphous carbon thin films (grown by PLD technique) are irradiated with nanosecond ArF excimer laser (laser wavelength=193 nm, pulse duration=20 ns) using laser energy density 0.6-1.0 Jcm⁻². The pulsed laser annealing (PLA) technique melts the B-doped amorphous carbon film in a highly super undercooled state, and quenched rapidly. The whole process is completed within 200-250 ns. This leads to conversion of amorphous carbon films into B-doped quenched carbon structure where B is doped beyond thermodynamic solubility.
limit via solute trapping. The undercooling is controlled by thermal conductivities of the substrate (sapphire in this case) and as-deposited diamond-like carbon thin films and laser parameters (laser energy density (0.6-1.0 J/cm²), laser wavelength (193 nm) and pulsed laser width (20 ns)). The thermal conductivities of the as-deposited diamond-like carbon thin films can be controlled by varying the ratio of sp²/sp³-hybridized carbon. The formation of B-doped Q-carbon is dependent on the laser parameters and physical properties of the substrate, which control the solidification velocity. The solidification velocity (v) is directly related to the undercooling by the equation: 
\[ v = \frac{D \cdot f}{\lambda \cdot f_D} \left(1 - e^{\frac{(T_m - T_u) \Delta S}{k T}}\right), \]
where, \( D \), \( f \), \( \lambda \), \( f_D \), \( k \), \( T \), \( T_m \), \( T_u \) and \( \Delta S \) denote the diffusivity of the amorphous carbon (~10⁻⁸ m²/sec in liquid state), fraction of the available sites, atomic jump distance, geometrical factor associated with diffusion (~1), Boltzmann constant, temperature, melting temperature, undercooling temperature, and the change in entropy, respectively. An increase in the value of \( T_u \) decreases the value of chemical free energy barrier for carbon to amorphous B-doped Q-carbon phase transformation. This also increases the velocity of the melt front. Therefore, the values of undercooling dictate the production of Q-carbon from the carbon melt. If the cooling rate is slow (low undercooling and low solidification velocity ((~5 m/sec))), nano and microdiamonds are formed whereas with high cooling rates (large undercooling and large solidification velocity (>10 m/sec)) amorphous Q-carbon is formed.¹⁸,²³,²⁶-²⁹ At intermediate velocity, a composite of Q-carbon and diamond is formed. The characterization of the B-doped Q-carbon phase was carried out using Raman spectroscopy, electron energy-loss spectroscopy (EELS), field emission scanning electron microscopy (FESEM) and superconducting quantum interference device (SQUID) magnetometry. To characterize the Raman active vibrational modes, Alfa300 R superior confocal Raman spectrooscope with a lateral resolution less than 200 nm was employed. Crystalline Si was used to calibrate Raman spectra, which has its characteristic Raman
active peak at 520.6 cm\(^{-1}\). High-resolution SEM with sub-nanometer resolution was carried out using FEI Verios 460L SEM to characterize the laser-irradiated (B-doped Q-carbon) films. To prepare the cross-sectional transmission electron microscope (TEM) samples, a FEI Quanta 3D FEG instrument having dual beam technology employing both electron and ion beam guns, was used. A low energy ion beam (5 kV, 10 pA) was used to cleanup the focused ion beam (FIB) surface damage. Aberration-corrected STEM-FEI Titan 80-300 was used in conjunction with EELS to acquire high-angle annular dark-field (HAADF) images and EELS spectra of B-doped Q-carbon thin films. The electron probe current used in the experiment was 38±2 pA. The EELS data was acquired with a collection angle of 28 mrads. Quantum design magnetic property measurement system (MPMS3) was used to measure temperature, field and time-dependent magnetic properties of thin films. Both the vibrating sample magnetometry (VSM) and direct current (DC) modes were used for measuring field, time and temperature-dependent magnetization. The magnetic flux-creep measurements were performed at isothermal conditions (up to 5000 secs) and magnetic field of 1 T after attainment of zero field conditions. The magnetic measurements were made with samples mounted parallel to the magnetic field. The temperature and field dependent resistivity measurements were performed in the physical property measurement system (PPMS).

7.4. Results and discussion

Figure 7.1(a) depicts temperature-dependent magnetic moment plots of B-doped Q-carbon at zero field cooled (ZFC) and field cooled (FC) conditions. As it is evident from the plots that there is an expulsion of magnetic field (Meissner diamagnetism) below the superconducting transition temperature (\(T_c\)) in B-doped Q-carbon. There is a sharp onset of diamagnetism at 36.0±0.5 K with complete diamagnetic shielding at lower temperatures. There also occurs penetration of the
magnetic field with an increase in the applied magnetic field in the field cooled conditions, which results in the upward shift of the magnetic moment curves below $T_c$. The temperature-dependent difference in the magnetic moment ($\Delta M = M_{FC} - M_{ZFC}$) at different applied magnetic field (20 Oe and 80 Oe) are shown as an inset in figure 7.1(a). There is a drastic difference between the temperature dependence of $\Delta M$ below and above $T_c$. Above $T_c$, there is no temperature dependence of $\Delta M$, thereby indicating a complete destruction of superconductivity (destruction of Josephson coupling) in B-doped Q-carbon. It should also be noted that $\Delta M$ increases with increasing applied magnetic field (below upper critical magnetic field). This suggests pinning of the magnetic vortices in the B-doped Q-carbon structure. The magnetic susceptibility ($\chi$) of B-doped Q-carbon samples are calculated as $\sim -0.02$ and $-0.09$ emu cc$^{-1}$Oe$^{-1}$ for FC and ZFC (at 5 K), respectively (inset of figure 7.1(a)). The ZFC magnetization shows the flux exclusion from the B-doped Q-carbon sample, whereas the FC magnetization indicates the flux expulsion. The shielding fraction is calculated from the ZFC curve whereas the superconducting volume fraction is calculated from the FC curve. A drastic difference between the ZFC and FC curves indicates pinning of the magnetic vortices in B-doped Q-carbon. The ZFC susceptibility ($-4\pi \chi$) represents the shielding fraction in a superconducting material. A complete shielding ($4\pi \chi < -1$) is observed in the B-doped Q-carbon samples, which indicates a high-quality superconducting phase. The superconducting volume fraction (Meissner fraction) is calculated from the FC curve at low applied magnetic field ($H < H_{c1}$). Without considering the demagnetization enhancement factor, the superconducting volume fraction is calculated to be $\sim 25\%$. Figures 7.1(b) and (c) show the temperature-dependent normalized first derivative of magnetic moment and second derivative of magnetic moment, respectively. The derivative method provides line shapes, characteristics peaks and crossover points which determine characteristic superconducting parameters.$^{30}$
pronounced peak ($T_c$) and FWHM ($\Delta T$) are observed at 35.5 K and 3.0 K, respectively. In figure 7.1(c), the temperature at which the curve crosses the zero line indicates $T_c$. The peak to peak width ($\Delta T'$) is calculated to be 0.5 K. The ratio of the widths calculated from the derivative plots ($\Delta T / \Delta T'$) is 6.0 and it indicates the characteristic of the superconducting transition line shape. The asymmetry of the transition is calculated to be $4.9 \times 10^{-3}$ using the relation: $(A-B)/(A+B)$. The line shape and asymmetry of the superconducting transition in B-doped Q-carbon indicate the presence of moderate electron-phonon coupling in this material.\cite{30,31}

The critical fields in B-doped Q-carbon superconducting phase are calculated using temperature dependent resistivity (at various magnetic field) and field- dependent magnetic moment (at various temperatures) measurements and the results are shown in figure 7.2. There is a sharp drop in the normalized resistivity ($\rho(T)/\rho(300)$) below $T_c$ in B-doped Q-carbon (shown in figure 7.2(a)). This sharp transition is also indicative of homogeneous superconductivity in this material. Higher magnetic fields are required to destroy the superconducting nature of B-doped Q-carbon, as it is evident from the lowering of $T_c$ and broadening of transition width with increasing magnetic field. The temperature corresponding to the zero-resistivity point vs magnetic field is shown as an inset in figure 7.2(a). To estimate the upper critical field ($H_{c2}$), the plot is extrapolated using the equation: $\frac{H_{c2}(T)}{H_{c2}(0)} = 1 - \left(\frac{T}{T_c}\right)^2$. The value of $H_{c2}(0)$ is calculated to be 5.6 T. The inset of figure 7.2(b) indicates an irreversible nature of the magnetic moment with increasing and decreasing magnetic field. This is attributed to intergranular and London currents (around the superconducting grains), which can trap the Abrikosov vortices and fluxons in an irreversible manner thereby causing a hysteresis behavior of the magnetic moment vs field plots.\cite{33} Above $T_c$, there is a complete loss of the hysteresis behavior indicating a complete dissolution of the Josephson coupling in the superconducting grains of B-doped Q-carbon. As it is evident from the figure 7.2(b) that there is a
decrease in the absolute value of magnetic moment with increasing temperature, a characteristic of superconducting materials.\textsuperscript{34} The plots also indicate type-II superconductivity in B-doped Q-carbon, having distinct values of lower critical field ($H_{c1}$) and $H_{c2}$ below $T_c$. The $H_{c1}$ and $H_{c2}$ are calculated from the point (magnetic field) at which the moment reaches its minimum value and the field at which $M(H)$ first deviates from the background, respectively. The values of $H_{c1}(0)$ and $H_{c2}(0)$ are calculated as 0.1 and 5.4 T, respectively. The anomalous drop of the lower critical field at low temperature\textsuperscript{26} requires further theoretical and experimental research (in B-doped Q-carbon which is currently underway). A similar drop in the lower critical field at low temperatures is also reported in amorphous carbon doped with sulphur.\textsuperscript{35} The Ginzburg-Landau parameter ($k$) is calculated to be 1.04 using the equation: $\frac{H_{c1}(0)}{H_{c2}(0)} = \frac{\ln(k)}{k^2 \times 2\sqrt{2}}$. Since the value of $k > 1/\sqrt{2}$, it shows that B-doped Q-carbon is a type-II superconductor. Figure 7.2(c) shows magnetization hysteresis loop at various temperatures (2, 11 and 21 K) below $T_c$. As it is evident from the hysteresis loops that there is irreversibility of the magnetization curves. This is due to pining of flux lines. The inset in figure 7.2(c) shows the irreversibility of the magnetization curves at 2 K. This results in a width (difference in M+ and M- values) which gives rise to critical current density. Addition of extrinsic impurities in superconductors increases the value of critical current density. But in the case of B-doped Q-carbon superconductor, there exists B-doped $sp^2$ hybridized carbon (non-superconducting entities) as pinning centers without adversely affecting $T_c$. Figure 7.2(d) depicts the critical fluctuations in B-doped Q-carbon. The figure indicates the presence of short-wave fluctuations ($n=-3.5$), mean-field region ($n=-1$ and -0.5), and critical region ($n=-0.2$). These characteristics explicitly explain the curvature of the resistivity plot near $T_c$.\textsuperscript{36} In the mean-field region (using Aslamazov-Larkin equation) the reduced conductivity ($\sigma'=\Delta\sigma/\sigma_0$) is expressed using the equation: $\frac{\Delta\sigma}{\sigma_0} = (AT')^n$.\textsuperscript{37} where $\sigma_0$ is the conductivity at 300 K, $\Delta\sigma$ is the difference between
room temperature conductivity and conductivity at a particular temperature, \( A \) is the temperature
independent constant, \( n \) is the critical exponent \((n = -0.5\) and \(-1.0\) for 3D and 2D critical
fluctuations, respectively) and \( T' \) is the reduced temperature defined using the relation:
\( T' = \left( T / T_c \right) - 1 \). The critical fluctuations occur close to \( T_c \) and the dimensionality of the fluctuations
(2D or 3D) are important superconducting parameters. There is a transition from 2D to 3D nature
of critical fluctuation near \( T_c \) in B-doped Q-carbon. The 2D to 3D crossover is seen at \( T/T_c = 1.01 \)
as compared to \( T/T_c = 1.11 \) in other high-temperature superconductors.\(^{35}\) Similar 3D fluctuations
are seen in other high-temperature superconductors: YBCO, LSCO.\(^{36}\) These fluctuations indicate
moderate to strong electron-phonon coupling in the superconducting state.

Figure 7.3 depicts the superconducting region in B-doped Q-carbon, which is enclosed by \( T_c, H_{c2} \)
and critical current density \((J_c)\). The values of \( J_c \) are calculated using the Bean’s formula:
\[ J_c = \left[ \frac{20\Delta M}{tw^2\left(l - \frac{w}{2}\right)} \right] \], where \( \Delta M \) is the difference in magnetization values (+M and -M) at a particular
magnetic field, and \( t, w, \) and \( l \) are the thickness, width and length, respectively, of the B-doped Q-
carbon sample. As it is evident from the \( J_c \) plots that there is a sharp decrease in the value of \( J_c \)
with an increase in the applied magnetic field, characteristic of a superconducting material. A
weaker field dependence of \( J_c \) at higher fields are also seen in B-doped Q-carbon due to the
presence of weakly connected superconducting grains. The value of \( J_c (0 \text{ Oe}) \) at 2 K is calculated
as \( 2.7 \times 10^9 \text{ A/cm}^2 \), which is considerably higher than oxide high-temperature superconductors.\(^{38,39}\)

The high values of critical current density may be due to unique pinning state associated with
mixing of \( sp^3 \) and \( sp^2 \) bonding in B-doped Q-carbon thin film.\(^{40}\) For the practical applications of
superconductors, there is a necessity to increase \( J_c \) which facilitates larger superconducting region
for the flow of dissipationless current. An increase in \( J_c \) is also conducive to lower flux creep rate,
which is a key to frictionless motors and other superconducting applications. Previous reports indicate that there is a considerable increase in $J_c$ with the introduction of extrinsic defects. These processes reduce $T_c$ of the material and thereby effectively reducing the superconducting region (volume). In the case of B-doped Q-carbon due to the ultrafast laser melting and subsequent quenching process, the structure is densely packed. This leads to an increase in the density of electronic states near Fermi level which facilitates high values of $T_c$ and $J_c$. The large values of $J_c$ at low temperature (2 K) are due to the presence of pinned states in the structure of B-doped Q-carbon. The B-doped Q-carbon contains an electronic mixture of $sp^3$ (~80%) and rest $sp^2$ hybridized carbon atoms. The superconductivity in this material is due to the formation of hole Cooper pairs, which are generated when boron is doped in the C- $sp^3$ hybridized structure. The presence of B-doped C- $sp^2$ entities in B-doped Q-carbon can increase the values of $J_c$ by introducing the pinning centers. At higher magnetic fields these pinned states can move thereby drastically reducing the values of $J_c$. Above the irreversibility field ($H^*$), the Lorentz forces on the magnetic vortices are large enough to facilitate their detachment from the pinning sites. This causes a reduction in the ability of a high-temperature superconductor to carry dissipation-free current. The value of $H^*$ is calculated to be ~2.5 T which is approximately half of $H_{c2}(0)$. A reduction of grain size in superconductors is also a viable path for increasing $J_c$. The size of the superconducting grains is comparable to the $\varepsilon_L$ in B-doped Q-carbon. The low grain size can also causes a tremendous increase in the value of $J_c$ in B-doped Q-carbon. Figure 7.3 also shows temperature-dependent $J_c$ measurements in B-doped Q-carbon. These data points correspond to the value of $J_c$ at a particular temperature at 0 Oe. There is a characteristic drop of $J_c$ with an increase in temperature and can be fitted with the equation: \[ \frac{J_c(T)}{J_c(0)} = 1 - \left( \frac{T}{T_c} \right)^{\frac{1}{2}} \] The magnetic field-dependent temperature measurements are also shown in the figure 7.3. These measurements
illustrate the characteristic nature of superconduction in B-doped Q-carbon. Three vertices of the figure 7.3 illustrate $T_c$ (36.0 K), $J_c$ (2.9×10^9 A/cm^2) and $H_{c2}$ (5.6 T), which are the three important parameters of a superconducting material. The values of critical current density are 2.20×10^8 and 1.72×10^8 A/cm^2 at 1T (10 K) and 2T (10 K), respectively. At 1T the values of critical current density are 2.37×10^8 and 2.20×10^8 A/cm^2 at 5 and 10 K, respectively. The high values of critical current density and $T_c$ will enable B-doped Q-carbon power transmission (superconducting) cables to carry a large amount of dissipation-less current. For example, a YBa$_2$Cu$_3$O$_{7-\delta}$ superconductor carrying a 150 A current (below $T_c$) can lead to an eightfold reduction of the heat load as compared to pristine Cu (in oxygen-free environment under similar operating conditions). Therefore, the use of B-doped Q-carbon in power transmission and superconducting magnets will drastically decrease transmission losses (in the form of resistive heat) and cost of materials processing (carbon-based material). The large values of $H_{c2}$ in B-doped Q-carbon will also facilitate its use in superconducting supercolliders operating at liquid He temperature. B-doped Q-carbon will also find its application in He-based close-cycle refrigeration systems, operating above 10 K. This novel carbon-based material can also be used in MRI systems, where magnetic flux densities of ~2T are used. Since B-doped Q-carbon has high values of $T_c$, $J_c$ and $H_{c2}$, it can sustain high magnetic fields and can also simplify cryogenic apparatus. These factors ultimately reduce the operational cost of superconducting-based frictionless motors. Electromagnetic pumping can also be achieved by using B-doped Q-carbon as electrodes. These superconducting pumps have no moving (mechanical) parts and work on the reactive thrust principle which helps in fluid propulsion. The large superconducting regime in B-doped Q-carbon shows that it can also be used in SMES devices (which can supply transient power at switching stations in a MAGLEV track) where the magnetic energy is stored in a superconducting coil energized with a circulating...
dissipation-less current. The use of B-doped Q-carbon as interconnects will also reduce propagation delays ($\approx$ resistance$\times$capacitance) between the electronic devices, thereby increasing the versatility of superconducting applications of B-doped Q-carbon. Since B-doped Q-carbon is totally biocompatible, it can be used for implantable devices.

Figure 7.4 depicts the time-dependent magnetic moment (flux creep) measurements in B-doped Q-carbon. The flux creep phenomenon follows the Anderson-Kim logarithmic time dependence\(^\text{44}\) (shown up to 5000 sec) with the reduced magnetic moment ($M(t)/M(t=0)$), as shown in figure 7.4(a). The motion of the pinned magnetic fluxes is associated with the flux creep which can be activated thermally. The probability of the thermally activated jumps increases exponentially with an increase in temperature. Thermally activated creep mechanism leads to dampening of supercurrents and reduction of magnetization, which thwart the high-temperature (below $T_c$) use of superconductors. The time-dependent magnetic moment data can be fitted using the equation:

$$\frac{M(t)}{M(t=0)} = 1 - S \times \ln(1 + \frac{t}{\tau_0}),$$

where $\tau_0$ denotes the time constant and $S = k_BT/U_p$. The fitted plots are shown in the figure 7.4(a) for various values of $T/T_c$. The important parameters governing the flux creep phenomenon are the pinning potential ($U_p$), isothermal magnetization relaxation ($S$), and $\tau_0$. The flux creep measurements are performed at a high magnetic field (1 T, field below upper critical field) which facilitate a strong interaction between the dense magnetic vortices. These measurements, therefore, yield better results of the pinning parameters related to the intervortex interaction phenomena. Figure 7.4(b) indicates an exponential dependence of the magnetic relaxation with temperature. The exponential relation between $S$ and $T_c$ is calculated as: $S \approx (e^{T/0.16T_c})$. This is associated with the average velocity of the thermally activated jumps (of magnetic flux lines) which is also exponentially related to the temperature. The inset in figure
7.4(b) shows the temperature-dependent change in magnetization loop width (ΔM). It shows a decrease in ΔM with temperature (up to $T_c$) which also causes a decrease in the pinning potential. The isothermal magnetic relaxation studies in B-doped Q-carbon indicate a strong flux creep near $T_c$. The strong thermal fluctuations near $T_c$ cause a giant creep of magnetic vortices and create a vortex liquid state. This reduces the effective pinning potential, as shown in figure 7.4(c). There is a complete reduction of the trapped flux (vortex state) above $T_c$ (normal state). Unlike in YBCO, where the pinning centers are formed due to the presence of dislocations in the CuO$_x$ layers,$^{45}$ in B-doped Q-carbon the B-doped $sp^2$ hybridized carbon entities may form the effective pinning centers. The pinning potential increases with decreasing temperature (as shown in figure 7.4(c)). The value of $U_p$ near $T_c$ is calculated as 0.75 eV, which is comparable to that in commercially available high-temperature superconductors (non-BCS YBCO, NBCO).$^{45}$ Figure 7.4(c) also shows the temperature-dependent time constant measurements in B-doped Q-carbon. The $\tau_0$ determines a transient state before the onset of the logarithmic magnetic relaxation (figure 7.4(a)). A transient time of $\sim 300$ sec is registered at temperatures close to $T_c$ which indicates a superior superconducting behavior of B-doped Q-carbon. As it is evident from the figure 7.4(a) that there is only $\sim 1.2\%$ decrease in magnetic moment at $T/T_c=0.97$, which indicates an immense applicability of B-doped Q-carbon in MRI and NMR inserts. A much higher change in magnetic moment ($\sim 20\%$) is seen in other high-temperature superconductors due to the formation of a frustrated glassy state.$^{46}$ The magnetic flux lines extend over a distance approximately equal to the London penetration depth in B-doped Q-carbon. The free energy barrier ($\Delta F$ near 0 K) of the flux bundle can be calculated as 688.02 T$^2$ nm$^3$ using the equation: $\Delta F = \left(\frac{H_{c2}(0)^2}{8\pi}\right)\lambda_L^3.$$^{47}$ The high values of critical current density (at low temperatures) in B-doped Q-carbon can be correlated with large values of free-energy barrier and pinning potential in its structure. The large pinning potential (in
superconductors) is a critical criterion for levitation and MRI applications.\textsuperscript{46} It should also be noted that the flux pinning strength and dimension of the critical fluctuations (near $T_c$) determine the irreversibility (hysteresis) of the M-H loops. In B-doped Q-carbon, the 3D nature of critical fluctuations and a high pinning potential result in the butterfly-like hysteresis (in the M-H plots), indicating superior superconducting characteristics of B-doped Q-carbon.

7.5. Conclusions

In conclusion, we presented the magnetic relaxation and three-dimensional critical fluctuations in a high-temperature superconductor: B-doped Q-carbon. These studies will eventually lead to the formation of commercially viable B-doped Q-carbon-based thermoelectric and various other superconducting devices. This superconducting phase is formed as a result of nanosecond laser melting in a super undercooled state and subsequent quenching of a amorphous carbon and boron composite layers. A sharp onset of diamagnetism is observed in B-doped Q-carbon at 36.0±0.5 K with complete diamagnetic shielding at lower temperatures (below $T_c$). The magnetization $\nu S$ temperature measurements also indicate similar results. There occurs a penetration of the magnetic field (with an increase in the applied magnetic field) in the field-cooled conditions, which results in the upward shift of the magnetic moment curves below $T_c$. The temperature-dependent resistivity measurements indicate an abrupt drop of resistivity below $T_c$ in B-doped Q-carbon. This sharp transition is indicative of homogeneous superconductivity in this material, which is possible due to the absence of B clusters in B-doped Q-carbon. The field-dependent resistivity $\nu S$ temperature plots indicate that a large magnetic field is required to destroy the superconducting nature of B-doped Q-carbon. With increasing magnetic field, there is a lowering of $T_c$ and subsequent broadening of the transition width in B-doped Q-carbon. Critical fluctuations measurements in B-doped Q-carbon show a transition from 2D to 3D (nature of critical fluctuation)
near $T_c$, which plays an important role in the superconducting transition. Using the power law, the value of $H_{c2}(0)$ is calculated to be $\sim 5.6$ T from the resistivity and magnetic plots. The magnetic moment vs field plots at various temperatures (below $T_c$) indicate an irreversible nature of the magnetic moment with increasing and decreasing magnetic field. This is due to the fact that intergranular and London currents (around the superconducting grains) can trap the Abrikosov vortices and fluxons in an irreversible manner, thereby causing a hysteresis behavior of the magnetic moment vs field plots in B-doped Q-carbon. Finally, we have also shown that the large values of $J_c$ ($\sim 2.7 \times 10^9$ A/cm$^2$) at low temperatures ($\sim 2$ K), which are attributed to the presence of pinned states in the structure of B-doped Q-carbon. To calculate the pinning potential in B-doped Q-carbon we have performed time-dependent isothermal magnetic moment studies, which follow Anderson-Kim logarithmic decay formalism. The values of pinning potential and transient time near $T_c$ are calculated to be 0.75 eV and $\sim 300$ sec, respectively, indicating superior superconducting properties of B-doped Q-carbon. Isothermal magnetic relaxation studies in B-doped Q-carbon also indicate a strong flux creep near $T_c$. Structural characterizations using Raman spectroscopy and EELS indicate a high $sp^3$ fraction ($\sim 84\%$) and rest $sp^2$ in the B-doped Q-carbon phase. The B-doped $sp^2$ hybridized carbon (non-superconducting entities), which is present in the B-doped Q-carbon, may act as effective pinning sites thereby increasing the values of pinning potential (near $T_c$), critical current density and upper critical field in this material. The motion of fluxoids in thermal gradients causes electromagnetic force ($e.m.f$) in a type-II superconductor. This leads to generation of potential difference, thereby leading to design of better thermoelectric devices (non-zero Peltier and Thompson coefficients). We have successfully demonstrated the motion of the fluxoids (by varying temperature and pinning potential) in B-doped Q-carbon. Since B-doped Q-carbon is a BCS ($s$-wave) superconductor, it can be interfaced with topological
insulators\textsuperscript{48} to create Majorana Fermions\textsuperscript{49} for quantum computing, sensing and secure communication applications. This discovery of high-temperature superconductivity in B-doped Q-carbon will stimulate further research in carbon-based superconductivity. Recent measurements show higher $T_c$ with increasing boron concentration. We have synthesized B-doped Q-carbon with B concentration close to 50%, and estimated $T_c$ over 114 K.
7.6. Figures:

![Figure 7.1](image)

**Figure 7.1.** (a) Magnetic moment vs temperature plots of B-doped Q-carbon at zero-field cooled (ZFC) and field cooled (FC) conditions; (b) The normalized first derivative of magnetic moment vs temperature showing $T_c=35.5$ K and $\Delta T=3$ K; and (c) The second derivative of magnetic moment vs temperature. The insets in (a) show the temperature-dependent difference of FC and ZFC at 20 and 80 Oe and susceptibility vs temperature of B-doped Q-carbon.
Figure 7.2. (a) Normalized resistivity vs temperature plots of B-doped Q-carbon at different applied fields (0, 1, 2, 3, 4 and 5 T); (b) Moment vs magnetic field plots at various temperatures (2, 6, 11, 16 and 21 K); (c) M vs H loops showing an irreversibility nature; and (d) Critical fluctuations in B-doped Q-carbon showing the crossover between 2D to 3D region. The insets in (a), (b), and (c) show variation of upper critical field with temperature, moment vs field at 21 K, and calculation of $J_c$, respectively.
Figure 7.3. Superconducting region plot showing $T_c$, $J_c$ and $H_c$ in B-doped Q-carbon.
Figure 7.4. (a) Time-dependent magnetic moment at 1 T; (b) Magnetic relaxation vs $T/T_c$ with the inset showing $\Delta M$ vs $T/T_c$; and (c) Pinning potential and time constant vs $T/T_c$. 
7.7. References


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8. Discovery of High-Temperature Superconductivity ($T_c = 55$ K) in B-Doped Q-Carbon

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8.1. Abstract

We have achieved superconducting transition temperature ($T_c$) of 55 K in 27 at% B-doped Q-carbon. This value represents a significant improvement over previously reported $T_c$ of 36 K in B-doped Q-carbon and is the highest $T_c$ for conventional BCS (Bardeen–Cooper–Schrieffer) superconductivity in bulk carbon-based materials. The B-doped Q-carbon exhibits type-II superconducting characteristics with $H_{c2}(0) \sim 10.4$ T, consistent with the BCS formalism. The B-doped Q-carbon is formed by nanosecond laser melting of B/C multilayered films in a super undercooled state and subsequent quenching. It is determined that $\sim 67\%$ of the total boron exists with carbon in $sp^3$ hybridized state, which is responsible for the substantially enhanced $T_c$. Through the study of the vibrational modes, we deduce that higher density of states near Fermi level and moderate to strong electron-phonon coupling lead to high $T_c$ of 55 K. With these results, we
establish that heavy B doping in Q-carbon is the pathway for achieving high-temperature superconductivity.

8.2. Introduction

Carbon based strongly-bonded materials have generated tremendous interest because of their potential for high-temperature superconductivity.\(^1\textsuperscript{,}^2\) For strongly coupled materials, \(T_c \approx 0.2[\lambda < \omega^2 \geq \Sigma_i(\eta_i/M_i)]^{0.5}\), where \(\lambda\) is the electron-phonon coupling constant related to ratio of spring constants, \(\omega\) is averaged phonon frequency, \(M\) is averaged atomic mass, and \(\eta\) is the McMillan-Hopfield parameter with units of spring constant and is related to strength of electronic response of electrons near the Fermi surface to atomic perturbations.\(^3\) Thus, using this as a guideline, the search for higher \(T_c\) need to focus on \(sp^3\) and \(sp^2\) strongly bonded carbon-based materials, which are doped with appropriate dopants to provide free carriers. This paradigm has led to search for superconductivity in doped diamond,\(^4\) nanotubes\(^2\) and buckyballs.\(^5\) The highest \(T_c\) in boron-doped SWNTs (single-wall nanotubes) ranged from 8-12 K and reached 19 K under pressure.\(^6\) The highest \(T_c\) in alkali-doped C\(_{60}\) has been reported to be 33 K.\(^7\) In search of high-temperature superconductivity in bulk materials, the reported \(T_c\) in boron-doped diamond reached 11 K with 5 at% boron concentration by using microwave plasma assisted chemical vapor deposition (MPCVD) techniques.\(^8\) Further increase in boron concentration to enhance \(T_c\) by using close to equilibrium technique, presents critical challenges.\(^9\) First, a highly nonequilibrium technique\(^10\) is needed to increase boron concentration, much higher than the thermodynamic solubility limit of 2 at%. Second, boron in substitutional carbon sites in diamond crystalline lattice creates strain (covalent radius of B=0.82 Å; and covalent radius of C=0.91 Å), which can lead to strain scattering and breaking up of Cooper pairs.
We recently reported a discovery, where amorphous carbon can be converted into Q-carbon or diamond by nanosecond laser melting in a super undercooled state and rapid quenching.\textsuperscript{11} In parallel, we can convert h-BN into Q-BN or c-BN.\textsuperscript{12} We reported $T_c$ of 25 K in B-doped diamond where estimated boron concentration was close to 17±1 at\%\textsuperscript{13,14} Here the diamond was formed by nanosecond laser melting of B-doped amorphous carbon and quenching rapidly from highly undercooled state. Under the rapid quenching, thermodynamic solubility limits are far exceeded by the phenomenon of solute trapping.\textsuperscript{13,14} By manipulating the undercooling by laser and substrate parameters to even higher values, we were able to produce B-doped Q-carbon with $T_c$ of 36 K at 17±1 at\%.\textsuperscript{13} The structure of Q-carbon is amorphous with 75-85\% sp\textsuperscript{3} and the rest sp\textsuperscript{2} bonded carbon. The boron in Q-carbon is bonded (67\%) to sp\textsuperscript{3} and the rest (33\%) to sp\textsuperscript{2} carbon.\textsuperscript{11} It should be mentioned that undoped Q-carbon is ferromagnetic with Curie temperature of over 580 K, and shows interesting properties, including room-temperature extraordinary Hall effect.\textsuperscript{11} Upon doping with boron, Q-carbon turns diamagnetic and exhibits superconducting behavior with $T_c$ increasing progressively with increasing B-concentration. The ferromagnetism in Q-carbon is destroyed with B-doping and it is completely eliminated at a critical concentration, and above which B-doped Q-carbon turns completely paramagnetic and superconducting. The superconducting transition temperature is found to increase from 36 K to 55 K with increasing B concentration from 17 at\% to 27 at\% in B-doped Q-carbon. It has also been shown that in 17 at\% B-doped Q-carbon, the upper critical magnetic field ($H_{c2}(T)$) follows $H_{c2}(0) [1-(T/T_c)^2]^{11}$ temperature dependence and is consistent with the BCS formalism.\textsuperscript{13} From the critical current density \textit{versus} field moments, the value of critical current density ($J_c (2T)$) in B-doped Q-carbon at 21 K is calculated to be $4.3\times10^7$ Acm\textsuperscript{2}, which indicates that this material can be used for the persistent mode of operation in MRI and NMR applications.\textsuperscript{14} Here we report that $T_c$ of 55 K has been reached, when B-concentration
in Q-carbon is further increased from 17±1 at% \((T_c = 37 \text{ K})\) to 27±1 at% via rapid laser melt quenching through the phenomenon of solute trapping.\(^{13,14}\)

8.3. Methods

A highly non-equilibrium pulsed laser deposition (PLD) technique was used to deposit alternating layers of boron and amorphous carbon thin films onto c-sapphire. The thickness of composite films ranges from 100-500 nm. The substrate temperature ranges from 300-550 K and \(1.0 \times 10^{-7}\) torr operating pressure (base pressure). The operating pressure was achieved by using an (oil-free) triscroll pump in conjunction with a turbo molecular pump. The PLD can be made highly non-equilibrium forward-directed process by controlling the laser spot size. A nanosecond KrF excimer laser (laser wavelength=248 nm, pulse duration=25 ns) was used for the PLD technique. In this process, the pulsed laser beam is rastered through the glassy carbon and boron (sector) targets mounted on the same target holder. The laser energy density in the PLD process ranges from 3.0-3.5 Jcm\(^2\). Prior to the start of the deposition process, the targets are pre-ablated to reduce the impurities in the as-deposited composite thin films. The change in B profile from multilayered structure to uniform distribution after laser annealing provides a direct evidence for melting. An increased laser-solid coupling, which is determined by optical absorption and reflection, is required during the pulsed laser annealing process. By putting C layers on the top, the reflectivity is reduced and absorption is enhanced since B is metallic it is highly reflective to the nanosecond laser pulse. This causes the formation of liquid metallic carbon and boron which thereby promotes liquid-phase diffusivity of boron in molten carbon. By using the two-dimensional diffusivity relation: \(x = 2\sqrt{Dt}\), where \(x, D\) and \(t\) indicate diffusion length, diffusivity and time, respectively we have determined the B/C periodicity. Using the value of \(D = 10^{-4}\) cm\(^2\)/sec (liquid phase diffusivity), \(t = 250\) ns, the B/C periodicity is calculated as 100 nm. The above-mentioned
periodicity in B/C layers causes simultaneous melting of B and C thereby causing solute trapping (of B) which leads to high-temperature superconductivity. By maintaining a constant (overall) thickness we can engineer the B and C layer thickness (ratio). This controls the B-doping in the Q-carbon phase. The melt-lifetime is controlled by varying the thermal conductivities of the as-deposited film and substrate. Therefore, alternating layers of B and C are essential to obtain the details of melting and alloying process. The as-deposited thin films are pulsed laser annealed (PLA) using nanosecond excimer ArF laser (laser wavelength=193 nm, pulse duration=20 ns, laser energy density 0.6-1.0 Jcm⁻²). The PLA process melts the B-doped carbon film in a highly super undercooled state and followed by ultrafast quenching. The whole process is completed within 200-250 ns. This non-equilibrium technique converts amorphous carbon films into B-doped quenched carbon (B-doped Q-carbon) structure where B concentration can exceed the thermodynamic solubility limit. We have shown that the B at% can be increased from 2 at% (in B-doped diamond) to 27 at% (in B-doped Q-carbon), which ultimately leads to high-temperature superconductivity.

The characterization of the superconducting B-doped Q-carbon phase was carried out using Raman spectroscopy, SIMS, EELS, HAADF, PPMS and SQUID magnetometry. Alfa300 R superior confocal Raman spectrocope with a lateral resolution less than 200 nm was employed to characterize the Raman-active vibrational modes in B-doped Q-carbon. A standard Si crystalline Si wafer was used to calibrate the unpolarized Raman spectra, which has its characteristic Raman peak at 520.6 cm⁻¹. Time-of-Flight Secondary Ion Mass Spectrometer (TOF-SIMS) with a lateral resolution of <300 nm was used to detect the presence of C, O, B, Al and other trace impurity elements (in ppm level) in the B-doped Q-carbon thin films. A FEI Quanta 3D FEG instrument having dual beam technology (where both electron and ion beam guns are used) was employed for
preparing thin (<80 nm) cross-sectional STEM samples. To clean up the FIB ion beam damage, a low energy ion beam (5 kV, 10 pA) was also used (after mounting the cross-sectional sample on a FIB grid). Aberration-corrected STEM-FEI Titan 80-300 was used in conjunction with electron energy-loss spectroscopy (EELS with a resolution of 0.15 eV) to acquire HAADF images and EELS spectra of B-doped Q-carbon thin films. An electron probe current of 38±2 pA and collection angle of 28 mrads were used during the EELS acquisition. Quantum design magnetic property measurement system (MPMS3) was used to measure magnetic properties of thin films. VSM and DC modes were used for measuring field- and temperature-dependent magnetization. The magnetic measurements were made with samples mounted parallel to the magnetic field (parallel to c axis). The SQUID magnetometer can detect magnetic field with ~10⁻⁸ emu sensitivity and has a working temperature range: 1.8-400 K. The temperature stability and magnetic field uniformity in SQUID are ±0.5 % and 0.01% over 4 cm (sample length), respectively. Temperature-dependent resistivity measurements were carried out in the physical property measurement system (PPMS) at zero magnetic fields. To study melt kinetics upon performing PLA, a temporal and spatial Gaussian is utilized as a heat source. The annealing was modeled using via 2-D Heat transfer mode in transient COMSOL Multiphysics and simulation of laser interaction with materials (SLIM).³³ The annealed region had a finer mesh size of 1 nm which increased to coarser values up to 100 nm in the sub-domain. The outer boundaries of the film were approximated with adiabatic conditions, while the annealed surface had radiative and conductive losses incorporated in it. The thermal conductivities were approximated as 3 Wm⁻¹K⁻¹ and 290 W m⁻¹K⁻¹ for solid and liquid amorphous carbon at high temperatures, respectively. For boron, the thermal conductivities were taken as 27 W m⁻¹ K⁻¹ and 10 W m⁻¹ K⁻¹ for solid and liquid metallic boron, respectively.⁴¹ The motion of melt-front during the onset of melting and regrowth was performed using the “Phase
change model” at melting temperatures for C and B, with the latent heat of melting and heat conduction as the driving force propagating the melt interface. The pulsed laser deposition (PLD) and pulsed laser annealing (PLA) are highly non-equilibrium techniques. In PLD the energy of the species exceeds the value of $k_B T$. Therefore, in conjunction with detailed experimental work (SQUID, PPMS, EELS, HAADF, Raman spectroscopy, SIMS) we have used SLIM and COMSOL theoretical simulations to explain high-temperature superconductivity in B-doped Q-carbon. It is needless to mention that further (experimental and theoretical) work is currently being undertaken to understand the kinetics of the highly non-equilibrium processing techniques.

8.4. Results and discussion

Figure 8.1 shows the details of temperature dependent magnetic and electrical measurements to determine $T_c$ in the B-doped Q-carbon. The magnetic susceptibility vs temperature ($M \ vs \ T$) measurements in zero field cooled and field cooled (50 Oe) conditions indicate the onset temperature of the superconducting state to be at ~55 K (as shown in Figure 8.1(a)). The large difference in magnetic susceptibility between the ZFC and FC conditions indicate the presence of flux pinning forces in the superconducting phase. The magnetic susceptibility vs temperature plots also indicate the presence of a paramagnetic signal (predominant at lower temperatures) which increases with increasing magnetic field. Similar paramagnetic influence has also been observed previously in other high-temperature superconductors.$^{15,16}$ The results from TOF-SIMS spectra indicate that the B-doped Q-carbon samples do not contain any impurities (within a resolution of about ppm). Figure 8.1(b) shows the magnetic moment vs magnetic field ($M \ vs \ H$) plots at 5, 10, 50 and 70 K. A significant hysteresis in the $M \ vs \ H$ plots below $T_c$ (at 5, 10 and 50 K) indicates type-II superconductivity in the B-doped Q-carbon samples. The hysteresis behavior is pronounced with the decrease in temperature. There is also an increase in the value of the
magnetization at lower temperatures. The M-H plots are irreversible in nature thereby indicating the penetration of the magnetic vortices (at higher fields). With the reversal of the sign of applied magnetic field, magnetic flux in the Shubnikov phase is trapped. Above $T_c$ (at 60 K), there is a complete loss of the hysteresis behavior and the sample exhibits a paramagnetic behavior. The magnetization curves are distorted (below $T_c$) due to the presence of an obvious paramagnetic signal. From the hysteresis plots, $H_{c1}$ can be estimated at the point where the (virgin) magnetization curve deviates from its linearity. The $H_{c2}$ is calculated from the extrapolation of the linear portion of the magnetization curve after it reaches its minimum. Figure 8.1(c) shows the superconducting, vortex and normal states of B-doped Q-carbon. Curve fitting of the lower critical field vs temperature shows a BCS nature following the power law: $\frac{H_{c}(T)}{H_{c}(0)} = 1 - \left(\frac{T}{T_c}\right)^n$. The values of $H_{c1}(0)$ and exponent ($n$) calculated as 0.04 T and 1.89, respectively. Similar curve fitting of the upper critical field vs temperature also reveals BCS type-II superconductivity in B-doped Q-carbon. The calculated values of $H_{c2}(0)$ and exponent are 10.47 T and 1.72, respectively. The value of $T_c$ calculated from the fitting relation is 55.0±0.5 K. The $H_{c2}(0)$ is also calculated as 12.31 T using the Werthamer-Helfand-Hohenberg (WHH) model\(^\text{17}\): $H_{c2}(0) = -0.69(dH_{c2}/dT)T_c$, where $dH_{c2}/dT$ denotes the slope at $T_c$. The Ginzburg-Landau coherence length ($\xi_L$) is calculated using the equation: $\xi_L = [\Phi_0/2\pi H_{c2}(0)]^{0.5}$, where $\Phi_0$ denotes the quantum of magnetic flux ($2.07 \times 10^{-15}$ T.m\(^2\)). Utilizing the value of $H_{c2}(0)$ as 10.47 T, $\xi_L$ is calculated to be 56.95 Å. The value of flux penetration depth ($\lambda_d$) can also be calculated using the equation: $\lambda_d = (\Phi_0/4\pi \lambda_d^2)\ln(\lambda_d/\xi_L)$. The value of $\lambda_d$ is calculated as 57.51 Å. The Ginzburg-Landau parameter ($k$) is calculated to be 1.01 (>1/2\(^{0.5}\)) which indicates that B-doped Q-carbon is a type-II superconductor.\(^\text{18}\) The zero-temperature energy gap ($\Delta(0)$) in B-doped Q-carbon is calculated as 8.53 meV using the relation: $\Delta(0) = 1.8 k_BT_c$ and $T_c=55$ K, which is ~55% more than that the earlier reported B-doped Q-carbon
(17 at% B) superconducting phase exhibiting $T_c$ of 36 K.\textsuperscript{13} The electron-phonon coupling can be calculated using the McMillan relation: \textbf{19} $T_c = \frac{\omega_{\log} \exp \left(- \frac{1.04(1+\lambda)}{\lambda - \mu^* (1+0.62\lambda)} \right)}{1.2}$, where $\omega_{\log}$ denotes the logarithmic average of phonon frequencies (= 67.4 meV), $\mu^*$ is the screened Coulomb repulsion pseudopotential (= 0.12), and $\lambda$ is the measure of average electron-phonon coupling. Using the value of $T_c$ as 55 K, the calculated value of $\lambda$ is 1.02, which is consistent with theoretical calculations of Moussa and Cohen for B-doped diamond.\textsuperscript{9} The value of $J_c$ (0 Oe) at 5 K in B-doped Q-carbon ($T_c$=55 K) is calculated as $2.95 \times 10^8$ A/cm², which is considerably higher than that reported in other high-temperature superconductors.\textsuperscript{20,21}

Superconducting transition temperature in B-doped Q-carbon is also determined using temperature dependent resistivity measurements, as shown in Figure 8.1(d). The results indicate a gradual establishment of global phase coherence in an array of weakly coupled superconducting grains in B-doped Q-carbon. The onset of superconducting transition ($T_{c on}$) is observed at ~55 K, while the zero-resistivity ($T_{c off}$) condition is at ~25 K. Since B-doped Q-carbon exhibits a broad transition width ($\Delta T \sim 18$ K), $T_c$ can be determined by using the derivative plot of normalized resistivity vs temperature. The point of inflection of the derivative plot ($T_c$) is determined to be 50 K (indicated by *) and is shown in the inset of Figure 8.1(d). A broad transition width may result from the presence of mixed phases of lower B-concentration in highly doped superconductors containing weakly coupled superconducting grains.\textsuperscript{15} The onset of superconducting transition temperature and broad transition width are also in agreement with magnetic measurements shown earlier in Figure 8.1(a). This suggests the existence of mixed superconducting phases, possibly due to the ultrafast laser processing induced strain in B-doped Q-carbon, as reported earlier high pressure-induced superconductors.\textsuperscript{15}
The B-doped Q-carbon sample exhibiting $T_c = 55$ K is probed using annular dark field (ADF) imaging in a scanning transmission electron microscope. The structure is further compared with the previously reported B-doped Q-carbon sample having $T_c = 36$ K.$^{13}$ A schematic of the applied method for tuning the amount of B using sector targets is shown in Figures 8.2(a) and (c). To incorporate larger doping concentration of B in Q-carbon, nanosecond pulsed laser annealing (PLA) was done on the parent films containing multilayers of B and C, deposited by pulsed laser deposition with a larger sector of B, as shown in the Figure 8.2(a). As a result, B-doped Q-carbon film was observed along with a top amorphous layer, which later was confirmed as pure B. The cross-sectional (ADF) image of the sample is shown in Figure 8.2(c), where top B layer is clearly interfaced with B-doped Q-carbon film. On the other hand, B-doped Q-carbon sample, reportedly exhibiting $T_c \sim 36$ K is obtained using smaller B sector (Figure 8.2(c)), consists of only B-doped Q-carbon layer without any top layer.$^{13}$ The results elucidate that the B-doped Q-carbon with $T_c$ of 55 K clearly have a different nanostructure constitution as compared to the one reported earlier with a single layer of B-doped Q-carbon ensuing a $T_c$ of 36 K, as shown in Figure 8.2(d).

To understand the structure of B-doped Q-carbon showing $T_c$ of 55 K, detailed electron energy-loss spectroscopic (EELS) analysis was performed as shown in Figure 8.3. Figure 8.3 illustrates the compositional maps of B (Figure 8.3(c)) and C (Figure 8.3(d)) corresponding to the ADF image of B-doped Q-carbon (Figure 8.3(b)). Figure 8.3 clearly demonstrates a homogeneous distribution of B in Q-carbon film, while the top layer consists of pure B.$^{22}$ The average B concentration is determined to be $27\pm 1$ at\% in the B-doped Q-carbon region using EELS quantification.$^{23}$ It is noteworthy to mention that the estimated concentration of doped B is much higher ($27\pm 1$ at\%) than our previously reported B-doped Q-carbon ($17\pm 1$ at\% B).$^{13}$ In another interesting observation, it is evident that there is a distinct 2-3 nm thick interposing layer between 27 at\% B-doped Q-
carbon and pure B. This layer contains estimated B concentration of 45±2 at%. It is noteworthy that this layer is atomically sharp, indicating a distinct entropy and phase presumably with higher $T_c$ and thus causing the transition onset at high temperatures. The representative EELS spectra (as-acquired and background subtracted) from B-doped Q-carbon, interface and pure B are shown in Figure 3A, displaying B-K (188 eV) and C-K (284 eV) edges. The B-K edge from the B region exhibits the characteristics of pure B.\textsuperscript{22} On the other hand, it contains $\pi^*$ and $\sigma^*$ peaks for both B and C in B-doped Q-carbon. These characteristic peaks ($\pi^*$ and $\sigma^*$) indicate the presence of C and B bonded in both $sp^3$ and $sp^2$ hybridization state, as was also reported previously.\textsuperscript{13} The $sp^3$ fraction of C in B-doped Q-carbon is estimated to be ~71% which is consistent with Raman spectroscopy results. Based on the analysis of B-K edge in Q-carbon, $sp^3$ bonded fraction of B is estimated to be ~67%, suggesting a total of ~18 at% B doping in $sp^3$ sites of Q-carbon, which gives rise to superconductivity. Overall, in a key result, phase segregation of B-doped Q-carbon and amorphous B with a distinct interface is observed in the sample where B doping in Q-carbon is as high as ~27 at% due to highly non-equilibrium nature of the quenching process.

To obtain a detailed bonding characteristics in B-doped Q-carbon, Raman spectroscopy is performed. Figure 8.4(a) depicts unpolarized Raman spectra of 27 at% B-doped Q-carbon ($T_c$=55 K) and 17 at% B-doped Q-carbon ($T_c$=36 K) samples using 532 nm as the excitation source. The peak fitted spectra of 27 at% B-doped Q-carbon ($T_c$=55 K) using Raman-active vibrational modes of C at 1105 cm\(^{-1}\), 1330 cm\(^{-1}\), and 1567 cm\(^{-1}\) is shown in the inset, concluding $sp^3$ fraction to be ~71% which is in excellent accordance with the EELS results. In other carbon-based highly doped samples, with the increase in doping percentages, there is an increase in graphitization.\textsuperscript{24,25} In an interesting finding, a significant blue shift of ~10 cm\(^{-1}\) of the diamond peak ($F_{2g}$) in heavily B-doped Q-carbon samples (27 at%) is seen as compared to 17 at% B-doped Q-carbon samples.
(shown in inset). This shift is correlated to the inherent hydrostatic pressure induced by the highly non-equilibrium laser processing of B-doped Q-carbon. This intrinsic hydrostatic pressure gives rise to an increase in the phonon frequency and a decrease in charge transfer by modulating the bonds of B-C in the B-doped Q-carbon structure. An increase in phonon frequency also results in a strong electron-phonon interaction which leads to a high superconducting transition temperature. The upshift in phonon frequency \( (F_{2g}) \) occurs due to a reduction in the free lattice vibrations. This phonon mode \( (F_{2g}) \) is a characteristic of the out-of-plane vibrations of tetrahedra (coordination number = 4) in diamond. Similar upshifts are also observed in the radial breathing modes of B-doped CNT thereby causing an increase in the superconducting transition temperature \( (T_c) \).\textsuperscript{26-28} Up to pressures of 40 GPa, the Raman shift of the diamond peak can be calculated using the following equation: \( \omega(P) = \omega_0 + a_1P + a_2P^2 \) where, \( \omega_0, a_1 \) and \( a_2 \) are 1333.0 cm\(^{-1}\), 2.83 cm\(^{-1}\) GPa\(^{-1}\) and \(-3.65 \times 10^{-3}\) cm\(^{-1}\) GPa\(^{-2}\), respectively.\textsuperscript{29} The intrinsic hydrostatic pressure calculated using the above equation in Q-carbon is -1.06 GPa (compressive). It is well-known that the average value of the electronic density of states will decrease with increasing pressure due the pressure-induced band broadening. However, the pressure dependence of electronic density of states near the Fermi energy level can be very different.\textsuperscript{30} \( T_c \) depends on the structural details and the topology of the Fermi surface in a superconducting material. The pressure-induced redistribution of electronic charges between different bands can also alter the position of the Fermi level thereby increasing the electronic density near the Fermi level.\textsuperscript{31} This plays a vital role in increasing \( T_c \) in B-doped Q-carbon. The blue shift indicates an increase in the electronic density of states near Fermi level with increasing B doping concentration in B-doped Q-carbon, thereby causing a high-temperature superconductivity. The experimental evidence of increasing electronic density of states near Fermi level is presented in Figure 8.4(b) by using electronic Raman spectra (between 100-500 cm\(^{-1}\)) of
B-doped Q-carbon ($T_c = 55$ K and 36 K) and as-deposited B-C thin films. It is evident from the spectra, distinct shallow acceptor states are observed in the B-doped Q-carbon samples as compared to the as-deposited B-C thin films. In the heavily doped (27 at%) B-doped Q-carbon sample ($T_c = 55$ K), distinct energy levels at 14.0, 22.7 and 34.6 meV are present in comparison with the energy levels at 13.3 and 33.3 meV in the 17 at% B-doped Q-carbon sample ($T_c = 36$ K). The vibrational mode at 445 cm$^{-1}$ correspond to sapphire substrate (marked by *). The energy level at 14.0, 22.7 and 34.6 meV corresponds to 1s to 2s, 1s to 3s and 1s to 4s electronic transitions, respectively, consistent with those observed in heavily B-doped diamond samples.$^{32}$ Among these energy levels, the most important one corresponds to 1s to 4s transition due to its proximity to the valence band maximum. This appears at 34.6 meV in 27 at% B doped Q-carbon while at 33.3 meV in 17.0 at% B doped Q-carbon. These are three key observations from the spectra: (i) broadening, (ii) blue-shift and (iii) enhanced intensity in this energy states are seen by increasing B doping concentrations in Q-carbon. The broadening in the energy level indicates the increased overlapping of the wavefunctions of acceptor (excited) states ($n$s). This causes an increase in the electronic density of the acceptor states leading to an increase in $T_c$ in high-temperature superconductors. The blue-shift indicates formation of acceptor energy levels near the valence band maximum, thereby stabilizing the formation of Cooper pairs at higher thermal energy. There is also a considerable increase in Raman intensity (which is directly proportional to the electronic density of states) with increasing B at% from 17.0 to 27.0 % and is shown as an inset in the Figure 4B. According to the McMillan formula, which is valid for $\lambda < 1.5$, $\lambda$ is related to the electronic density of states near Fermi energy ($N(E_F)$) by the following equation: $\lambda = N(E_F) \times V$ where, $V$ denote the electron-phonon coupling potential. Therefore, the higher value of $T_c$ in the heavily B-doped Q-carbon sample ($T_c = 55$ K) is related to an increase in the electronic density of states at the Fermi
level and $\lambda$, as compared to the 17 at% B-doped Q-carbon sample ($T_c = 36$ K) sample. Based on the electronic Raman results for B-doped Q-carbon, the schematic energy diagram of B acceptor states and electronic transitions present in B-doped Q-carbon and B-doped diamond$^{14}$ (formed by HFCVD process) are shown in Figure 4C. It clearly illustrates that the evolution of a shallow acceptor energy level at $\sim$34.6 meV results from the enhanced B concentration (27 at%) which is much closer to the valence band maximum as compared to the energy level at $\sim$33.3 meV in 17% B-doped Q-carbon. This causes an increase in the density of the electronic acceptor states near the Fermi level, which is primarily responsible for high-temperature superconductivity in B-doped Q-carbon.

Finally, to understand the evolution of interesting morphology in heavily B doped (27 at%) Q-carbon under nanosecond laser annealing, we employ the SLIM (simulation of laser interaction with materials) program$^{33}$ and COMSOL Multiphysics and simulate the laser-solid interactions (Figure 8.5). The thermal profiles of C-B layered structures and pure C film on Al$_2$O$_3$ are shown in Figure 8.5. This calculation first establishes that the energy threshold for the homogeneous melting amorphous C/B thin films is $\sim$0.6 J/cm$^2$ (i.e. no melting of the top C layer occurs at 0.4 J/cm$^2$). This homogeneous metallic melt triggers the liquid phase diffusion process, where the dopant concentrations can exceed the retrograde thermodynamic solubility limits (2 at% B in diamond). The B-profile broadening in Figure 8.6(a) is consistent with the diffusivity of B in liquid phase ($\sim$10$^{-4}$ cm$^2$/sec). As it is evident from the thermal profile, the onset of melting occurs at $\sim$20 ns (after the laser is incident on the layered structure). The dotted lines $T_m^C$ and $T_m^B$ denote the melting point of C and B, respectively. A flatter temperature profile with time is indicative of the formation of homogeneous melt of the C-B layer. The C-B profile is also compared with the simulation results of similar thickness of C layer on sapphire. B stays in the melt state for $\sim$57 ns
even after the solidification of C in C-B layered structure. It leads to zone-refining of the insoluble B melt from the solidified B-doped Q-Carbon layer and finally results in the observed structure of 27 at% B-doped Q-carbon. The progression of laser induced melting and solidification in C-B multilayer structure is shown as an inset in Figure 8.5. Various stages of this process illustrate the faster solidification in C as compared to B, thus leading to solute trapping of B in Q-carbon and the evolution of zone-refined B-doped Q-carbon structure. This nanosecond pulsed laser annealing process (<100 ns) leads to the formation of shallow acceptor electronic states and strong electron-phonon coupling in 27 at% B-doped Q-carbon. The strong electron-phonon coupling and high density of states near the Fermi level lead to the high-temperature superconductivity in B-doped Q-carbon.

Figure 8.6(a) indicates the TOF-SIMS profile of the superconducting B-doped Q-carbon sample ($T_c=55$ K). An effective laser-material coupling is achieved using the C as the top layer in the B-C layered composite structure. This leads to laser-induced melting and subsequent rapid quenching process thereby leading to the formation of highly B-doped Q-carbon structure. The periodic variation of SIMS spectral intensity of B and C is flattened out after the PLA process (shown in Figure 8.6(a)). This indicates a complete melting (of C and B) followed by liquid phase diffusivity. From dopant profile broadening, the diffusivity coefficient was derived to be $\sim 2\times10^{-4}$ cm$^2$/sec. A Boron enriched layer (~45 at% B) is formed at the interface (between metallic B and 27 at% B-doped Q-carbon) and is shown in Figure 8.6(b). The atomistic details of this highly-doped layer is discussed in the EELS section. The uniformity of B/C concentration profile in the B-doped Q-carbon thin film is an important criterion for high-temperature superconductivity (and is also shown in Figure 8.6(b)).
Figure 8.7(a) depicts the magnetic moment *versus* temperature plots at ZFC and FC conditions for the sapphire substrates employed in the present study. This indicates a non-superconducting nature of the substrates, which is critical for the present study. All the magnetization curves shown in the manuscript are subtracted from the sapphire substrate background. Figure 8.7(b) shows the magnetic moment *versus* temperature plots at various FC magnetic fields (50 and 100 Oe). With an application of the external magnetic field, there occurs a field expulsion which causes the magnetic moment to attain positive values. This is a characteristic behavior of a superconducting material. Figure 8.7(c) indicates the (virgin) magnetization curve (where the measurements start from 0 Oe applied field) of B-doped Q-carbon sample performed at various temperatures (5, 7, 30, 40, 50, 52 K). The paramagnetic contribution is subtracted in the above-mentioned plots. The lower critical field ($H_{c1}$) can be estimated at the point where the (virgin) magnetization curve deviates from its linearity (shown by *) and the upper critical field ($H_{c2}$) as the extrapolation of the linear portion of the magnetization curve after it reaches its minimum.

The electron-phonon coupling can be calculated using the McMillan equation: $T_c = \frac{<\omega>_{log}}{1.2} \exp\left(-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right)$ where, $<\omega>_{log}$ denotes the logarithmic average of phonon frequencies (= 67.4 meV), $\mu^*$ is the screened Coulomb pseudopotential (= 0.12), and $\lambda$ is the measure of average electron-phonon coupling. Using the value of $T_c$ as 55 K, the calculated value of $\lambda$ is ~1.02, which is consistent with theoretical calculations of Moussa and Cohen for B-doped diamond and is shown in the Figure 8.8(a). The supplementary fig. 8.8(b) shows the variation of $T_c$ and $\lambda$ with increasing B at% in B-doped diamond, which is calculated using DFT. The Figure 8.8(b) shows the value of B at% and $\lambda$ (at $T_c=55$ K) as 26.77 and 1.02, which is in excellent accordance with the concentration determined by EELS. As it is evident from the figure 8.8(b),
there is a decrease in the value of $T_c$ above 30 at% B doping due to the onset of lattice instability.\textsuperscript{9} The lattice distortions will decrease and increase $<\omega>$ and $\lambda$, respectively.\textsuperscript{9}

Figure 8.9(a) represents the semi-log plot of critical current density ($J_c$) versus applied magnetic field in B-doped Q-carbon ($T_c$=55 K). $J_c$ is calculated using the Bean’s formula: $J_c = \frac{20\Delta M}{tw^2(l-w/3)}$, where $\Delta M$ denotes the difference in magnetization values (+M and -M) at a particular magnetic field (calculated from the M-H loops), and $t$, $w$, and $l$ are the thickness, width, and length of the sample, respectively. The plot indicates a decrease in the value of $J_c$ with an increase in the applied magnetic field, which is a characteristic property of a superconductor. The value of $J_c$ (0 Oe) at 5 K in B-doped Q-carbon ($T_c$=55 K) is calculated as $2.95 \times 10^8$ A/cm$^2$, which is lower than that calculated in 17 at% B-doped diamond: $T_c$=36 K ($1.82 \times 10^9$ A/cm$^2$). This decrease in the critical current density can be envisaged due to an increase in the paramagnetic contribution in the heavily B-doped sample ($T_c$=55 K). Nevertheless, the values of $J_c$ in B-doped Q-carbon samples are considerably higher than that found in other high-temperature superconductors.\textsuperscript{20,21,34} Large values of $J_c$ are critical for practical applications (of superconductors). The large values of $J_c$ in B-doped Q-carbon samples are due to their small dimensions. The inset of Figure 8.9(a) indicates the magnetic field dependence on $J_c$ for B-doped Q-carbon samples having $T_c$ = 36 and 55 K. As it is evident from the plot that there is a significant flattening of the $J_c$-H plot in the heavily B-doped Q-carbon sample ($T_c$=55 K) above ~750 Oe (shown by *). This indicates a higher value of the upper critical field in the 27at% B-doped Q-carbon (10.47 T) as compared to 17 at% B-doped Q-carbon (5.40 T) sample. The irreversibility field (H*) in the heavily B- doped Q-carbon samples is ~ 94 % greater than in the 17 at% B-doped Q-carbon samples. This indicates a larger ability to
carry dissipation-free current (at higher magnetic fields) in the 27 at% B-doped Q-carbon as compared to 17 at% B-doped Q-carbon thin films.

Figure 8.9(b) represents the semi-log plot of \( J_c \) (0 Oe) \textit{versus} temperature. The temperature dependence of the critical field (at 0 Oe) at lower temperatures can be fitted using the equation: 

\[
J_c(T) = J_c(0) [1-(T/T_c)],
\]

where \( J_c(0) \) indicates the critical current density at \( \sim 0 \) K. The value of \( J_c(0) \) is calculated to be \( 3.31 \times 10^8 \) A/cm\(^2\). The plot indicates a higher value of \( J_c \) (4.2 K) in B-doped Q-carbon (~\( 10^8 \) A/cm\(^2\)) as compared to other high-temperature superconductors: Nb-Ti, Nb\(_3\)Sn and YBCO (< \( 10^5 \) A/mm\(^2\)). The energy per unit volume of the superconducting state (\( \Delta G_{ns} \)) relative to the normal state can be calculated using the equation:

\[
\Delta G_{ns} = -0.5 \mu_0 H_c^2,
\]

where \( H_c \) and \( \mu_0 \) denote upper critical field (at \( \sim 0 \) K) and magnetic permeability (in vacuum), respectively.

Considering the values of \( H_c \) as 27.02 and 10.54 T in Nb\(_3\)Sn and 27 at% B-doped Q-carbon, respectively, \( \Delta G_{ns} \) (of B-doped Q-carbon) = 0.15 \times \( \Delta G_{ns} \) (of Nb\(_3\)Sn) is calculated. This indicates that a lesser energy is required for the expulsion of magnetic field in B-doped Q-carbon as compared to that in Nb\(_3\)Sn which thereby causes the tremendous increase in the value of \( J_c \) (in B-doped Q-carbon). Similarly, \( \Delta G_{ns} \) (of 17 at% B-doped Q-carbon) = 0.26 \times \( \Delta G_{ns} \) (of 27 at% B-doped Q-carbon). This explains the increase in the value of \( J_c \) in 17 at% B-doped Q-carbon as compared to 27 at% B-doped Q-carbon. A weaker dependence of \( J_c \) at higher fields is also observed in B-doped Q-carbon and can be due to the presence of a large number of (weakly-coupled) superconducting and paramagnetic regions. The larger values of \( J_c \) at lower temperatures are due to the presence of pinned states in the B-doped Q-carbon structure. These pinned states cause magnetic flux pinning, thereby increasing the superconducting transition width and \( J_c \). The depairing current density is calculated as \( 4.61 \times 10^{10} \) A/cm\(^2\) using the equation: \( j_0 = \)
\[ \frac{\Phi_0}{(3\sqrt{3\pi}\lambda^2\xi)} \], where \( \Phi_0 \), \( \lambda \) and \( \xi \) represent the flux quantum, penetration depth and coherence length, respectively. This indicates that we have achieved \( \sim 0.72\% \) of the depairing current density at \( \sim 0 \) Oe (due to the presence of weakly coupled superconducting grains). Figure 8.9(b) also indicates a crossover at \( \sim 20 \) K between the Ambegaokar-Baratoff (AB) and Ginzburg-Landau (GL) models. AB model predicts a critical current density dependence of \( (1-T/T_c) \), whereas GL predicts as \( (1-T/T_c)^{1.5} \). The AB model is followed at lower temperatures due to the presence of weak Josephson coupling and is predominantly observed in granular superconductors (weakly-linked superconducting grains). After 20 K there is a shift from the AB to GL model due to the presence of current-induced gap suppression effect. There is an increase in the crossover point with increasing B-doping \%. This is due to the presence of paramagnetic (non-superconducting) regions in the highly doped samples which leads to the formation of Josephson coupling. The crossover point also indicates the temperature at which the Josephson coupling energy is equal to the superconducting condensation energy. The ratio \( (\varepsilon_0) \) of Josephson coupling energy to the superconducting condensation energy in a superconductor can be calculated using the equation:

\[ \varepsilon_0 = \frac{1}{0.882 \left(1 - \frac{T_x}{T_c}\right)}, \]

where \( T_x \) denotes the crossover temperature (20 K). The value of \( \varepsilon_0 \) is calculated as 0.72. The ratio \( \varepsilon_0 \) is also inversely proportional to the electronic density of states present near the Fermi level \( (N(0)) \). The value of \( \varepsilon_0 \) is less than 1 thereby indicating an increase in the density of states near the Fermi level. This increase in \( N(0) \) and high value of phonon vibration frequency (observed from Raman spectroscopy) can give rise to a strong electron-phonon coupling, thereby resulting in high-temperature superconductivity in B-doped Q-carbon structure.

The blue-shift of \( E_{2g} \) peak in Raman spectra indicates an increase in the electronic density of states in B-doped Q-carbon thereby causing high-temperature superconductivity. With an increase in the
laser-induced pressure in B-doped Q-carbon, there is a significant upshift of the $E_{2g}$ vibrational mode which also indicates a stronger electron-phonon coupling. The upshift of the above-mentioned Raman active vibrational mode is due to the suppression of free lattice vibration.\textsuperscript{6} There is a reduction of charge transfer which is caused as a result of a decrease in the B-C bond under laser-induced pressure. This improves the alignment of the Fermi energy level to the Van Hove singularity (VHS) points in the electronic density of states. This results in an increased value of $T_c$ in highly (27 at%) B-doped Q-carbon thin films. However, the change in the phonon frequency for the G vibrational mode in B-doped Q-carbon is minimal. This indicates a negligible change in the in-plane strain of the graphitic entities formed in the superconducting material. There occur Raman active vibrational modes in the range 475-1225 cm$^{-1}$ in B-doped diamond samples due to maxima in the phonon density of states (PDOS).\textsuperscript{39} The presence of these peaks in B-doped diamond thin films indicates distortion and defects in the diamond lattice. These peaks also originate from the local vibrational modes of B pairs in the interstitial sites ($n$-type).\textsuperscript{40} The absence of these Raman active vibrational modes in B-doped Q-carbon samples indicates B doping in the electrically active sites of Q-carbon, which leads to an increase in the superconducting transition temperature.

8.5. Conclusion

In conclusion, type-II high-temperature superconductivity with a $T_c$ of 55.0±0.5 K is achieved in B-doped Q-carbon thin films. These results show a huge improvement in previously reported $T_c$ of 36 K in B-doped Q-carbon films and represents the highest experimentally reported $T_c$ for BCS superconductivity in bulk carbon-based material. Such high $T_c$ is attributed to the heavy B doping (27 at%) in Q-carbon, accomplished by nanosecond laser induced homogeneous melting and subsequent quenching of B-C layer. This synthesis process can enhance the dopant concentrations
beyond the thermodynamic solubility limit, via solute trapping, which can be incorporated into substitutional sites (electrically active) without affecting their energy levels and ionization efficiencies. The upper critical magnetic field (\(H_{c2}(T)\)) in B-doped Q-carbon follows \(H_{c2}(0) [1- (T/T_c)^{1.72}]\) temperature dependence and is consistent with the BCS formalism. The electronic Raman spectra of B-doped Q-carbon (27 at% B) reveal an acceptor energy level at \(~34.6\) meV, situated closer to the valence band maximum as compared to that in 17 at% B-doped Q-carbon (~33.3 meV) and HFCVD grown B-doped diamond (~35.3 meV). The high electron-phonon coupling (\(\lambda=1.02\)) and increased electronic density of states near the Fermi energy level result in the high-temperature superconductivity in this highly doped phase. We also envisage an increase in the electron-phonon coupling with increasing B concentration thereby causing a dramatic increase in the superconducting transition temperature. This discovery of high-temperature superconductivity in 27 at% B-doped Q-carbon will stimulate further research in strongly-bonded carbon-based materials in the search for near room temperature superconductivity. Higher \(T_c\) (>55 K) is expected for the 45±2 at% phase and current efforts are being made to increase the fraction of this phase by manipulating the laser and substrate variables.
8.6. Figures:

Figure 8.1. (a) Magnetic moment vs temperature plots of B-doped Q-carbon thin film showing $T_c \sim 55$ K; (b) depicts M-H loops at a various temperatures below (5, 10, 50 K) and above (60 K) $T_c$; (c) Upper critical field and lower critical field in B-doped Q-carbon thin films along with the WHH curve; and (d) Normalized resistivity vs temperature with the inset showing the maximum resistivity drop at $\sim 50$ K. The error bars (5%) are shown in figure (c).
Figure 8.2. Schematic showing the process of synthesizing the parent as-deposited films for B-doped Q-carbon with (a) larger and (c) smaller B sector target; (b) ADF image of B-doped Q-carbon with 27 at% B-doping concentrations. Figure (b) shows the formation of bilayer structure of B-doped Q-carbon (bottom layer) and excess B (top layer); and (d) ADF image of B-doped Q-carbon containing lower concentration of B (17 at%), illustrating no formation of excess B layer.
Figure 8.3. (a) Representative EELS spectra containing B-K (188 eV) and C-K (284 eV) from different regions marked in (b); (b) Cross-sectional HAADF image of the B-doped Q-carbon where top layer is identified as pure B, while bottom layer is B-doped Q-carbon; (c) EELS elemental distribution maps of B; and (d) EELS elemental distribution maps of C. Figures (c) and (d) show uniform distribution of ~27 at% B in Q-carbon region, while having the presence of high concentration (~45 at%) B doping at the interface region.
Figure 8.4. (a) Raman spectroscopy of B-doped Q-carbon thin films having $T_c = 36$ and 55 K, with the insets showing 70.4% $sp^3$ in B-doped Q-carbon ($T_c = 55$ K) and a Raman shift (blue shift) of $\sim 10$ cm$^{-1}$ in the high $T_c$ sample; (b) Electronic Raman spectra of B-doped Q-carbon (having $T_c = 36$ and 55 K) and as-deposited B-C sample; and (c) Energy-level schematic diagram of B acceptor states in 17 at% B-doped Q-carbon (green band: 33.3 meV) and 27 at% B-doped Q-carbon (34.6 meV). The sapphire peak in figure (b) is indicated by *.
**Figure 8.5.** Temperature vs time profile after PLA using 0.6 J/cm² laser energy density simulated using SLIM programming with the inset showing depth dependent temperature profiles at different stages calculated using COMSOL Multiphysics. The dotted lines in the figure correspond to the melting point of carbon ($T_m^C$) and boron ($T_m^B$). In the B-doped Q-carbon structure, B stays in the liquid phase for ~57 ns after the solidification of C.
Figure 8.6. SIMS profiles of (a) 27 at% B-doped Q-carbon structure formed after PLA technique; and (b) B/C concentration profile showing the presence of a highly B-doped (~44at% B) Q-carbon phase at the interface between B and 27 at% B-doped Q-carbon thin film.
Figure 8.7. Magnetic moment vs Temperature plots of (a) sapphire substrate; (b) B-doped Q-carbon at different applied fields; and (c) calculation of critical fields in B-doped Q-carbon thin films at different temperatures.
Figure 8.8. (a) Variation of $T_c$ with $\lambda$ for B-doped Q-carbon; and (b) variation of $T_c$ and $\lambda$ with at% B in B-doped diamond\textsuperscript{9} (the blue dotted line corresponds to 27 B at% in B-doped diamond).
Figure 8.9. (a) Variation of $J_c$ with magnetic field for B-doped Q-carbon ($T_c=55$ K) at 10 and 20 K with the inset showing the variation of $J_c$ with magnetic field for B-doped Q-carbon samples ($T_c=36$ and 55 K) at 5 K; and (b) temperature dependence of $J_c$ in B-doped Q-carbon ($T_c=55$ K) showing the crossover between the AB and GL model at ~20 K.
8.7. References


9. Structure-property correlations in a phase-pure high-temperature superconductor with a record BCS $T_c = 55$ K

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9.1. Abstract

Here, we report the detailed structure-property correlations of a phase-pure B-doped Q-carbon high-temperature superconductor having a superconducting transition temperature ($T_c$) of 55 K. This superconducting phase is a result of nanosecond laser melting and subsequent quenching of a highly super undercooled state of molten B-doped C. The temperature-dependent resistivity at different magnetic fields and magnetic susceptibility measurements indicate a type-II Bardeen-Cooper-Schiffer superconductivity in B-doped Q-carbon thin films. The magnetic measurements indicate that the upper and lower critical fields follow $H_{c2}(0)[1-(T/T_c)^{1.77}]$ and $H_{c1}(0) [1-(T/T_c)^{1.19}]$ temperature dependence, respectively. The structure-property characterizations of B-doped Q-carbon indicate a high density of electronic states near the Fermi-level and large electron-phonon coupling. These factors are responsible for $s$-wave bulk type superconductivity with enhanced $T_c$ in B-doped Q-carbon. The time-dependent magnetic moment measurements indicate that B-doped Q-carbon thin films follow the Anderson-Kim logarithmic decay model having high values of pinning potential at low temperatures. The crossover from two-dimensional to three-dimensional
nature of Cooper pair transport at $T/T_c = 1.02$ also indicates a high value of electron-phonon coupling which is also calculated using the McMillan formula. The superconducting region in B-doped Q-carbon is enclosed by $T_c = 55.0 \text{ K}$, $J_c = 5.0 \times 10^8 \text{ A/cm}^2$, and $H_{c2} = 9.75 \text{ T}$ superconducting parameters. The high values of critical current density and pinning potential also indicate that B-doped Q-carbon can be used for persistent mode of operation in MRI and NMR applications. The Cooper pairs which are responsible for the high-temperature superconductivity are formed when B exists in the $sp^3$ sites of C. The electron energy loss spectroscopy and Raman spectroscopy indicate a 75% $sp^3$ bonded C and 70% $sp^3$ bonded B in the superconducting phase of B-doped Q-carbon which has 27 at% B and rest C. The dimensional fluctuation and magnetic relaxation measurements in B-doped Q-carbon indicate its practical applications in frictionless motors and high-speed electronics. This discovery of high-temperature superconductivity in strongly-bonded and light-weight materials by using non-equilibrium synthesis will provide the pathway to achieve room-temperature superconductivity.

9.2. Introduction

The hybridization of $s$ and $p$ orbitals in C atoms can lead to the formation of various allotropes and phases which have interesting magnetic and electrical properties. The evolution of high-temperature superconductivity in C is due to its light-weight strongly-covalent bonded atoms and large Debye temperature ($\theta_D$). The superconducting transition temperature ($T_c$) can be further increased by doping C structures thereby forming high density of electronic states ($N(0)$) near the Fermi energy level ($E_F$) with moderate to large electron-phonon coupling. The van Hove singularities in low-dimensional C structures can also introduce high electronic density of states near $E_F$. The superconductivity in carbon-based materials has been experimentally reported in graphite intercalation compounds at high pressure (CaC$_6$, $T_c = 15 \text{ K}$ at 7.5 GPa).
carbon nanotubes \((T_c = 20 \text{ K})\),\(^4\) multi-walled carbon nanotubes \((T_c = 12 \text{ K})\),\(^5\) alkali metal-doped C\(_{60}\) \((T_c = 33 \text{ K})\),\(^6\) K-intercalated picene \((T_c = 18 \text{ K})\),\(^7\) B-doped diamond \((T_c = 11 \text{ K})\),\(^8\) etc. The superconductivity in the carbon-based materials follows the well-established Bardeen–Cooper–Schrieffer formalism where \(T_c\) is governed by the equation: 
\[
T_c = 1.13 \theta_D e^{-1/(N(0)\nu)},
\]
where \(\nu\) denotes the Cooper pairing potential. Recently, a unconventional superconductivity \((T_c = 1.7 \text{ K})\) is also demonstrated in the interface states of graphene layers twisted at an angle of \(1.1^o\).\(^9\) The discovery of high-temperature superconductivity below 203 K in H\(_2\)S under high-pressure has stimulated significant research in light weight, strongly-bonded, and strongly-correlated electron-phonon systems.\(^10\) Therefore, for carbon-based superconductivity, B-doped diamond was an optimal choice where increasing B concentration in the substitutional sites increased \(T_c\) from 4 to 11 K.\(^8,\(^11\) Though theoretical predictions claim that \(T_c\) in B-doped diamond can be increased up to 55 K with \(~\) 20 at\% B,\(^1\) but experimentally the increase in B beyond 5 at\% presents formidable challenges in terms of internal strains, dopant clustering, and thermodynamic solubility limits.\(^12\) Therefore, highly non-equilibrium methods (based upon energetics of plasma and lasers) and strongly-bonded light weight amorphous materials are required to attain high-temperature superconductivity.

Recently, we have reported the formation of novel phase of carbon (Q-carbon) and BN (Q-BN) by melting and subsequent quenching of highly undercooled state of molten C and BN, respectively by using a high-powered nanosecond ArF excimer laser.\(^13,\(^14\) The Q-carbon phase is a new state of carbon with distinct structure and entropy, and contains four-fold \(sp^3\) (75-85\%) and rest three-fold \(sp^2\) bonded carbon. The formation of the highly dense and amorphous Q-carbon phase is dependent on the degree of undercooling which is controlled by laser energy density and thermal conductivities of the substrate and the as-deposited thin film. The process of undercooling is
similar to applying high pressure and therefore it leads to the formation of strongly-bonded light weight materials having moderate to strong electron-phonon coupling. Undoped Q-carbon is a room-temperature ferromagnet,\textsuperscript{15} which turns into a superconductor upon B-doping. We have reported high-temperature superconductivity in B-doped Q-carbon having $T_c$ of 36 K and 55 K.\textsuperscript{16,17} But in our previous samples exhibiting $T_c = 55$ K, we had an additional layer of zone-refined B on the top and so the 55 K layer was part of a composite structure. Therefore, the B-doped Q-carbon thin films did not exhibit optimum superconducting characteristics (sharp transitions, large critical current density, low flux creep, \textit{etc}). In the present research, we have solved this problem and synthesized phase-pure 55 K B-doped Q-carbon superconducting thin films (with no B zone-refined layer) which have shown superior superconducting properties for practical applications. In this paper, we present details of experimental procedures, temperature- and field-dependent magnetization, critical current density \textit{vs} temperature, resistance \textit{vs} temperature at different magnetic fields, critical fluctuations, temperature-dependent flux creep, and structure-property correlations (Raman and electron energy loss spectroscopy, scanning electron microscopy, high-angle annular dark field microscopy, and electron diffraction) of phase-pure B-doped Q-carbon thin films. We have also discussed the origin and nature of BCS superconductivity in the B-doped Q-carbon thin films and their potential applications in superconducting devices. Therefore, we envisage that highly non-equilibrium processing techniques can lead to development of potential high-temperature superconductors which can be directly used for practical applications.

\textbf{9.3. Experimental}

The pulsed laser deposition (PLD) is used to deposit alternating layers of boron and amorphous carbon thin films onto $c$-sapphire substrates. For the PLD process, KrF excimer laser (laser wavelength=248 nm, pulse duration=25 ns) is used. The total thickness of the films ranges from...
400-500 nm. The B and C sector targets are mounted on the same target carrousel which is rotated using a stepper motor. The back surface of the B target should be properly flushed with the C target so that no ablation of C occurs when the laser beam is rastered on the B target. The substrate temperature and the operating pressure are maintained at 450 K and 1.0×10⁻⁷ Torr. This operating pressure is maintained by using an oil-free scroll pump and turbomolecular pump. Prior to the deposition, the B and C targets are pre-ablated by using the KrF nanosecond laser to remove loose particles and surface contaminants. Then the pulsed laser beam is rastered (repetition rate=10 Hz) through the C and B (sector) targets. The laser energy density used during the deposition process ranges from 3.0-3.5 Jcm⁻². Subsequently, these B-C thin films are irradiated with nanosecond ArF excimer laser (laser wavelength=193 nm, pulse duration=20 ns). The laser energy density used ranges between 0.6-1.0 Jcm⁻². The pulsed laser annealing technique melts the B-C composite films in a highly undercooled state which is followed by quenching. The process is completed within 200-250 ns. This leads to the formation of superconducting B-doped Q-carbon thin films. By using the two-dimensional diffusion equation \( X=2(D*t)^{0.5} \), the diffusivity coefficient \( D \) is calculated as \( \sim 2\times10^{-4} \text{ cm}^2/\text{sec} \) which suggests melting and liquid phase diffusivity. This helps to incorporate B (in excess of its thermodynamic solubility limit) in the electrically active sites of \( sp^3 \)-bonded C.

The characterizations of the B-doped Q-carbon thin films were carried out by using Raman spectroscopy, FESEM, EELS, HAADF, SQUID magnetometer, and PPMS. The Raman spectroscopy was performed using a Alfa300 R superior confocal spectroscope which has a 200 nm lateral resolution. The Raman instrument was pre-calibrated by using crystalline Si sample that has a sharp Raman peak at 520.6 cm⁻¹. The FEI Verios 460 L was used to perform the high-resolution FESEEM analysis, which has a sub-nanometer resolution. For preparing the cross-sectional TEM samples, FEI Quanta 3D FEG (having dual beam technology) was used. The
focused ion beam damage was cleaned up by using a low energy (5 kV, 10 pA) ion beam. To acquire the HAADF and EELS we have used the aberration-corrected STEM-FEI Titan 80-300 electron microscope. Using the monochromator, the EELS was tuned up to provide an energy resolution of 0.15 eV. The electron probe current and collection angle used were 38 pA and 28 mrads, respectively. The JEOL 2000 FX electron microscope was used for performing the selected area electron diffraction (SAED) of the B-doped Q-carbon thin films. A 200 kV electron beam from a LaB6 source was used for the electron diffraction experiments. The magnetic measurements were performed in the SQUID Quantum design magnetic property measurement system (MPMS3). Both the VSM and DC modes were used for the magnetic measurements. The samples were mounted parallel and 90 degrees to the applied magnetic field. The temperature stability in the magnetometer was ±0.5 % and the magnetic field uniformity is 0.01% over 4 cm (sample length). The magnetic field strength as high as 7 Tesla (with a field charging resolution of 0.33 Oe) was used to perform the field dependent measurements in B-doped Q-carbon samples. The magnetic flux creep measurements were carried out in a magnetic field of 1 T under isothermal conditions in SQUID magnetometer. The temperature-dependent resistance and critical fluctuation measurements were carried out in the physical property measurement system (PPMS) at different magnetic fields (1-7 T).

9.4. Results and discussion

The magnetization moment vs temperature plots in zero field cooled (ZFC) and field cooled (FC) conditions are shown in figure 9.1(a). The B-doped Q-carbon superconducting thin films are mounted parallel (0 degree) and perpendicular (90 degree) to the external magnetic field during the temperature-dependent magnetization measurements. The samples are cooled in an external magnetic field of 100 Oe during the FC measurements. It is clearly evident that there occurs a
sharp decrease in the value of magnetic moment (to negative values) below 55.0 K which is the superconducting transition temperature of this material. This is also known as the Meissner effect where magnetic flux expulsion occurs when a sample is cooled below the superconducting transition temperature. Beyond the superconducting transition temperature there is no temperature dependence of magnetic moment which indicates a complete destruction of Josephson coupling (or superconductivity). A large difference in the magnetic moment values between the ZFC and FC curves indicates the presence of large flux pinning forces in the material (which cause the pinning of magnetic vortices). This leads to trapping of magnetic flux in the FC condition thereby causing an upshift of the negative magnetic moments. The magnetic susceptibility ($\chi$) of B-doped Q-carbon superconducting samples are calculated as $\sim -0.05$ and $-0.09$ emu cc$^{-1}$Oe$^{-1}$ for ZFC (0 degree) and ZFC (90 degree) at 5 K, respectively. The values of $\chi$ are calculated as $\sim -0.03$ and $-0.04$ emu cc$^{-1}$Oe$^{-1}$ for FC (0 degree) and FC (90 degree) at 5 K, respectively. The ZFC magnetization shows the flux exclusion from the B-doped Q-carbon sample, whereas the FC magnetization indicates the flux expulsion. Therefore, the shielding and superconducting volume fractions can be calculated from the ZFC and FC curves, respectively. The shielding fraction ($-4\pi \chi$) is calculated to be 0.63 when the superconducting samples are mounted parallel to the magnetic field. A complete shielding occurs when the samples are mounted perpendicular to the field which is also the reason for the 94.5% increase in the negative magnetic moment at the perpendicular position (as compared to the parallel position). The superconducting volume (Meissner) percentages are calculated to be 37.68 % and 50.24 % for 0 degree and 90 degree orientations, respectively. The insets of figure 9.1(a) show temperature-dependent first-order and second-order derivatives of magnetic moment. The derivative method is usually used to calculate the line shapes, characteristic peaks, and crossover points which determine the characteristic
superconducting parameters. The peak of the first-order derivative curve and the point at which the second derivative plot crosses the x-axis indicate the value of $T_c (~55 \text{ K})$. The asymmetry of the transition is calculated to be $1.9 \times 10^{-2}$ using the relation: $(A-B)/(A+B)$. The ratio of the widths calculated from the derivative plots ($\Delta T /\Delta T'$) is 1.08 and it indicates the characteristics of the superconducting transition line shape. The line shape and asymmetry of the superconducting transition in B-doped Q-carbon samples indicate the presence of strong electron-phonon coupling which is also calculated using McMillan equation. Figure 9.1(b) indicates magnetic moment vs magnetic field at isothermal conditions. As it is clearly evident from the figure that at room temperature, B-doped Q-carbon thin films exhibit a paramagnetic character. For temperatures below $T_c$, the superconducting thin films show a “butterfly-like” magnetic hysteresis character which is a characteristic of type-II superconductors. The M-H plots indicate an irreversible nature of the magnetic moment with increasing and decreasing magnetic field. This is attributed to intergranular and London currents (around the superconducting grains), which can trap the Abrikosov vortices and fluxons in an irreversible manner thereby causing a hysteresis behavior of the magnetic moment vs field plots.\(^{18}\) Above $T_c$, there is a complete loss of the hysteresis behavior (paramagnetic nature) indicating a complete dissolution of the Josephson coupling in the superconducting grains of B-doped Q-carbon. The decrease in the absolute value of magnetic moment with increasing temperature in B-doped Q-carbon thin films is a characteristic property of superconducting materials.\(^ {19}\) The values of lower and upper critical fields ($H_{c1}(T)$ and $H_{c2}(T)$) are calculated from the magnetic hysteresis loops. With increasing magnetic field, the value of magnetic moment increases up to a certain amount of field and then it decreases thereafter. The magnetic field value for the largest value of negative magnetic moment in the 4\(^{th}\) quadrant denotes $H_{c1}(T)$. The values of $H_{c2}(T)$ are determined as the magnetic field at which the magnetic moment
goes to zero. As it is evident from the isothermal M-H plots that the width of the plots decreases with increasing temperature. Figure 9.1(c) depicts the critical magnetic field vs temperature plots for the B-doped Q-carbon thin films. Three distinct regions namely superconducting, vortex, and normal states are found in the superconducting thin films thereby ascertaining a type-II BCS nature of superconductivity (in the thin films). The $H_{c2}(T)$ is found to vary at a faster rate than predicted by the Werthamer-Helfand-Hohenberg (WHH) model. According to the WHH model, $H_{c2}(0) = -0.69(dH_{c2}/dT)T_c$, where $dH_{c2}/dT$ denotes the slope at $T_c$. Therefore, the value of $H_{c2}(0)$ is calculated to be 11.23 T which is also shown in figure 9.1(c). In the case of B-doped Q-carbon thin films, the value of $H_{c2}(0)$ is calculated by using the power law: $\frac{H_{c2}(T)}{H_{c2}(0)} = 1 - \left(\frac{T}{T_c}\right)^n$. The data points fit best to the value of $n = 1.77$ and the value of $H_{c2}(0)$ is calculated (as 9.75 T) from the intersection point of the upper critical curve with the Y axis. For the case of temperature-dependent $H_{c1}$ plot, the data points fit best to the value of $n = 1.19$ and the value of $H_{c1}(0)$ is calculated as 1106.40 Oe. There is an upward curvature ~0 K in the case of $H_{c1}(T)$, which can be explained by the increased $sp^2$ contribution in the bonding of B-doped Q-carbon. The B in $sp^2$ electronic sites also increases the value of pinning potential which is explained in the flux creep section. The values of $T_c$ calculated from the temperature-dependent upper and lower critical field plots are 55.45 and 54.99 K, respectively. The Ginzburg-Landau coherence length ($\kappa$) is calculated to be 58.10 Å by using the equation: $\kappa = [\Phi_0/2\pi H_{c2}(0)]^{0.5}$. In the above calculation, the values of $H_{c2}(0)$ and superconducting magnetic flux quantum ($\Phi_0$) are taken to be 9.75 T and 2.07×10^{-15} T.m², respectively. The value of penetration depth ($\lambda_d$) is calculated to be 59.50 Å by using the equation: $H_{c1}(0) = (\Phi_0/4\pi\lambda_d^2)\ln(\lambda_d/\kappa)$. Therefore, the Ginzburg-Landau parameter ($k$) is calculated to be 1.02 (>1/2^{0.5}) thereby confirming that the B-doped Q-carbon thin films are type-II $s$-wave BCS superconductors. The Ginzburg-Landau parameter can also be calculated to be 1.04
by using the equation: \( \frac{H_{c1}(0)}{H_{c2}(0)} = \frac{\ln(k)}{k^2 \times 2 \sqrt{2}} \). Therefore, similar values of \( k \) by using two different superconductivity equations instill the confidence about the superconducting parameter calculations. The zero-temperature energy gap (\( \Delta(0) \)) in B-doped Q-carbon thin films is calculated as 8.50 meV by using the equation: \( \Delta(0) = 1.8 k_B T_c \). According to BCS formalism, the energy gap in superconductors is a region around the Fermi energy level containing high electronic density of states. The size of the energy gap (meV) is much smaller than the energy scale of the band structure (eV). With increasing temperature, the superconducting energy gap decreases and vanishes above \( T_c \) giving rise to pseudogap states.

From the viewpoint of practical applications of a superconductor, it should have high values of upper critical field, transition temperature, and critical current density which is the maximum amount of dissipation less current that it can carry in the superconducting region. The critical current density (\( J_c \)) for the superconducting thin films is calculated using the Bean’s formula: \( J_c = \left[ \frac{20 \Delta M}{t w^2 \left( t - \frac{w^2}{2} \right)} \right] \), where \( \Delta M \) is the difference in magnetization values (+M and -M) at a particular magnetic field, and \( t, w, \) and \( l \) are the thickness, width, and length of the samples. The critical current density vs magnetic field plots at isothermal conditions are shown in figure 9.1(d). The value of \( J_c \) (0 Oe) at 5 K is calculated as 5.30×10^{8} A/cm^{2} which is considerably larger than in B-doped diamond^{11} and other high-temperature superconductors.^{20,21} Figure 9.1(d) shows a sharp decrease of \( J_c \) with increasing magnetic field at isothermal conditions. This is because at higher fields the Lorentz force, which is created on the magnetic vortices, causes depinning and thereby drastically reduces the critical current density. A smaller drop in \( J_c \) vs magnetic field plots (at a fixed temperature) is possible by introducing pinning centers which adversely affects \( T_c \). A weaker dependence of \( J_c \) at higher fields is also observed in B-doped Q-carbon thin films. This can be due
to the presence of a large number of weakly-coupled superconducting regions. The large values of $J_c$ at lower temperatures are due to the presence of $sp^2$ bonded pinning states. The B-doped $sp^2$ entities present in the B-doped Q-carbon structure enhance the flux pinning. Therefore, high current density is required to move the pinned vortices. However at large magnetic fields this phenomenon is negligible due to the presence of an external magnetic field which assists the movement of the pinned states. It is well known that in the absence of flux pinning a superconductor exhibits low values of $J_c$ due to the presence of flux lattice lines (FLL) which dissipate the energy and the superconductor eventually turns “normal”. The refinement of the superconducting grain size is, therefore, a viable approach to introduce pinning centers in a superconductor. This causes an increase in the value of $J_c$. But in the case of amorphous B-doped Q-carbon thin films, the non-magnetic inclusions (B-doped $sp^2$ entities) which are formed due to the ultrafast melting and quenching process, help to increase the value of $J_c$. The high values of $J_c$ can also be predicted from the sharp fall in the magnetic moment below $T_c$ and the large width of the magnetic moment vs field plots. The high critical current density of B-doped Q-carbon (at low magnetic fields) makes it an ideal candidate for low field NMR inserts. The temperature dependence of the critical field (at 0 Oe) is shown in the inset of figure 9.1(d). As it is evident from the figure that with increasing temperature, initially there is a sharp decrease in $J_c$ which is followed by a gradual fall of $J_c$. This is due to the transition from Josephson coupling (at lower temperatures) to current-induced gap suppression effect (at higher temperatures). The value of $J_c(0)$ is extracted as $7.10\times10^8$ A/cm$^2$ by extrapolating the curve to 0 K. At 5 K the value of $J_c(0 \text{ Oe})$ is calculated as $\sim10^8$ A/cm$^2$ which is one order magnitude higher than that found in YBCO, Nb-Ti, and Nb$_3$Sn high temperature superconductors. The energy per unit volume ($\Delta G_{ns}$) of the superconducting state relative to the normal state can be calculated by using the equation: $\Delta G_{ns} =$
−0.5\(\mu_0 H_c^2\), \(^{21}\) where \(\mu_0\) and \(H_c\) denote magnetic permeability (in vacuum) and upper critical field (at \(\sim 0\) K), respectively. The values of \(H_c\) in Nb\(_3\)Sn and B-doped Q-carbon are 27.0 T and 9.7 T, respectively. So, \(\Delta G_{ns}\) (of B-doped Q-carbon) \(\sim 0.13 \times \Delta G_{ns}\) (of Nb\(_3\)Sn). Therefore, the high values of \(J_c\) in B-doped Q-carbon thin films are due to the fact that the energy required to exclude the magnetic field is extremely low in the case of B-doped Q-carbon (0.13 \times energy required for Nb\(_3\)Sn superconductors). The depairing current density \(j_0\) in B-doped Q-carbon can be calculated by using \(j_0 = \frac{\phi_0}{(3\sqrt{3}\pi \lambda^2 \xi)}\), where \(\phi_0\), \(\lambda\) and \(\xi\) represent the flux quantum, penetration depth and coherence length, respectively. The depairing current density is calculated as \(1.55\times10^{11}\) A/cm\(^2\). Therefore, a further enhancement of the critical current density can be achieved in B-doped Q-carbon thin films by increasing the B concentration in the \(sp^2\) electronic sites (which may further enhance number density of pinning centers). The high values of critical current density (\(\sim 10^8\) A/cm\(^2\)) and \(T_c\) (55 K) will enable B-doped Q-carbon power transmission (superconducting) cables to carry a large amount of dissipation-less current. The use of B-doped Q-carbon in power transmission and superconducting magnets will drastically decrease transmission losses (in the form of resistive heat) and cost of materials processing (carbon-based material). The large values of \(H_{c2}\) (9.75 T) in B-doped Q-carbon will also facilitate its use in superconducting supercolliders operating at liquid He temperature. B-doped Q-carbon will also find its application in He-based close-cycle refrigeration systems, operating above 10 K. This novel carbon-based material can also be used in MRI systems, where magnetic flux densities of \(\sim 2\)T are used. Since B-doped Q-carbon has extremely high values of \(T_c\), \(J_c\) and \(H_{c2}\), it can sustain high magnetic fields without losing its superconducting properties. These factors ultimately reduce the operational cost of superconducting-based frictionless motors.
The electron-phonon coupling parameter (for phonon-mediated BCS superconductivity) can be calculated using the McMillan formula \( T_c = \frac{<\omega>_{\log}}{1.2} \exp\left(-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right) \), where \(<\omega>_{\log}\) is the logarithmic average of phonon frequencies, \(\mu^*\) is the screened Coulomb pseudopotential, and \(\lambda\) is the measure of average electron-phonon coupling. Using the value of \(<\omega>_{\log}\), \(\mu^*\) and \(T_c\) as 67.4 meV, 0.1, and 55.0 K, respectively, the calculated value of electron-phonon coupling parameter \((\lambda)\) is 1.01. This value is also consistent with the theoretical calculations of Moussa and Cohen for highly B-doped diamond.\(^1\) This value of \(\lambda\) is indicative of strong electron-phonon coupling in B-doped Q-carbon. The value of the electron-phonon coupling in B-doped amorphous Q-carbon is ~5 times that in 2 at% B-doped diamond \((T_c=4\text{ K})\).\(^1\) This suggests stronger electron-phonon coupling in B-doped Q-carbon as compared to B-doped crystalline diamond, thereby leading to high-temperature BCS superconductivity in B-doped Q-carbon. The BCS superconductivity can also be explained by the relation between \(\lambda\), the density of states at the Fermi energy \((N(0))\), mass \((M)\), average square of electron-phonon matrix element \((<I^2>)\), and the characteristic phonon frequency averaged over the phonon spectrum \((<\omega^2>)\). The average electron-phonon coupling parameter is related to the above three variables by the equation \(\lambda = (N(0) <I^2>)/(M <\omega^2>)\). For the case of B-doped Q-carbon thin films, there is an increase in the value of \(N(0)\), the atomic mass is also quite low, and there exists strong covalent bonds. These factors cause an increase in the value of electron-phonon coupling parameter which along with the high dopant concentrations lead to high-temperature superconductivity in B-doped Q-carbon. Due to the presence of \(\sigma\) and \(\pi\) electronic states in B-doped Q-carbon, there can exist two distinct superconducting gaps. It has been shown that the critical magnetic fields can be analyzed according to a theoretical model.\(^23\) In this model, the \(\sigma\) and \(\pi\) electronic states are separated by a Josephson contact (interband coupling). At lower temperatures the contribution from the \(\pi\) electronic states are predominant, and this gives
rise to an upward curvature in lower critical field in the doped thin films (having a significant $\pi$ fraction). This can be explained by increased electronic scattering in the $\pi$ band of the doped superconductor. As it is evident from the inset of figure 9.1(c), the $H_{c1}$ follows an upward curvature at lower temperatures. This is due to the presence of $\pi$ electronic states in B-doped Q-carbon, which also play an important role in critical current density and flux creep of this novel material.

Figure 9.2(a) depicts the sharp fall in resistance when B-doped Q-carbon thin films are cooled down below the superconducting transition temperature. The sharp transition is also indicative of homogeneous and bulk superconductivity in the thin films. The resistance vs temperature measurements are also performed at different magnetic fields. As it is evident from figure 9.2(a) that large magnetic fields are required to completely destroy the superconducting nature of B-doped Q-carbon. With increasing magnetic field, there occurs a lowering of $T_c$ and broadening of transition width. This is a characteristic property of a high-temperature superconductor and it also helps us to calculate the value of upper critical field. To estimate the upper critical field ($H_{c2}$), we have used the power law $\frac{H_{c}(T)}{H_{c}(0)} = 1 - \left(\frac{T}{T_c}\right)^2$. The extrapolated value of $H_{c2}(0)$ is calculated to be 10.0 T which is closer to the value of upper critical field calculated from the magnetic measurements. Figure 9.2(a) indicates a semiconducting nature of B-doped Q-carbon thin films above the superconducting transition temperature. Since, the thin films are heavily doped, they can be considered to be degenerate semiconductors. The superconducting degenerate semiconductors have strong intervalley and intravalley electron-phonon coupling which assist in increasing the $T_c$.

Theoretical calculations and experimental results have also suggested that high concentration of impurities in strongly bonded semiconductors leads to high temperature superconductivity. $^{24-26}$ The high dopant concentration in Q-carbon thin films gives rise to high density of electronic states near the Fermi level. This helps to increase the number of electronic states available for scattering
which assists in increasing the BCS parameter \(N(0) \times V\). In B-doped Q-carbon superconducting thin films, the high \(T_c\) is also caused by a large number of attractive intervalley phonons which increase the dielectric screening and reduce the repulsive Coulomb interaction. The electron-phonon coupling constant is large which also indicates a strong intervalley coupling in the novel superconducting material. Figure 9.2(b) shows a clear evidence of the onset of zero-resistance superconducting state below \(~55\) K. The onset of superconductivity \((T_{c\_on})\) and zero-resistivity \((T_{c\_off})\) conditions are observed at \(59.8\) and \(55.4\) K, respectively. The onset of superconductivity characterizes the critical fluctuations (formation and electrical transport of Cooper pairs) in a superconductor and are explained later. The sharp superconducting transition in B-doped Q-carbon indicates the presence of a high-quality superconducting phase. Figure 9.2(c) shows the first-order resistance-temperature derivative plot. The transition width \((\Delta T)\) is calculated to be \(2.9\) K. This transition width is comparable to that of high-temperature oxide superconductors\(^27\) but much wider than that observed in single-crystal metallic superconductors \((\sim 10^{-4} \text{ K})\).\(^28\) The transition width (at \(0\) T) is also dependent on the crystalline nature of a sample, with the single-crystal sample having a narrower transition than their polycrystalline or amorphous counterparts. Therefore, the transition width in B-doped Q-carbon is influenced by its amorphous nature. Figure 9.2(d) depicts the critical fluctuations in B-doped Q-carbon thin films. The figure indicates the presence of mean-field region \((n=-1\) and -0.5), and critical region \((n=-0.2)\). The critical fluctuations explicitly explain the curvature of the resistivity plot near \(T_c\).\(^29\) In the mean-field region the reduced conductivity \((\sigma/\sigma_0)\) is expressed by using the Aslamazov-Larkin equation: \[\frac{\Delta \sigma}{\sigma_0} = (AT')^n\],\(^30\) where \(\sigma_0\) is the conductivity at \(300\) K, \(\Delta \sigma\) is the difference between room temperature conductivity and conductivity at a particular temperature, \(A\) is the temperature independent constant, \(n\) is the critical exponent \((n = -0.5\) and -1.0 for 3D and 2D critical fluctuations, respectively), and \(T'\) is the reduced
temperature calculated using the relation: \( T' = \left( \frac{T}{T_c} - 1 \right) \). The critical fluctuations occur extremely close to \( T_c \) and the dimensionality of the fluctuations (2D or 3D) are important superconducting parameters. A close observation also indicates that the mean field region starts from 59.9 K which is also the \( T_{c_{\text{on}}} \) state for the B-doped Q-carbon thin films. There is a transition from 2D to 3D nature of critical fluctuation near \( T_c \) in the superconducting thin films. The 2D to 3D crossover is observed at \( T/T_c = 1.02 \) as compared to \( T/T_c = 1.11 \) in other high-temperature superconductors.\(^{29}\) With decreasing temperatures, the 3D fluctuations are therefore predominant in B-doped Q-carbon. Similar nature of 3D fluctuations is also seen in other high-temperature superconductors: YBCO, LSCO.\(^{29}\) The critical fluctuations measurements also indicate that the \( T_c \) \( \text{off} \) condition occurs at 55.6 K which is extremely close to the previously calculated value of \( T_c \text{off} \).

Below the mean field region, the critical region starts, indicating the onset of zero-resistivity condition. The presence of these critical fluctuations shows moderate to strong electron-phonon coupling in the superconducting state.

Figure 9.3 depicts the isomagnetic time-dependent magnetic moment measurements in B-doped Q-carbon thin films at different temperatures (5, 20, 30, 40, and 45 K). The flux creep measurements are performed at a high magnetic field (1 T, field below upper critical field) which facilitates a strong interaction between the dense magnetic vortices. These measurements are also known as magnetic flux creep where the propagation of flux field lines (magnetic vortices) with increasing time at isothermal and isomagnetic conditions are observed. The flux creep phenomenon in the superconducting thin films follows the Anderson-Kim logarithmic time dependence.\(^{31}\) The reduced magnetic moment \((M(t)/M(t=0))\) vs time (in log scale) plots are shown in figure 9.3(a). The decrease in the value of reduced magnetic moment with time indicates that the motion of the pinned magnetic fluxes is associated with the flux creep which is activated
thermally ($k_B T$). The plots also indicate that the probability of the thermally activated jumps increases exponentially with an increase in temperature. It is also known that the thermally activated creep mechanism leads to dampening of supercurrents and reduction of magnetization. Therefore, large flux creep thwarts the high-temperature (near $T_c$) use of superconductors. As it is evident from the time-dependent reduced magnetic moment plot that there is only $\sim 4\%$ decrease in the magnetic moment at 45 K (and 1 T). Therefore, there exists a strong pinning potential (discussed below) in B-doped Q-carbon thin films which restrict the thermally activated creep mechanism. An extremely low decrease of magnetic moment with increasing time, indicates the immense applicability of B-doped Q-carbon thin films in MRI and NMR inserts. A much higher change in magnetic moment ($\sim 20\%$) is observed in other high-temperature superconductors due to the formation of a frustrated glassy state. The time-dependent magnetic moment data in the superconducting thin films are fitted using the Anderson-Kim logarithmic equation: $\frac{M(t)}{M(t=0)} = 1 - S \times \ln(1 + \frac{t}{\tau_0})$, where $\tau_0$ denotes the time constant and $S$ denotes the isothermal magnetization relaxation. The values of pinning potential (at different temperatures) can be calculated by using the equation: $U_p = \frac{k_B T}{S}$. The Anderson-Kim fitted plots are shown in the figure 9.3(a) for various values of $T/T_c$. The critical parameters which govern the flux creep phenomenon are the pinning potential, isothermal magnetization relaxation, and time constant. Figure 9.3(b) indicates an exponential dependence of the isothermal magnetization relaxation with reduced temperature ($T/T_c$). The exponential relation between $S$ and $T_c$ is calculated as: $S \approx (e^{T/0.07T_c})$. The plot indicates that after a $T/T_c$ value of 0.7, there occurs a massive thermally activated flux creep in the B-doped Q-carbon thin films. The thermally activated creep is associated with the average velocity of the thermally activated jumps (of magnetic flux lines) which are exponentially related to
temperature. The temperature-dependent isothermal magnetization studies indicate a strong flux
creep near $T_c$. The strong thermal fluctuations near $T_c$ also create a vortex liquid state thereby
reducing the effective pinning potential (shown in inset of figure 9.3(b)). At 5 K, the pinning
potential is calculated as 0.14 eV which is comparable to various non-BCS high-temperature oxide
superconductors.\textsuperscript{33} It is also observed that there is a minimal change of pinning potential with
temperature (up to $T/T_c = 0.6$). In most of the superconductors the thermally activated creep starts
at low temperatures unlike in B-doped Q-carbon (due to the presence of homogeneously dispersed
pinning centers). In high-temperature oxide non-BCS superconductors and most of the BCS
superconductors, the pinning centers are formed due to the presence of dislocations in the oxide
layers and addition of external non-magnetic impurities, respectively.\textsuperscript{33} In B-doped Q-carbon, the
B-doped $sp^2$ hybridized carbon entities form the effective pinning centers. These electronic states
are formed as a result of the ultrafast melting and quenching process of molten B and C. Therefore,
these inclusions are uniformly distributed throughout the B-doped Q-carbon structure. This
increases the potential applications of B-doped Q-carbon thin films in superconducting pumps,
transmission lines, and MAGLEV tracks. The inset in figure 9.3(b) also indicates the temperature-
dependent time constant measurements in the novel superconducting thin films. The time constant
determines a transient state before the onset of the logarithmic magnetic relaxation. A transient
time of ~400 sec is registered at temperatures close to $T_c$ which indicates a superior
superconducting behavior of B-doped Q-carbon thin films. Below the superconducting transition
temperature, the magnetic flux lines extend over a distance approximately equal to the London
penetration depth which is 59.4 Å in B-doped Q-carbon thin films. The free energy barrier ($\Delta F$
near 0 K) of the flux bundle can be calculated as 793.14 T$^2$ nm$^3$ using the equation:
$$\Delta F = \left( \frac{H_{c2}(0)}{B_\pi} \right)^2 \lambda_L^3.$$\textsuperscript{34} The large value of free energy barrier of the flux bundle and pinning potential in B-
doped Q-carbon thin films cause high values of critical current density. In B-doped Q-carbon thin films, the 3D nature of critical fluctuations (near $T_c$) and a high pinning potential also result in the butterfly-like hysteresis (in the M-H plots), indicating superior superconducting characteristics of B-doped Q-carbon. Figure 9.3(c) depicts the superconducting region in B-doped Q-carbon, which is enclosed by $T_c$, $H_{c2}$, and $J_c$. The three vertices of figure 9.3(c) illustrate $T_c$ (55.0 K), $J_c$ ($7.10 \times 10^8$ A/cm$^2$), and $H_{c2}$ (9.75 T), which are the three important parameters of a superconducting material. Outside the superconducting region, the material is in the normal (conducting) state.

Figure 9.4(a) indicates high-resolution SEM image of superconducting B-doped Q-carbon thin films. The B-doped Q-carbon is formed near the sapphire interface, above which quenched carbon layer forms after quenching. This layer shows nanoscale cracks exposing the B-doped Q-carbon film underneath. These cracks are formed because of an order of magnitude higher coefficient of thermal expansion of amorphous carbon overlayer than that of the B-doped Q-carbon. The tensile strain ($\Delta \alpha \times \Delta T$) is estimated to be $\sim 5 \times 10^{-6} \times 4000 = 0.02$ or 2%. The cross-sectional HAADF image indicates the formation of the thin layer of B-doped Q-carbon close to the sapphire substrate where maximum value of undercooling occurs. The B-doped Q-carbon has negative electron affinity and therefore it glows under the application of a stage (voltage) bias. The inset of figure 9.4(a) shows the formation of diamond at the triple points of the B-doped Q-carbon filamentary structure. The formation of diamond from the highly undercooled B-doped Q-carbon structure occurs by homogeneous nucleation and has $<110>$ out-of-plane orientation. A heterogeneous nucleation of diamond is favored on $c$-sapphire substrate, which has $<111>$ out-of-plane orientation. The cross-sectional HAADF image along with SAED pattern are shown in figure 9.4(b). The HAADF image shows the formation of $\sim 90$ nm thick superconducting B-doped Q-carbon thin film on $c$-sapphire substrate. A layer of Pt is deposited on the top of B-doped Q-carbon to minimize Ga$^{3+}$ damage.
During focused ion beam operations. The SAED ring pattern conclusively prove that B-doped Q-carbon is amorphous in nature. The intensity profile plot is superimposed on the electron diffraction pattern, which shows the presence of first and second nearest neighbors, corresponding to 111 (center) and 220 (edge) of diamond tetrahedra. This is consistent with our geometrical modeling of these phases. The room-temperature EEL spectroscopy (figure 9.4(c)) helps us to calculate the B-at% present in the B-doped Q-carbon structure. The EEL spectrum obtained from different points from the B-doped Q-carbon thin film shows the K edges of B and C. The core-loss EEL spectrum from points 1 and 2 depict the characteristic $\pi^*$ and $\sigma^*$ peaks of B and C. The $\pi^*$ and $\sigma^*$ are the antibonding (high-energy) electronic states of $\pi$ and $\sigma$ bondings. The presence of these antibonding electronic states indicates that B and C atoms are present in both $sp^3$ and $sp^2$ hybridized states. The similar nature of EEL spectrum from point 1 and point 2 indicates a homogeneous nature of bonding states in the B-doped Q-carbon structure. This is a characteristic of bulk superconductivity needed for practical applications in transmission lines, MAGLEV tracks, superconducting pumps, etc. The EEL spectrum from point 3 (substrate) shows a complete absence of B and C K edges. By using the EELS quantification routine, the B concentration is calculated as 27.0 at% and rest is C (73.0 at%).

Figure 9.4(d) depicts the unpolarized Raman spectroscopy of as-deposited (before PLA) and B-doped Q-carbon (after PLA) thin films. The Raman spectroscopy is performed at 300 K using 532 nm excitation wavelength. It is clearly evident from the spectrum that there is a significant increase in the $sp^3$-bonded C fraction (from 0.65 to 0.76) after the nanosecond laser melting and subsequent quenching process. In the range between 1000-1800 cm$^{-1}$ the Raman spectrum can be deconvoluted into three Raman-active vibrational modes. The peaks are centered around 1100, 1300, and 1600 cm$^{-1}$. The first peak corresponds to $sp^2$ dangling bonds at the surface of $sp^2$-bonded...
entities. The second and third peaks correspond to $sp^3$ and $sp^2$ bondings in C, respectively. The undoped phase of ferromagnetic Q-carbon which is formed by nanosecond laser irradiation and subsequent quenching process, contains 75-85% $sp^3$ bonding and rest $sp^2$. In the case of B-doped diamond superconducting thin films ($T_c = 4$ K) a sharp peak centered at 1332 cm$^{-1}$ and a broad graphitic peak at 1560 cm$^{-1}$ are predominantly observed in Raman spectroscopy. Therefore, the Raman spectra for B-doped Q-carbon thin films ($T_c = 55$ K) are different from that observed in B-doped diamond. This indicates that the $sp^3$ and $sp^2$ bonding states play an important role in high-temperature superconductivity. There occurs a quantum mechanical interference between the zone-center Raman active optical phonon and the continuum of electronic states created by B atoms in B-doped Q-carbon. This phenomenon gives rise to asymmetry and red-shift of the Raman-active vibrational modes in the B-doped Q-carbon thin films. The red-shifts ($w.r.t$ the as-deposited thin film) in the $sp^3$ and $sp^2$ bonded C (in B-doped Q-carbon thin films) are 15.75 and 29.02 cm$^{-1}$, respectively. The red-shifts also indicate that B is doped in substitutional sites of $sp^3$ and $sp^2$ bonded C. The Raman red-shifts also indicate a large value of electron-phonon coupling which is also calculated using McMillan formula. The B-doping in $sp^3$ C leads to high-temperature superconductivity via the formation of Cooper pairs whereas the B-doping in $sp^2$ C introduces pinning centers which increase critical current density and decrease the flux creep near $T_c$. In the case of B-doped diamond superconducting thin films, extra peaks are observed between 400-1200 cm$^{-1}$. These peaks occur due to maximas in the phonon density of states, which suggest strain-induced distortion in the diamond lattice upon B-doping. The presence of these extra peaks also indicates the presence of B pairs in interstitial sites of diamond which drastically reduce the superconducting transition temperature. The absence of these extra peaks in B-doped Q-carbon suggests that the B atoms are present in the electrically active sites thereby rendering improved
superconducting properties (high $T_c$, $J_c$, and $H_{c2}$, and low flux creep). The formation of B-doped Q-carbon thin films occurs *via* liquid phase which explains the presence of B in the electrically active sites of C. The Raman spectroscopy also shows that the deformation potential of the hole states (after B-doping) is caused by the C-C bond stretching (red-shift of Raman peaks). Therefore, phonon coupling is the main cause of high $T_c$ in B-doped Q-carbon thin films.

The electronic Raman spectra of superconducting B-doped Q-carbon and as-deposited B-C thin films are shown in figure 9.4(e). The results show distinct shallow acceptor energy levels centered at 14.7, 25.0, 36.7, and 46.6 meV in B-doped amorphous Q-carbon, which are not present in the as-deposited thin films. The peak near 420 cm$^{-1}$ corresponds to $c$-sapphire (substrate), which is present in the as-deposited and B-doped Q-carbon thin films. The first electronic Raman peak at 14.7 meV corresponds to 1s to 2s electronic transition, whereas the other two correspond to 1s to 3s and 1s to 4s transitions. The electronic transitions pertaining to 1s to 4s orbitals are interesting as they are situated extremely close to the valence band maximum (VBM). Previous reports have confirmed that at low B concentrations ($<1\times10^{18}$ cm$^{-3}$) the electronic transitions pertaining to only 1s($p_{3/2}$) $\rightarrow$ 1s($p_{1/2}$) at 16 cm$^{-1}$ occur. The Lyman series electronic transitions corresponding to 1s to ns transitions ($n = 2, 3,$ and 4) are observed at higher B concentrations in the substitutional sites of $sp^3$ bonded C. It has been also observed that at higher B concentrations there occur spin-orbit splitting and therefore two peaks show up which correspond to $p_{3/2}$ and $p_{1/2}$ electronic states. The spin-orbit splitting is found to be 10 meV in the case of B-doped Q-carbon as compared to 6 meV in B-doped diamond. This indicates a significant overlap of the electronic acceptor states in B-doped Q-carbon thereby increasing the density of the electronic states near the Fermi level. Therefore, Raman studies conclusively show that formation of new acceptor states, increase in
electronic density of states near $E_F$, and large electron-phonon coupling cause superior superconducting properties in B-doped Q-carbon thin films.

Figure 9.4(f) illustrates the peak-fitted $\pi^*$ and $\sigma^*$ antibonding electronic states present in the C K edge in B-doped Q-carbon thin films. The $sp^3$ bonded C is calculated to be 78% (and rest $sp^2$) which is similar to that calculated from Raman spectroscopy (figure 9.4(d)). The $\pi^*$ and $\sigma^*$ peaks are seen at 283 and 289 eV, respectively. Figure 9.4(g) depicts the $\pi^*$ and $\sigma^*$ antibonding electronic states present in the B K edge in the novel superconducting thin films at 191 and 198 eV, respectively. The K edges of B and C in B-doped Q-carbon thin films are centered at different energy levels and the peak shapes are different as compared to pristine B and C atoms. These indicate a cumulative change in the local (electronic) environment of B atoms caused due to doping in the B-doped Q-carbon structure. The $sp^3$ bonded B is calculated to be 70% (and the rest is $sp^2$). Therefore, 19 at% B is present in the $sp^3$ sites which leads to the formation of positively charged holes. These holes pair up below the superconducting transition temperature to give rise to high-temperature superconductivity in B-doped Q-carbon thin films. On the other hand, 8 at% B is present in the $sp^2$ sites which act as pinning centers thereby increasing the values of $J_c$ and $H_{c2}$. The $sp^2$ bonded B is also responsible for low flux creep near $T_c$, thereby facilitating the use of this novel superconducting material in MRI and NMR inserts.

Previous reports have indicated that $T_c$ rises monotonically with increasing B concentration (in the substitutional sites) in B-doped diamond. The highest value of $T_c$ (11 K) was achieved in diamond-5% B thin films synthesized using PECVD (plasma enhanced CVD) technique. It has also been observed experimentally that the presence of substitutional disorder (with increasing B concentration) can quench $T_c$ in B-doped diamond by opening an energy gap in the valence states.
At higher B concentrations, B-doped diamond enters into the dirty type-II BCS superconductor regime where scattering of Bloch states by impurities does not play an important role. Therefore, increasing the $T_c$ by increasing B concentration in the diamond structure beyond the thermodynamic solubility limit is not an optimal solution to attain high-temperature superconductivity. In the case of B-doped Q-carbon, the substitutional B in the diamond tetrahedra, which are randomly packed, does not cause lattice distortion even at concentrations exceeding thermodynamic solubility limits. This ultimately causes high $T_c$ and improved superconducting properties in the B-doped Q-carbon structure. The substitutional B in B-doped Q-carbon acts as shallow acceptor states lying extremely close to the valence band maximum. This gives rise to the formation of holes (Cooper pairs) which strongly couple with the phonons thereby giving rise to high $T_c$. Increased B concentration from 5 to 27 at% (in the substitutional sites) causes an increase in the electron-phonon coupling strength leading to an increase in the $T_c$. The density of electronic states near the Fermi energy level is predominantly characterized by the electronic states in substitutional B atom. Therefore, an increase in the electronic density of states near the Fermi level is directly related to the rise in $T_c$ in heavily doped materials. Theoretical studies have also predicted that in the superhard material, BC$_3$ with 16.7 at % of B ($T_c$=38 K), the electronic density of states near the Fermi energy level is 2.1 times higher than that in 2% B-doped diamond ($T_c$=4 K). The phonon density of states and energy calculations in BC$_3$ reveal that the higher energy (115-160 meV) and lower energy modes (<100 meV) correspond to C-C and B vibrations, respectively. There is also an increase in the intensity of phonon density of states at low energy level with increasing dopant concentration. Similar nature of the increase in the phonon density of states (at low energy) are also observed in highly B-doped Q-carbon structure from the electronic Raman spectroscopy. The large values of elastic constant and strong chemical bonds in
super hard materials leads to the formation of high-energy phonons and increased electronic charge densities which can lead to high $T_c$. The $\sigma$ and $\pi$ band contributions in B-doped Q-carbon give rise to high $J_c$, $H_{c2}$, and pinning potential. The upward curvature of the temperature-dependent $H_{c1}$ plot is indicative of $\pi$ band scattering that leads to low flux creep near $T_c$ in B-doped Q-carbon. The $H_{c1}(\sigma)$ fraction is calculated to be 0.61 from the temperature-dependent $H_{c1}$ plot. This is in excellent agreement with the B $\sigma$ electronic state fraction (0.70) calculated from the B K edge in EELS. Therefore, the $sp^2/sp^3$ ratio plays an important role in the superconducting properties of B-doped Q-carbon.

The SLIM (simulation of laser interaction with materials) programming is used to simulate the laser-solid interactions which determine the formation of the novel high-temperature superconducting phase. The SLIM calculations involve an accurate finite difference method to calculate the threshold energy density, melt depth, and solidification velocity of the pulsed laser annealed samples. The threshold energy ($E_{th}$) required for melting the layers of amorphous C and B thin film is calculated to be ~0.4 J/cm$^2$ by using the equation $E_{th} = \frac{K_sT_m\zeta^{0.5}}{(1-R_l)D^{0.5}}$, where $K_s$ is the thermal conductivity of amorphous carbon ($=0.3\times T^{-0.53}$ W cm$^{-1}$K$^{-1}$), $T_m$ denotes the difference between the substrate temperature of $c$-sapphire and melting temperature of amorphous carbon ($=3523$ K), $\zeta$ is the pulsed laser width ($=20$ns), $R_l$ denotes the reflectivity of the amorphous carbon at 193 nm ($=0.1$), and $D$ is diffusivity of amorphous carbon at room temperature ($=2$ cm$^2$ sec$^{-1}$).

With the increase in the pulse energy density, there occurs an increase in the thickness of the melted region. Therefore, 0.6 J/cm$^2$ pulse energy is used to melt the 500 nm composite layer of B and C. As the laser pulse terminates, the melt front recedes back to the surface. The initial stages of solidification see a low velocity but quickly reach the maximum when the steady state condition
is achieved. The maximum melt depth ($\Delta x$) is calculated by using the equation: 

$$\Delta x = (1 - R_l)(E - E_{th})/(C_v T_m + L),$$

where, $C_v$ denotes the volume heat capacity of amorphous carbon at its melting point (= 2.1 J cm$^{-3}$ K$^{-1}$), and $L$ is the latent heat of fusion of amorphous carbon (= 19775 J cm$^{-3}$). The melt in velocity ($v_{in}$) is calculated using equation: 

$$v_{in} = \frac{LC^2}{K_l \zeta (E - E_{th})^2 K_1} / L\Delta x,$$

where $\Delta T$ denotes the temperature difference between maximum temperature and melting point of amorphous carbon. The homogeneous melt cools down with high solidification velocities (10-20 m/sec). This causes sufficient undercooling (pressure) to form highly dense and B-doped amorphous Q-carbon. The formation of a homogeneous melt (after the super undercooling process) triggers the liquid phase diffusion (diffusivity $\sim 10^{-4}$ cm$^2$/sec), where the dopant concentrations can exceed the retrograde thermodynamic solubility limits. Again the growth velocity ($v$) is directly related to the undercooling by the following equation: 

$$v = \frac{D_{\infty f}}{\lambda f_D} \left(1 - e^{-(T_m-T_u)\Delta S/kT}\right),$$

where, $D_{\infty}, f, \lambda, f_D, k, T, T_m, T_u$ and $\Delta S$ denote the liquid diffusivity, fraction of the available sites, atomic jump distance, geometrical factor associated with diffusion, Boltzmann constant, temperature, melting temperature, undercooling temperature, and the change in entropy, respectively. Therefore, an increase in the value of undercooling favors the formation of the amorphous and highly doped superconducting phase. The increase in B concentration favors the formation of shallow acceptor states near the Fermi level, which cause high temperature superconductivity in amorphous B-doped Q-carbon thin films.

9.5. Conclusions

A type-II BCS superconductivity is experimentally observed in phase-pure B-doped Q-carbon thin films. This novel phase is formed as a result of nanosecond laser melting and subsequent quenching of highly undercooled state of molten B and C. This synthesis process can enhance the dopant...
concentrations beyond the thermodynamic solubility limits via solute trapping. Therefore, the
dopants (B) can be incorporated into substitutional (electrically active) sites (of \(sp^3\) bonded C)
without affecting their energy levels and ionization efficiencies. The liquid phase diffusivity (~\(10^{-4}\)
cm\(^2\)/sec) of B in C leads to an increase in the atomic concentration of B in C beyond the retrograde
thermodynamic solubility limits. The atomic\% of B in B-doped Q-carbon thin films is found to be
27.0 as compared to 2.0 in B-doped diamond (\(T_c = 4\) K). Therefore, the increase in B at\% plays an
important role in increasing the electronic density of states near the Fermi energy level which
increases the \(T_c\) in B-doped Q-carbon. The superconducting transition temperature and upper
critical field (at 0 K) are calculated to be 55.0 K and 9.75 T, respectively. The magnetic moment
measurements indicate that the upper and lower critical fields follow \(H_{c2}(0)\) \([1-(T/T_c)^{1.77}]\) and
\(H_{c1}(0)\) \([1-(T/T_c)^{1.19}]\) temperature dependence, respectively. The magnetic moment vs temperature
plots indicate that a complete shielding occurs when the samples are mounted perpendicular to the
field which is also the reason for the 94.5\% increase in the negative magnetic moment at the
perpendicular position (as compared to the parallel position). The temperature-dependent lower
critical field plot indicates an upward curvature ~0 K which can be explained by the increased \(sp^2\)
contribution in the structure of B-doped Q-carbon. The B in \(sp^2\) electronic sites increases the value
of pinning potential which reduces the magnetic flux creep near \(T_c\). The value of the electron-
phonon coupling in B-doped amorphous Q-carbon is ~ 5 times than that in 2 at\% B-doped diamond
\((T_c=4\) K). In B-doped Q-carbon thin films we have observed the onset of superconductivity \((T_{c on})\)
and zero-resistivity \((T_{c off})\) conditions at 59.8 and 55.4 K, respectively. The upper critical field
calculated from the electrical measurements is ~10 T. The critical fluctuation measurements
indicate that the 2D to 3D crossover occurs at \(T/T_c = 1.02\) (by using the Aslamazov-Larkin
equation) which is comparable to other high-temperature superconductors. The magnetic flux
creep measurements in B-doped Q-carbon thin films follow the Anderson-Kim logarithmic time dependence. After a $T/T_c$ value of 0.7, there occurs a massive thermally activated flux creep in the superconducting thin films. At low temperatures, the pinning potential is calculated as 0.14 eV which is comparable to various high-temperature oxide superconductors. The B-doped $sp^2$ hybridized carbon entities form the effective pinning centers which increase the potential applications of B-doped Q-carbon thin films in superconducting pumps, transmission lines, and MAGLEV tracks. The FESEM, HAADF, and SAED pattern indicate the formation of large-area amorphous superconducting thin films. The EELS and Raman spectroscopy of B-doped Q-carbon thin films illustrate that ~75% of C exists in the $sp^3$ bonded state (and rest is $sp^2$). The presence of the antibonding electronic states in EELS indicate that B and C atoms are present in both $sp^3$ and $sp^2$ hybridized states. The detailed EELS quantification reveals that 70% of B exists as $sp^3$ and therefore 20 at % of B is doped in the $sp^3$ electronic states of Q-carbon. This causes the formation of positive holes, resulting in superconductivity below 55 K. The Raman spectroscopy indicates a red-shift of Raman active modes in B-doped Q-carbon thin films. This indicates a large value of electron-phonon coupling which is also calculated using the McMillan formula. The electronic Raman spectra of B-doped Q-carbon thin films reveal an acceptor energy level at ~46 meV with the spin-orbit splitting energy value of ~10 meV. The presence of this electronic state near the valence band maximum indicates an increase in the density of shallow acceptor electronic states near the Fermi energy level. Therefore, the strong electron-phonon coupling and increases density of state attribute to the high $T_c$ in the novel material. The large values critical current density ($\sim 10^8$ A/cm$^2$) in B-doped Q-carbon and their dependence with temperature and magnetic field indicate potential applications. The values of critical current densities are significantly high as compared to typical oxide superconductors (BSCCO $\sim 10^5$ Acm$^{-2}$ at 4.2 K), which are important consideration.
for practical applications. This discovery of high-temperature superconductivity in phase-pure B-doped Q-carbon thin films will stimulate further research in strongly-bonded carbon-based materials in the search for near room temperature superconductivity.
9.6. Figures:

Figure 9.1. Magnetic characteristics of B-doped Q-carbon thin films (a) Magnetic moment vs temperature plots for 0 and 90 degree orientations, (b) Magnetic moment vs field at various temperatures, (c) Magnetic field vs temperature plots showing upper critical field and lower critical field (in the inset), (d) Critical current density vs magnetic field plots at various temperatures with the inset showing critical current density vs temperature plots at $B = 0$ T.
Figure 9.2. Electrical characteristics of B-doped Q-carbon thin films (a) Resistance vs temperature plots at different magnetic fields with the inset showing the upper critical field vs temperature plot, (b) Resistance vs temperature plot at B = 0 T showing the $T_{c\,on}$ and $T_{c\,off}$ states, (c) First derivative plot showing the transition width as 2.9 K, and (d) Critical fluctuation measurements showing 2D to 3D crossover at $T/T_c = 1.02$. 
Figure 9.3. Magnetic flux creep of B-doped Q-carbon thin films (a) Time-dependent reduced magnetic moment at various temperatures, (b) Isothermal magnetization relaxation vs reduced temperature plots with the inset showing pinning potential and time constant vs reduced temperature, and (c) 3D plot of the superconducting region.
Figure 9.4. Structural characterizations of B-doped Q-carbon thin films (a) FESEM of B-doped Q-carbon with the inset showing nucleation of diamond at the triple points, (b) HAADF image of B-doped Q-carbon formed on c-sapphire substrate with the inset showing SAED pattern of amorphous B-doped Q-carbon, (c) Room-temperature EEL spectra from various points on the HAADF image showing B and C K edges, (d) Raman spectra showing $sp^3/sp^2$ bonding states in as-deposited and B-doped Q-carbon thin films, (e) Electronic Raman spectra showing the shallow acceptor states near the valence band maximum, (f) and (g) High-resolution EEL spectrum of C and B K edges, respectively.
9.7. References


10. Formation and Characterization of Nano- and Microstructured Twinned Cubic Boron Nitride

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10.1. Abstract

Nano- and microstructures of phase-pure cubic boron nitride (c-BN) are synthesized by employing nanosecond pulsed laser annealing technique at room temperature and atmospheric pressure. In the highly non-equilibrium synthesis process, nanocrystalline h-BN is directly converted into phase-pure twinned c-BN from a highly undercooled melt state of BN. By changing the nucleation and growth rates, we have synthesized a wide range of sizes (90 nm to 25 μm) of c-BN. The electron diffraction patterns indicate the formation of twinned c-BN with [111] as the twin axis. The twinning density in c-BN can be controlled by the degree of undercooling and quenching rate. The formation of twins predominantly occurs prior to formation of amorphous quenched BN (Q-BN). Therefore, the defect density in nano c-BN formed at higher undercooling is considerably larger than that in micro c-BN, which is formed at lower undercooling. The temperature-dependent Raman studies indicate a considerable blue-shift of ~6 cm⁻¹ with decrease in temperature from 300 to 78 K in nano c-BN as compared to micro c-BN. The size-effects of c-BN crystals in Raman spectra are modeled using the spatial correlation theory, which can be used to calculate the
correlation length and twin density in c-BN. It is also found that the Raman blue-shift in nano c-BN is caused by the anharmonic effects and the decrease in Raman linewidth with decreasing temperature (300 to 78 K) is caused by three- and four-phonon decay processes. The bonding characteristics and crystalline nature of the synthesized c-BN are also demonstrated by using electron energy-loss spectroscopy and electron backscatter diffraction, respectively. We envisage that the controlled growth of phase-pure nano and microstructures of twinned c-BN and their temperature-dependent Raman-active vibrational mode studies will have a tremendous impact on low-temperature solid-state electrical and mechanical devices.

10.2. Introduction

Diamond and c-BN (space group= Fd3m) being the first and the second hardest materials known have excited the researchers from their inception and have generated tremendous scientific and technological interests. Besides hardness, diamond and c-BN have many other desirable properties, making them ideal materials for high-power, high-frequency, and radiation-hardened devices. Diamond and c-BN complement each other in view of much higher temperature stability and oxidation resistance of c-BN compared to diamond. Unlike diamond, c-BN is chemically inert and thermally stable to ferrous materials at high temperature. Doping of diamond structures (n-type) for transistor applications is difficult and can be overcome by c-BN, which can be doped to form p and n-type semiconductors. The properties of c-BN include: structure stability over a wide range of temperature (1200 K) and pressure (4 GPa), extreme hardness (48 GPa), chemical inertness, high thermal conductivity (740 Wm⁻¹K⁻¹) and melting point (3246 K), large optical band gap (6.4 eV), etc. These properties render c-BN to be used widely as pressure sensors, tools for high-speed machining, microelectronic devices, protective coatings, etc. Since diamond and c-BN are metastable materials at ambient temperatures and pressures, they have been synthesized at
high-temperature and pressure in limited quantities in bulk form. To address thin film synthesis, diamond has been synthesized by chemical vapor deposition (CVD) at high temperatures under corrosive atmospheres. The formation of epitaxial diamond has been extremely challenging due to the formation of interfacial soft amorphous carbon and disordered graphite. The c-BN thin film synthesis is more challenging, as CVD methods are not well established and physical vapor deposition (PVD) methods based upon energetic nitrogen ions have led to less than 85% phase-pure c-BN. These processes render a soft interfacial layer (of h-BN), thereby reducing adhesion and thwarting the usage of c-BN in mechanical moving parts, biomedical and electronic devices. Other methods of processing of nano and micro c-BN rely on the direct conversion of h-BN to c-BN at high temperature (1773 K) and pressure (8 GPa) in the presence of a catalyst or solvent. The energetic ion bombardment synthesis of c-BN causes structural damage and stress accumulation, thereby adversely affecting the properties of the synthesized c-BN. It should also be noted that for high-speed c-BN based electronic devices, epitaxially grown single crystalline c-BN is crucial. Nanoscale materials have better physical and mechanical properties than their bulk counterparts and are now being sought after for high-speed electrical and mechanical devices. The nanostructures of wide band gap semiconductors such as diamond, AlN, Q-carbon, and c-BN have negative electron affinity, thereby rendering them promising candidates for electron emission devices. It should also be mentioned that the twinning in diamond and c-BN leads to ultrahigh hardness and toughness through the Hall-Petch effect, where twins block the motion of dislocations. Therefore, there is a continuous drive to synthesize nano and microstructures of twinned c-BN in a controlled way from h-BN at room-temperature and atmospheric pressure.
Due to the high activation barrier, the pressure required for the direct phase transformation of h-BN to c-BN far exceeds the equilibrium pressure (at 300 K). It is well known that formation of the liquid phase of BN will drastically reduce the activation barrier \(^{22}\) and will facilitate the direct conversion of soft h-BN to extremely hard c-BN phase. Therefore, highly non-equilibrium techniques should be adopted to synthesize phase pure c-BN. Recently, we reported a major breakthrough in synthesis and processing of diamond by direct conversion of amorphous carbon into diamond and Q-carbon at ambient temperature and atmospheric pressure in air.\(^{23,24}\) In this discovery, phase-pure c-BN and new amorphous phase, Q-BN\(^ {25}\) are formed by nanosecond laser melting of BN and quenching subsequently to form these phases by controlling the undercooling. By controlling the undercooling, we are able to form nano c-BN to micro c-BN and Q-BN at a higher undercooling. In addition, nanoneedles, microneedles, large-size grits, and thin films can be formed over a large area. The formation of twinning in c-BN is controlled by the quenching rates from the BN melt. Twinning in c-BN can be used to enhance hardness further \(via\) restricting the motion of dislocations and obtaining Hall-Petch enhancement in hardness from the spacing between the twins.\(^ {16}\)

In the present research, the emphasis is on the synthesis of phase-pure nano- and micro c-BN with variable twin content. The low-temperature characterization of Raman-active vibrational modes of nano-and micro c-BN is carried out to study the details of bonding characteristics. The bulk nucleation results in random c-BN, whereas interfacial growth can lead to aligned, textured, and epitaxial growth by domain matching epitaxy.\(^ {26}\) When c-BN is epitaxially aligned with the substrate (\(c\)-sapphire) useful structures for electronic devices are formed. Low-temperature (cryogenic) aspects of nano and microstructures of c-BN have not been studied as compared to high temperature and pressure conditions. Cryogenic operations (of materials) can offer certain
advantages including higher operational speeds, shorter signal transmission times, lower power
dissipation, improved digital and analog circuit performance (increased signal/noise ratio), etc.
Currently, there is an urgent push for high-power, high-frequency, and high-speed radiation
hardened devices, which can be addressed by c-BN nano and microstructures. Twinning needs to
be minimized for electronic devices, but it improves mechanical properties by enhancing hardness
as well as toughness. These nano- and microstructured materials have been characterized using
various state-of-the-art techniques: temperature-dependent micro-Raman spectroscopy (300 to 78
K), high-resolution scanning electron microscopy (SEM), high-resolution transmission electron
microscopy (TEM), selected area electron diffraction (SAED), electron energy-loss spectroscopy
(EELS), and electron backscatter diffraction (EBSD) for structure-property correlations and their
impact on novel applications.

10.3. Experimental

Pulsed laser ablation of h-BN in a laser MBE chamber was performed to deposit nanocrystalline
h-BN with thicknesses ranging from 50-500 nm onto c-sapphire substrates at room temperature.
The substrates were cleaned in acetone vapor followed by ultrasound sonication in methanol and
drying (the substrates) in nitrogen. The thickness of as-deposited h-BN is varied by the number of
laser shots (1 laser shot~1Å). Thicker h-BN films are used for the formation of micro and large-
area c-BN after the pulsed laser annealing process, whereas thinner films are used for the formation
of nano- c-BN (after PLA). The large density of grain boundaries in nanocrystalline h-BN (grain
size~25 nm) facilitates melting of h-BN during the pulsed laser annealing process (due to enhanced
laser - h-BN coupling). The PLD was performed in a laser MBE chamber which is maintained at
a base pressure of 3×10⁻⁸ Torr. This base pressure is achieved by using a roughing (dry) pump in
conjunction with a turbo mechanical and cryo pump. ArF excimer laser (pulse duration = 20 ns,
wavelength = 193 nm, energy density = 3.0-3.5 Jcm$^{-2}$) is used for the deposition of nanocrystalline h-BN thin films. The laser was operated at a constant high-voltage mode (22 kV) and 10 Hz (10 laser shots per second) repetition rate during the PLD process. Therefore, for deposition of 5000 Å thick nanocrystalline h-BN onto c-sapphire, ~9 minutes of PLD was required. The size of laser spot on the h-BN target during the deposition was 0.06 cm$^2$, which translates into an energy density of ~3.0-3.5 Jcm$^{-2}$, required for laser-assisted ablation of h-BN target. Prior to the start of the deposition, pre-ablation of the target (200 laser shots at 10 Hz repetition rate) was performed. Since PLD is a highly non-equilibrium technique (due to the forward-directed nature of the laser plume), the stoichiometry of the target is preserved on the film. After PLD, the films were irradiated (for PLA) using pulsed ArF laser having energy densities of 0.6 Jcm$^{-2}$ to 1.0 Jcm$^{-2}$ at room temperature and atmospheric pressure. Only one laser pulse of the nanosecond laser (ArF) is required to convert nanocrystalline h-BN into phase-pure nano c-BN structures (and amorphous quenched-BN). Multiple laser shots (up to 3) are required to grow the c-BN nano nuclei present in the amorphous Q-BN structure to micro and large-area c-BN. PLA is also a highly non-equilibrium technique due to its ultrafast nature of melting and subsequent quenching (of the laser annealed thin film). The PLA process is completed in less than 200 ns. The PLA process melts and subsequently quenches the super undercooled state of BN thereby forming nano and microstructures of c-BN. Increasing the undercooling leads to the formation of Q-BN, which is amorphous in nature. The undercooling can be controlled by varying the thermal conductivities of as-deposited h-BN and substrate (sapphire) and laser energy density (0.6-1.0 Jcm$^{-2}$). Various state-of-the-art characterization techniques are used to determine the morphology, bonding characteristics, temperature and size-dependent phonon vibrational modes, and crystal structure (twinning and crystal orientation w.r.t the substrate) of c-BN. Unpolarized micro-Raman spectroscopy, SEM, TEM, EELS, and EBSD
were performed on the nano and microstructures of c-BN. Horiba Xplora PLUS confocal Raman microscope (0.5 μm spatial resolution) in conjunction with Labspec software were used to perform the temperature and size-dependent Raman studies in nano and micro c-BN. The excitation source was a 532 nm laser of the Raman instrument was calibrated using a crystalline Si wafer (Raman-active peak at 520.6 cm\(^{-1}\)) prior to the measurements. The temperature-dependent Raman measurements were performed in the Linkam stage (variable temperature stage purged with Ar) attached to the Raman microscope. For accurate measurements, the stage was thermally stabilized for 2 minutes prior to Raman spectra acquisition. FEI Verios 460L SEM (having sub-nanometer resolution) was used to characterize the laser irradiated films. FEI Quanta 3D FEG microscope having a dual beam technology, which uses both electron and ion beam guns was used for preparing thin cross-sectional samples for TEM and EELS. EBSD measurements were performed in the above-mentioned microscope using an EBSD HKL Nordlys detector. The lateral resolution of the EBSD detector was less than 10 nm, and it can map out the Kikuchi diffraction pattern (for determination of structures) of nano and microstructures of c-BN. JEOL-2000FX and 2010F STEM/TEM (point-to-point TEM resolution 0.18nm; STEM-Z resolution 0.08nm with information limit of 0.06nm) were used in conjunction with EELS, to collect high-resolution TEM images, bright field imaging, micro-diffraction (selected area electron diffraction), and EELS spectra with a resolution of 0.15 eV. This helped to determine the crystal structure (orientation and twinning) and bonding characteristics in c-BN, which is formed by our highly non-equilibrium technique.

10.4. Results and discussion

Figures 10.1(a-d) show the formation of nano, micro and large-area c-BN formation from h-BN by the PLA process. The average size of the nanocrystals is ~90 nm. The formation of c-BN
nanocrystals is dependent on the nucleation and growth velocity, which are controlled by undercooling during the PLA. The PLD deposited h-BN is of nanocrystalline nature, which is melted in a highly undercooled state (at 2800 K) during the PLA process. This leads to a complete conversion of h-BN to c-BN after the quenching from melt. The growth velocity \( v \) is directly related to the undercooling by the equation:

\[
v = \frac{D_\infty f}{\lambda f_D} \left( 1 - e^{-\frac{(T_m - T_u)\Delta S}{kT}} \right),
\]

where, \( D_\infty \), \( f \), \( \lambda \), \( f_D \), \( k \), \( T_m \), \( T_u \), and \( \Delta S \) denote the liquid diffusivity of the BN (~10\(^{-8}\) m\(^2\)/sec in liquid state), fraction of the available sites, atomic jump distance, geometrical factor associated with diffusion, Boltzmann constant, temperature, melting temperature, undercooling temperature, and the change in entropy, respectively. An increase in the value of \( T_u \) decreases the value of chemical free energy barrier for h-BN to amorphous Q-BN or crystalline c-BN phase transformation. This also increases the velocity of the melt-front. Therefore, the values of undercooling dictate the formation of amorphous Q-BN and crystalline c-BN from the BN melt. If the cooling rate is slow (low undercooling and low solidification velocity), crystalline c-BN is formed whereas with high cooling rates (large undercooling and large solidification velocity), amorphous Q-BN is formed.

For facilitating the homogeneous nucleation of c-BN from the super undercooled state, the Gibbs free energy of the c-BN nuclei \( (\Delta G_T) \) is governed by the equation:

\[
\Delta G_T = \frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^2 \gamma_s,
\]

where \( \Delta G_v \) denotes the difference between free energies per unit volume of c-BN solid and the super undercooled liquid, \( \gamma_s \) denotes c-BN/super undercooled liquid interfacial energy, and \( r \) denotes nuclei radius (of c-BN). Thermodynamically, the nucleation of c-BN is difficult due to large values of \( \gamma_s \). But using ultrafast non-equilibrium techniques, undercooling can be achieved which assists the crystal nucleation. The critical size of nuclei \( (r^*) \) can also be calculated (at \( \frac{d\Delta G_T}{dr} = 0 \)) using:

\[
r^* = \frac{2\gamma_s T_m}{\Delta H_f \Delta T},
\]

where \( T_m, \Delta H_f, \) and \( \Delta T \) denote melting point, latent heat of fusion, and
undercooling, respectively. Similarly, the critical free energy ($\Delta G_{T^*}$) for the formation of $r^*$ can also be calculated and is proportional to $\Delta T^{-2}$. The driving force for the solidification is directly proportional to the degree of undercooling. With the increase in undercooling, there is a decrease in the value of $\Delta G_{T^*}$ and $r^*$. This facilitates an increase in the rate of nucleation (at large undercooling values). This leads to amorphization (large undercooling) and twinned (medium undercooling) and defect-free crystal (small undercooling) formation (figure 10.1(e)). The degree of undercooling can be controlled by laser parameters (energy density 0.6-1.0 Jcm$^{-2}$) and thermal conductivities of the as-deposited thin film and the substrate. However, it should also be noted that, for heterogeneous nucleation of c-BN (on c-sapphire substrate), low undercooling favors crystal growth as the critical free energy for the formation of $r^*$ is lower as compared to homogeneous nucleation. This facilitates the formation of c-BN crystals closer to $T_m$, where crystal growth is predominant than nucleation. Figure 10.1(b) depicts the initial stages of formation of c-BN microcrystallites (shown by arrow) from nanocrystalline h-BN (inset of figure 10.1(b)) on c-sapphire. The size of the c-BN crystals is ~1 μm. When sufficient time for growth (from the BN melt) is given, large micro-crystals (~5 μm) and single-crystal films of c-BN are formed (figure 10.1(c) and (d)). The inset in figure 10.1(c) indicates the formation of micro c-BN from Q-BN, which is amorphous in nature (formed at high undercooling conditions). The single-crystal films of c-BN can be grown directly on c-sapphire, when super undercooled state of BN grows directly on sapphire, which provides a template for the epitaxial growth by domain matching epitaxy paradigm. The growth velocity ($v_{growth}$) in the liquid BN phase determines the dimension of the single crystal c-BN formed. The growth velocity is calculated to be ~10 msec$^{-1}$ using: 
$$v_{growth} = \frac{K_s T_m}{((D\tau)^{0.5}\rho L)}$$
where $K_s$, $T_m$, $D$, $\rho$, and $L$ denote thermal conductivity of sapphire substrate at 2800 K (5.65 Wm$^{-1}$K$^{-1}$), melting point of BN (2800 K), thermal diffusivity (10$^{-8}$ m$^2$/sec), density
of liquid c-BN (3.45 gcm⁻³), latent heat of c-BN (1800 Jg⁻¹). In the highly superundercooled state, the rate of nucleation \( (r_n) \) is extremely high. The rate of nucleation can be calculated using:

\[
 r_n = C_1 \exp\left(-\frac{C_2}{(1 - T/T_m)^2 T/T_m}\right)
\]

where \( C_1 \) and \( C_2 \) are constants. Therefore, when \( T \ll T_m \), the rates of nucleation are extremely high. The formation of large microcrystals of c-BN occurs due to explosive crystallization. The process of explosive crystallization is exothermic in nature, thereby leading to a stable growth of microcrystals (of c-BN). Figure 10.1(d) shows the formation of large-area c-BN with the inset showing large microcrystals (~5 \( \mu \)m) of c-BN, which are highly faceted. Therefore, direct conversion of h-BN to c-BN is possible using the highly non-equilibrium technique.

High-resolution TEM (figure 10.2(a)) and SAED (figure 10.2(b)) studies of micro and nano c-BN show the presence of twins (crystal defects). The nano-twinned structures are energetically more favorable than their nanograin counterparts (as the energy of twin boundaries is an order of magnitude less than that of grain boundaries). The presence of twin boundaries also enhances the hardness of a material (as twins are a barrier to dislocation glides). In the present work, we have demonstrated the formation of twins in nano and micro c-BN by controlling the extent of undercooling. With increasing the values of undercooling (by changing the thermal conductivities of as-deposited nanocrystalline h-BN and substrate and laser parameters) we have achieved a highly twinned structure. The bright field HRTEM image in figure 10.2(a) shows the presence of twins and high dislocation density in micro c-BN. The dislocations terminate in the twinned region (twin thickness < 100 nm). Since the \{111\} twins are visible the edge dislocations are of \( a/6<112> \) type. The top left inset and right bottom inset in figure 10.2(a) depict the formation of twins in nano c-BN (twin thickness < 5 nm). The top right inset in figure 10.2(a) illustrates the heterogeneous nucleation of epitaxial c-BN (formed by rapid crystallization) on sapphire. The
SAED pattern of c-BN (figure 10.2(b)) depicts the <110> cross-section, which has characteristics diffraction spots from {111} and {002} planes. The <110> texture growth of c-BN is similar to that in Si formed under rapid unseeded crystallization. The c-BN crystals are epitaxially aligned to the substrate (c-sapphire). The electron diffraction pattern of the substrate (c-sapphire) is shown in the inset of figure 10.2(b). The SAED pattern depicts <2̅110> cross-section of the substrate. The out-of-plane epitaxial arrangement is: <111> of c-BN aligned with <0001> sapphire. The in-plane epitaxial arrangements are: <110> c-BN // <2̅110> sapphire and <112> c-BN // <1̅101> sapphire. According to the DME paradigm, to accommodate the planar lattice misfit, 16 (2̅110) planes of sapphire match with 15 {110} half-planes of c-BN. The SAED pattern (figure 10.2(b)) also shows the presence of twin spots (marked in circles). The twin axis [1̅1̅1̅] forms the twin spots 1/3(1̅15), 1/3(11̅2), 2/3(1̅14), 1/3(771) of (1̅1̅1̅), (002), (220), and (1̅1̅3) diffraction spots, respectively (shown in figure 10.2(b)). Similar twinned structures in Si were also observed in previous studies. There occurs a rotation of 180° about the twin axis to form the twin spots. For cubic materials, the reciprocal lattice vectors of twin spots are calculated using the equation (10.1):

\[ h^* = \frac{p(hk + 2ql + 2tr) - h(q^2 + r^2)}{p^2 + q^2 + r^2} \]  

(10.1)

where, [pqr] is the twin axis and hkl is rotated 180° about the twin axis. The twin density for micro and nano c-BN is calculated to be ~ 10^8 and 10^{12} cm^{-2}, respectively. The SEM images in figures 10.2(c)-(f) indicate twinning in c-BN formed by ultrafast quenching and solidification technique. The SEM images show high density of twinning in c-BN. The mirroring of crystal facets is indicative of the twinned structure. These heavily twinned structures result from super undercooling process, where the solidification velocities are less than that in Q-BN but more than single-crystal c-BN formations. The size of c-BN crystallites is ~ 0.5×5×5 μm^3. Since the melt
lifetime is \( \sim 150 \) ns, the growth velocities exceed 3 msec\(^{-1}\). This indicates rather rapid recrystallization of c-BN from the superundercooled state. Such high values of crystal growth rate also indicate laser-induced liquid phase growth of c-BN from h-BN. Figure 10.3 depicts the electron backscatter (Kikuchi) diffraction performed using EBSD detector in FEI microscope. This technique provides electron diffraction pattern to determine the phase, crystallinity, and orientation of the phase formed (nano or micro) with respect to the substrate. The resolution of this technique (\( \sim 10 \) nm) is directly proportional to the probe size of the incident electron beam, which can be controlled by accelerating voltage and beam current. The secondary electron images and Kikuchi diffractions of nano c-BN from two different spots are shown in figures 10.3(a-d). A similar analysis is performed on micro c-BN and is shown in figure 10.3(e). The simulated Kikuchi patterns (of c-BN) are overlaid on the diffraction patterns for a better representation of the diffracting planes. As it is evident from figure 10.3, the Kikuchi bands are more prominent in the case of micro c-BN due to an increase in the electron interaction volume of electrons with the sample (in micro c-BN). The dynamical simulations of the EBSD Kikuchi pattern for regions A and B are shown in figure 10.3 (f-g). The crystal orientations (shown in the inset of figure 10.3(f-g)) correspond to twin formation in the c-BN structure. When the solidification rates exceed certain values (>5 msec\(^{-1}\)), twinned structures of c-BN are formed. Similar twin formations are also experimentally shown for Si, where the maximum melt growth is observed for (001) as compared to (111) close-packed surfaces.\(^{32-34}\) The production of these defects can also enhance the crystal growth rate, particularly for slower growing surfaces (by nucleation). The formation of twins predominantly occurs prior to complete amorphization.\(^{33}\) Therefore, the defect density in nano c-BN (formed at higher undercooling) should be considerably larger than that in micro c-BN (formed near \( T_m \)), which is discussed in detail below. If the solidification rates are increased to higher
values (>10 msec⁻¹), the transient melt is highly super undercooled and rapid growth defect multiplication takes place at the melt/solid interface. This leads to the formation of highly dense amorphous Q-BN thin films, which have been shown to possess novel mechanical and electrical properties.

The details of bonding characteristics (of c-BN) are probed using electron energy-loss spectroscopy (figure 10.4(a)). The background corrected spectrum along with the experimental spectrum and background are shown in figure 10.4(a). The c-BN formed via highly non-equilibrium synthesis technique shows the B-K edge peaks at 198.2 (σ* antibonding state), 216.6, and 234.5 eV. The EEL spectrum also shows N-K edge peaks at 408.4 (σ*) and 436.7 eV. The characteristic fine post-edge structures in EELS indicate long-range periodicity (crystalline structure) in c-BN. The long-range periodic structure of crystalline c-BN gives rise to modulation to the density-of-states, as it is evident from the σ* region in EELS. The high optical band gap of c-BN (6.4 eV) gives rise to the core-hole effect, which is also observed from the EELS profile of c-BN. In high band gap materials, the core-hole effect is dominant, as the rescreening of the hole by valence electrons is not complete. Other prominent phases of BN, h-BN and w-BN have their characteristic B and N K-edges at 192 and 402 eV (1s to π* transition) which are completely absent in the EEL spectra of laser annealed c-BN. This also proves a complete conversion of h-BN to c-BN via laser melting and ultrafast quenching process. The temperature-dependent vibrational modes (of the synthesized nano and micro c-BN) are studied using Raman spectroscopy. Figure 4(b) indicates the unpolarized Raman spectra of micro and nano c-BN synthesized via the highly non-equilibrium technique. The Raman spectrum of micro c-BN indicates phonon vibrational modes centered at 1055 (transverse optical: TO) and 1305 (longitudinal optical: LO) cm⁻¹ (in figure 10.4(b) and 10.5(a), respectively). Interestingly, in nano c-BN (as compared to micro c-BN) there
occurs ~35 cm\(^{-1}\) red-shift of the TO mode due to phonon confinement and ~20 cm\(^{-1}\) blue-shift of the LO mode due to electro-optical effect, which is discussed in detail below. The Raman peak ~1325 cm\(^{-1}\) in nano c-BN spectrum is not due to the presence of BC\(_2\)N phases (which also have peak ~1325 cm\(^{-1}\)). Furthermore, BC\(_2\)N phase has no Raman-active peak ~1020 cm\(^{-1}\). BC\(_2\)N phases also have distinct electron diffraction pattern and EELS, which are not observed in the present study. The blue-shift of LO mode in nano c-BN can be due to internal strain fluctuations and formation of twinned structure. It is well known that the size and shape of nanoparticles affect the Raman spectra. If the size of the nanoparticles is less than the wavelength of the laser (532 nm), the induced electromagnetic field in the nanoparticle strongly influences the Raman scattering modes. The electromagnetic field can influence the electro-optical effect in c-BN nanoparticles, thereby causing the blue-shift. The Raman spectra of nano and micro c-BN show no evidence of peak ~1365 cm\(^{-1}\) (E\(_{2g}\) mode), which is characteristics of h-BN. The spectra also indicate a complete absence of peaks ~1260 cm\(^{-1}\), which is predominantly observed for amorphous BN entities. These results are consistent with a complete conversion of h-BN to c-BN \textit{via} melting and super undercooling process. Since c-BN has a zinc blende structure, it has one optical phonon mode at Γ which is Raman-active. Due to the ionic character of BN, this triply degenerate vibrational mode splits into TO and longitudinal LO modes. In the case of h-BN, there is no splitting of the Raman-active mode centered at 1365 cm\(^{-1}\), due to the planar structure of h-BN (where the contributions from the two planes cancel out each other). Unlike TO phonons, the intensity of LO phonons can be enhanced by external electrical field. The LO modes are strongly affected by light due to the electro-optical (EO) effect. The TO modes are only affected by the deformation-potential interaction, and thereby provides an excellent marker for size, temperature, and pressure dependent studies. The electro-optical effect is predominantly observed in
nanomaterials, where symmetry-breaking occurs due to reduction in size (phonon-confinement). The study of electro-optical effect in semiconductors is interesting as it leads to the development of novel optoelectronic materials (optical modulators and waveguides).\textsuperscript{41} The EO effect is determined by the Faust-Henry coefficient ($C$), which is calculated using the equation (10.2):

$$C = -\left[\left(\frac{I_{LO}}{I_{TO}}\cdot\frac{\omega_{LO}}{\omega_{TO}}\cdot\left(\frac{\omega_{l}-\omega_{TO}}{\omega_{l}-\omega_{LO}}\right)^3\right) - 1\right]^{-1}\left[\frac{\omega_{LO}^2-\omega_{TO}^2}{\omega_{TO}^2}\right]$$  

(10.2)

where, $I_{LO}$, $\omega_{LO}$, and $\omega_{l}$ indicate intensity, phonon frequency, and incident laser frequency, respectively. The ratio of ionic and electronic term contributing to the EO effect is directly proportional to $C$. The value of $C$ (at 300 K) is calculated as -0.83 and 4.16 for micro and nano-cBN as compared to -1.53 for mm-sized c-BN\textsuperscript{40} prepared by HPHT techniques. This shows a higher ionic character in nano c-BN as compared to micro c-BN. Therefore, the splitting of triply degenerate vibrational modes (TO and LO) at the Brillouin zone is increased in nano c-BN. There occurs a drastic change in the value of $C$ to -0.21 (in nano c-BN) at 78 K. This requires a further study of the phonon scattering process in nano c-BN, which is discussed below.

Measurements of temperature-dependent Raman shifts and change in line widths help in determining the type of phonon-interactions in materials. Previous results in c-BN have confirmed interesting Raman shifts and change in line widths at higher temperatures (above 500 K),\textsuperscript{42-45} but no studies at cryogenic temperatures. However, low-temperature applications of c-BN based electronic devices require a detailed study of the material properties (phonon-interaction) for a better understanding. As it is evident from figures 10.4(c) and (d), there is a considerable shift of Raman peak (TO mode) to higher wavenumbers (blue-shift) with a decrease in temperature (300 to 78 K) in nano c-BN as compared to micro c-BN. Similar behavior of blue-shift is also found for the LO mode (figures 10.5(b) and (c)). There is also a decrease in the Raman linewidths with
decrease in temperature in c-BN. The decrease in linewidths is more prominent in micro c-BN as compared to nano c-BN. The temperature-dependent Raman shifts and change in linewidths can be understood in terms of an oscillator (the molecule) that interacts with the anharmonic potential (created by the electric field) within which the atoms move. At lower temperatures, there is a decreased phonon-phonon interaction, thereby resulting in less scattering and higher lifetime of these optical phonons. This leads to a decrease in the Raman linewidth with decreasing temperature. This phenomenon is well-established in micro c-BN which has well-defined phonon interactions. Therefore, the decrease in linewidth with decreasing temperature is prominently observed in micro crystals of c-BN. The temperature-dependent Raman shift and change in linewidths in nano c-BN are discussed in detail below.

The change in Raman frequency with crystallite size is investigated (figure 10.6) using the theory of phonon confinement as described in the spatial correlation model.\textsuperscript{46,47} According to this model, for the case of ideal crystals, only phonons near the center of the Brillouin zone \((q = 0)\) contribute to the Raman spectrum. In a real crystal, phonons can be confined by grain boundaries, stacking faults, impurities, \textit{etc}. This results in the uncertainty of phonon momentum and therefore phonons having \(q \neq 0\) contribute to the Raman spectrum. As discussed above, since the TO mode is affected only by the deformation-potential interaction, Raman peak fitting is performed in this mode. The normalized intensity \((I(\omega))\) of a Raman-active peak can be fitted using the equation (10.3):

\[
I(\omega) \approx \int_0^1 \frac{\exp(-qs/4\pi)^2 \pi q^2 dq}{[\omega - \omega(q)]^2 + [I_0/2]^2}
\]

where, \(\omega(q), S,\) and \(I_0\) indicate one-dimensional phonon dispersion curve, correlation length (defect-free phonon propagation length or mean free path), and natural linewidth \((2.1 \text{ cm}^{-1})\) of micro-sized strain free c-BN, respectively. For c-BN crystals having twins or other crystal defects,
the mean free path of phonon (S) will be less than the size of the crystal. The phonon dispersion curve for the TO mode can be calculated using the equation (10.4):

$$\omega(q) = \sum_{n=0}^{6} A + B_n \left( \frac{q}{a} \right)^n$$

(10.4)

where, \(a\) denotes the lattice constant of c-BN and \(A, B_n\) are the dispersion constants. The inset of figure 10.6(a) shows the plot of phonon dispersion curve \((\omega(q))\) vs reduced wavevector \((q/q_{max})\) of TO mode in c-BN, calculated theoretically.\(^{48}\) The value of \(q_{max}\) is \(2\pi/a\). Therefore, at the center of the Brillouin zone (\(\Gamma\)), \(q = 0\) and at the face-center (X) of the crystal, \(q = q_{max}\). As discussed before, there is no Raman shift at \(q = 0\) (Brillouin zone). There is a gradual decrease in the value of Raman shift when \(q\) approaches \(q_{max}\). The theoretical calculations provide a better estimate of the curvature of \(\omega(q)\), whereas the experimental approach gives an accurate value of Raman shift at the Brillouin zone \((q = 0)\). Therefore, the dispersion curve is rigidly shifted to 1055 cm\(^{-1}\) at \(q = 0\) from the theoretical calculations. As it is evident from the phonon dispersion curve that a downshift of Raman frequency of the TO mode in c-BN is caused by the deviation (or shift) from \(q = 0\) point. A 35 cm\(^{-1}\) red-shift in nano c-BN corresponds to \(q/q_{max} = 0.37\), which contributes to the phonon vibrational modes in nano c-BN. On the other hand, \(q/q_{max} = 0.05\) contributes to the phonon vibrational modes in micro c-BN. Figure 10.6(a) shows the fitted curves (equation (10.3)) along with the experimentally acquired (normalized) Raman spectra of nano and micro c-BN. The curve fitting helps us to determine the correlation lengths \((S)\) in nano and micro c-BN. The correlation length is calculated as 50 and 24 nm for the case of micro and nano c-BN, respectively. These values are in good agreement with the earlier calculated \(S\) values in micro and nano c-BN.\(^{49}\) We have also plotted the intensity vs Raman shift for c-BN microcrystals having \(S = 1000\) nm (or 1 \(\mu m\)). As it is evident from figure 10.6(a), there is an increase in FWHM with
decrease in $S$. This indicates that low values of $S$ correspond to high values of defect density in a crystal. The plots of weighing function (exp($-(qS/4\pi)^2$)) vs correlation length (figure 10.6(b)) show an increasing influence of regions with large $q$ for small correlation length to the shape of Raman peak. The temperature-dependent Raman shift (frequency) can be fitted using the polynomial equation: $\nu(T) = a_0 + a_1 T + a_2 T^2$, where $a_0$, $a_1$, and $a_2$ indicate coefficients. The fittings for LO and TO vibrational modes in nano c-BN are shown in figure 10.6(c). For the TO vibrational mode, the values of $a_0$, $a_1$, and $a_2$ are 1341.89 cm$^{-1}$, -0.08 cm$^{-1}$/K, and 1.19×10$^{-4}$ cm$^{-1}$/K$^2$, respectively. For the LO vibrational mode, the values of $a_0$, $a_1$, and $a_2$ are 1025.93 cm$^{-1}$, -0.06 cm$^{-1}$/K, and 8.81×10$^{-5}$ cm$^{-1}$/K$^2$, respectively. The values of the temperature-dependent coefficients for micro c-BN are $a_1 = -0.01$ and $-0.003$ cm$^{-1}$/K for TO and LO modes, respectively and $a_2 = -1.45 \times 10^{-5}$ and $-1.46 \times 10^{-5}$ cm$^{-1}$/K$^2$ for TO and LO modes, respectively.$^{45}$ The different values of temperature-dependent coefficients in nano and micro c-BN suggest different modes of phonon relaxation (in nano and micro c-BN), which is also related to the correlation length.

The temperature-dependent Raman shift is the result of both vibrational frequency change (as volume increases at higher temperature) and self-energy shift that arises from phonon coupling. The latter term can be defined as the change in the average vibrational energy at constant volume. The Raman shift due to thermal expansion ($\nu_G(T)$) can be calculated using the equation (10.5):

$$\nu_G(T) = \nu(0). \exp\left(-M \int_0^T \alpha dT\right)$$

(10.5)

where, $\nu(0)$ and $\alpha$ indicate Raman shift at 0 K and linear thermal expansion coefficient, respectively. The term $M$ depends on the nature of vibrational mode and is equal to 4.5 for TO mode and 3.6 for LO mode.$^{50}$ The Raman shift due to thermal expansion is shown for the TO and
LO modes in figure 10.7(a) and (b), respectively. As it is evident from the figures that there is an increase in the difference between the experimentally observed Raman shift and that due to volume expansion with an increase in temperature (up to 300 K). This is due to the self-energy (anhmonic contribution ($\nu_{an}(T)$)) of the system, which can be calculated using: $\nu_{an}(T) = \nu_{obs}(T) - \nu_C(T)$. In other strongly-bonded materials like diamond, $\nu_{an}(T)$ also behaves in a similar fashion. As it is evident from the inset of figure 10.7(b), the $\nu_{an}(T)$ contribution for LO mode is greater than that in TO mode. Earlier results have shown that in the case of micro c-BN, the $\nu_{an}(T)$ is more prominent in TO mode as compared to LO mode. This may be because the optical-electric effect is pronounced in nano c-BN as compared to micro c-BN. The temperature-dependent Raman linewidth of the TO and LO modes in c-BN can be explained by an increased probability of phonon decay (at high temperatures). This occurs due to the increase in the phonon occupation at high temperatures. The TO mode can decay via three or three and four phonon processes. The temperature-dependent linewidth ($\Gamma(T)$) for a three and four phonon processes can be calculated using equation (10.6):

$$
\Gamma(T) = A \left( 1 + 2 \left\{ \exp \left( \frac{\hbar \nu}{2kT} \right) - 1 \right\}^{-1} \right) + B \left( 1 + 3 \left\{ \exp \left( \frac{\hbar \nu}{3kT} \right) - 1 \right\}^{-1} + 3 \left\{ \exp \left( \frac{\hbar \nu}{3kT} \right) - 1 \right\}^{-2} \right) \quad (10.6)
$$

where, A and B are constants and $\nu$ Raman frequency of the TO (or LO) mode at 300 K. For a pure three-phonon process, $B=0$. As it is evident from the equation (10.6), that with decreasing temperature, the Raman linewidth decreases and approaches the value of A for a three-phonon process and (A+B) for three and four phonon processes (at T=0 K). Figures 10.7(c) and (d) indicate that there occurs three- and four-phonon processes at low-temperatures (77-300 K) for TO and LO modes in nano c-BN. Therefore, it is conclusively shown that the anharmonic effects in nano c-
BN cause Raman blue-shift, and the decrease in Raman linewidth with decreasing temperature is caused by three- and four-phonon decay processes.

10.5. Conclusions

In conclusion, we have successfully shown that nanocrystalline h-BN (~25 nm) can be converted directly into phase-pure c-BN at ambient temperature and atmospheric pressure in air. The sizes of c-BN (90 nm to 25 μm) and crystal twinning can be varied by changing the quenching rates, which changes the nucleation and growth of c-BN. The selected area electron diffraction patterns also indicate the formation of heavily twinned c-BN with [1̅1̅1] as the twin axis. The formation of crystal twins predominantly occurs before the formation of amorphous Q-BN. The twin density in nano c-BN (formed at higher undercooling) is calculated to be ~10^{12} cm^{-2}, which is four-order larger than that in micro c-BN (formed near melting temperature). The temperature-dependent Raman studies (300 to 78 K) show a considerable blue-shift of ~6 cm^{-1} in nano c-BN as compared to micro c-BN. The spatial correlation model is also used to demonstrate the size-effect of c-BN crystals on the Raman-active vibrational modes (TO and LO). The model is also employed to calculate the correlation lengths (50 and 24 nm for the case of micro and nano c-BN, respectively), which lead to a better understanding of the rapid-crystallization process from the BN melt. The anharmonic effects in Raman frequency and decrease in Raman linewidths in c-BN with decreasing temperature can also be caused by three and four phonon decay process. The atomic structure, bonding characteristics (σ* antibonding electronic state), and phonon vibrational modes of the synthesized c-BN crystals have been studied by high-resolution SEM, TEM, EELS, EBSD, and temperature-dependent Raman spectroscopy. The twinned diamond with twinned c-BN structures will lead to potential ultrahard materials. We are collaborating with Prof. E. Riedo,
CUNY, New York for the Modulated NanoIndentation (MoNI) method. This method has been used to measure the effective stiffness (indentation modulus) of Q-carbon structures (harder than diamond) while using CVD diamond and sapphire as standards. The detailed mechanical properties of the c-BN structures will be reported elsewhere. We envision, that the controlled synthesis of nano and microstructures of twinned c-BN using nanosecond excimer laser and their temperature-dependent studies will have a significant impact on low-temperature electrical and mechanical devices.
10.6. Figures:

**Figure 10.1.** FESEM of (a) nano c-BN formed after pulsed laser annealing (PLA) with the inset showing dense nanostructures of c-BN, (b) Initial stages of formation of micro c-BN with the inset showing nanocrystalline (~25 nm) h-BN, which is converted to phase-pure c-BN, (c) Formation of large micro-crystals of phase pure c-BN with the inset showing the transformation of Q-BN to c-BN, (d) Large-area c-BN formed after the PLA process with the inset showing highly faceted crystal structure of c-BN, and (e) Change in Gibbs free energy vs radius showing the formation of twinned c-BN by increasing the degree of undercooling.
Figure 10.2. (a) HRTEM of c-BN showing twins and dislocation with the top left inset showing twin in micro c-BN, top right inset showing epitaxial growth of c-BN on c-sapphire, and lower inset showing twin in nano c-BN, (b) Selected area electron diffraction (SAED) pattern of twinned c-BN showing the twin axis and twin diffraction spots (with the inset showing $<-2110>$ diffraction of the c-sapphire substrate), (c)-(f) FESEM of twins in various structures of c-BN formed after PLA. By changing the undercooling, twinning of c-BN is formed. The scale bar in top left inset and top right inset of figure (a) are 1 and 100 nm, respectively.
Figure 10.3. (a) and (c) Secondary electron images of nano c-BN, (b) and (d) EBSD Kikuchi pattern of nano c-BN showing the characteristic Kikuchi pattern of c-BN in red, (e) Secondary electron image of micro c-BN with the insets showing Kikuchi patterns of micro c-BN from region A and B, and (f-g) Dynamical simulation of the EBSD Kikuchi patterns for regions A and B with the inset showing crystal orientation.
Figure 10.4. (a) Core-loss EELS of phase pure c-BN showing antibonding electronic states ($\sigma^*$) of B and N, (b) Raman spectra of nano and micro c-BN at 78 K showing TO (Γ) vibrational mode, (c) Temperature-dependent Raman shift in nano c-BN, and (d) Temperature-dependent Raman shift in micro c-BN. As it is clearly evident that there is a considerable blue-shift in nano c-BN with decreasing temperature as compared to micro c-BN. The width of the red window is same in figures (c) and (d).
Figure 10.5. (a) Normalized Raman spectra of nano and micro c-BN at 78 K showing LO (Γ) vibrational mode, (b) Temperature-dependent Raman shift in nano c-BN, and (c) Temperature-dependent Raman shift in micro c-BN. As it is clearly evident that there is a considerable blue-shift in nano c-BN with decreasing temperature as compared to micro c-BN. The width of the red window is same in figures (b) and (c).
Figure 10.6. (a) Modeling of normalized intensity vs Raman shift (using spatial correlation model) in nano and micro c-BN formed after PLA with the inset showing theoretically calculated phonon dispersion (Raman shift vs q/q max) for TO mode in c-BN, (b) Weighing function vs q/q max for nano and micro c-BN, and (c) Raman shift vs temperature for LO and TO modes in nano c-BN.
Figure 10.7. Temperature-dependent Raman analysis for nano c-BN: (a) Raman shift vs temperature for TO vibrational mode along with the shift due to thermal expansion, (b) Raman shift vs temperature for LO vibrational mode along with the shift due to thermal expansion with the inset showing the anharmonic shift vs temperature for TO and LO modes, (c) Raman linewidth vs temperature for TO mode showing the prominent presence of three and four phonon processes, and (d) Raman linewidth vs temperature for LO mode showing the prominent presence of three and four phonon processes.
10.7. References


11. Direct Conversion of Carbon Nanofibers into Diamond Nanofibers Using Nanosecond Pulsed Laser Annealing

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11.1. Abstract

Here, we show the direct conversion of carbon nanofibers (CNFs) into diamond nanofibers (DNFs) by irradiating CNFs with ultrafast ArF nanosecond laser at room temperature and atmospheric pressure. The nanosecond laser pulses melt the tip of CNFs into a highly undercooled state, and its subsequent quenching results in the formation of DNFs. This formation of DNFs is dependent on the degree of undercooling which is controlled by nanosecond laser energy density and one-dimensional heat flow characteristics in CNFs. The conversion process starts at the top and it extends with the number of pulses. Therefore, our highly non-equilibrium nanosecond laser processing opens a new frontier for the synthesis of exciting pure and doped diamond structures at ambient temperatures and pressures for a variety of applications.
11.2. Introduction

The wonders and challenges in carbon have fueled several exciting opportunities and scientific discoveries for more than half a century.\textsuperscript{1,2} The conversion of the sixth most abundant element in the Earth’s crust, carbon into diamond at room temperatures and atmospheric pressures, has always been a matter of great interest to the carbon scientific community.\textsuperscript{3} Many approaches have been undertaken in the past to convert graphite into diamond at high temperatures and pressures (HPHT), plasma enhanced chemical vapor deposition (PECVD), microwave annealing at high temperature and pressure, and in the presence of a catalyst.\textsuperscript{4-6} There are reports of diamond formation from carbon nanotubes and fibers at low temperatures and pressures using spark plasma sintering, ballistic fracturing, and chemical processing, which exhibits limited yield and control.\textsuperscript{7-11} The conversion of carbon nanotubes and fibers into diamond has been also reported at high temperatures and high pressures \textit{via} the formation of intermediate quasi-spherical onion-like structures.\textsuperscript{12-15} Interesting nanostructures of diamond are also formed onto CNTs after hydrogen plasma treatment.\textsuperscript{16,17} The formation of nanocrystalline diamonds from CNTs using hydrogen chemisorption is similar to that in chemical vapor deposition (CVD) process, where atomic hydrogen is responsible for creating carbon containing species and formation of diamonds.\textsuperscript{18} Similar growth of diamonds (on Si) encapsulated in graphitic shells has been also reported using the post-treatment of (atomic) hydrogen.\textsuperscript{7} But there was a relatively low yield (~10\%) with little control of the dimensions of the diamond structures formed. Recently, picosecond laser assisted formation of new phases of carbon (T-carbon) nanowires from CNTs was also observed.\textsuperscript{19} Since this conversion requires first-order phase transformation, the role of picosecond lasers was not clarified.\textsuperscript{19} Previous result on conversion of CNTs to quadrilateral crystals of diamond using continuous wave CO\textsubscript{2} laser show sporadic growth of diamonds in a Fe-C alloy system.\textsuperscript{20} As a
result, a method for direct conversion of carbon nanofibers into diamond at ambient temperatures and atmospheric pressures in air will be a major step forward in this field.

This report presents a novel processing route to facilitate the one-step conversion of carbon nanofibers into diamond nanofibers using nanosecond ArF laser at room temperature and atmospheric pressure without any need for catalysts and atomic hydrogen to stabilize sp$^3$ diamond bonding. The formation of nanodiamonds is an optimal choice for nanomechanical systems and drug delivery due to its high biocompatibility and ease of functionalization.$^{21,22}$ Therefore, controlled conversion of graphitic structures to DNFs is a matter of great scientific interest with a tremendous technological impact. The formation of diamond utilizing a low-thermal budget route will revolutionize its use in electronic, biomedical, and photonic devices.$^3$ Again, the formation of diamond (large band gap material) on graphite will facilitate better design of field-effect transistors having high mobility (due to one-dimensional structure) and large thermal conductivity.$^{23}$ Thermodynamically, the low-energy conversion of graphite into diamond is extremely difficult owing to the high surface energy of diamond, which results in a positive value of the change in Gibbs free energy.$^{24}$ In our ultrafast pulsed laser annealing process, undercooling (non-equilibrium) route is utilized and the conversion (of graphite into diamond) is possible as increasing the degree of undercooling results in high nucleation rates and lowers the Gibbs free energy barrier.$^{25}$ The restriction of the heat flow (in one-dimensional amorphous CNFs) causes the formation of DNFs. We report a detailed characterization of DNFs using transmission electron microscopy (TEM), selected area electron diffraction (SAED), electron backscatter diffraction (EBSD), high-resolution scanning electron microscope (SEM), electron dispersive X-ray spectroscopy (EDX), electron energy-loss spectroscopy (EELS), and Raman spectroscopy.
11.3. Experimental

The CNFs are synthesized in a tube furnace-CVD chamber thermally baked at 800°C. Highly sensitive mass flow controllers are used to introduce Ar (450 sccm) and H₂ (10 sccm) in the tube furnace prior to the CVD processing. The temperature in the CVD furnace is ramped up to 800°C and thermally soaked for 10 min. At this temperature, 25 sccm of C₂H₄ is introduced in the furnace for 30 minutes. After that, the Ar and H₂ gases are flown in the tube furnace and the flow of C₂H₄ was switched off. The temperature is then ramped down to room temperature for 2 hours. The prepared CNFs are ultrasonicated to remove unwanted metallic impurities. These CNFs are irradiated in air with ArF laser pulses (pulse duration = 20ns, wavelength = 193nm, energy density = 0.6-1.0 Jcm⁻²). Due to the restriction of heat flow in one-dimensional CNFs, melting of amorphous carbon to a highly undercooled state occurs. The undercooled state is subsequently quenched to form nanostructures of diamond at the CNF tip. With increasing the number of nanosecond laser pulses, the entire fibers are converted into diamond. The CNFs (before and after PLA processing) are dispersed in ethanol and transferred onto copper TEM grids. To facilitate the bleeding of electronic charges, the sample is sandwiched between two copper grids and then mounted in the TEM sample holder. These structures are characterized by TEM, SAED, EBSD, SEM, and Raman spectroscopy (using 532 nm excitation laser). High-resolution SEM (and EDX) and EBSD measurements are carried out using FEI Verios 460L SEM and FEI Quanta 3D FEG FIB-SEM, respectively. EBSD technique helps for phase identification (by Kikuchi patterns) and the structural morphology is characterized using SEM. JEOL 2000 FX is used for performing the TEM and SAED of the CNFs and DNFs. A 200 kV electron beam from LaB6 source (having lattice resolution of 0.14 nm) is used for the TEM imaging and diffraction purposes. A HORIBA Xplora PLUS confocal Raman microscope having 0.5 μm spatial resolution and 532 nm excitation
source is used for determining the Raman active vibrational characteristics (at 300 K) of the CNFs and DNFs. The Raman mappings are performed by using a motorized XY stage installed in the confocal Raman microscope. The XPS instrument having PHOIBOS 150 analyzer is used for the XPS survey and high-resolution scans. The X-ray energy (10-14 kV) is derived from the Al/Mg source and the analyzer has less than 1 eV resolution. The XRD 2θ scans are performed by using the Rigaku D-MAX/A diffractometer with Cu-Kα radiation (wavelength = 0.154 nm).

11.4. Results and discussion

Figure 11.1 depicts the conversion of CNFs to DNFs after the nanosecond pulsed laser annealing with a single laser pulse. Before the PLA processing (figure 11.1(a)), the CNFs have smooth edges and ends, as CNFs comprise of amorphous graphitic carbon. Upon PLA, there occurs a formation of highly undercooled state of molten carbon at the tip of the fibers (due to the restriction of heat flow in one-dimensional CNFs). The PLA process is an ultrafast technique and is completed in less than 50 ns. Therefore, the highly undercooled state of molten carbon is quenched to nucleate nanostructures of diamond at the tip of the CNFs. In the tips and bends of the CNFs, the undercooling is the highest, where nanodiamonds are formed. Figure 11.1(b) shows the formation of nanostructures of diamond at the tip of the CNFs after the PLA technique. The formation of DNFs starts with nucleation of diamond from the highly undercooled state of molten carbon (formed after PLA). The formation of diamonds occurs by a homogeneous nucleation from the highly undercooled state of carbon. The change in Gibbs free energy ($\Delta G_T$) associated with the formation of DNFs consists of a gain in volume energy ($\sim r^3$) at the expense of surface energy ($\sim r^2$), where $r$ is the radius of diamond nucleus. The change in free energy can be calculated using the equation: $\Delta G_T = -\frac{4}{3} \pi r^3 \rho \frac{\Delta H_m}{T_m} \Delta T_u + 4 \pi r^2 r_s$, where $\rho$ is the density of diamond, $\Delta H_m$ is the
latent heat of melting, $M_m$ is the molar mass, and $r_s$ is the surface free energy between diamond nuclei and the undercooled state of carbon. The first term in the equation is the volume energy term (gain in free energy for the formation of diamond nucleus from the undercooled state) whereas the second one is the surface energy term. The degree of undercooling, $\Delta T_u$ is equal to $T_m - T_r$, where $T_m$ indicates melting point of graphite (~5000 K) and $T_r$ indicates the nucleation temperature (~4000 K). With an increase in the value of $\Delta T_u$, $\Delta G_T$ becomes more negative and a conversion of graphite (CNFs) to diamond (CNRs) is favorable. Again, the critical radius and change in Gibbs free energy (at $\frac{d\Delta G_T}{dr} = 0$) is inversely proportional to $\Delta T_u$ and $\Delta T_u^2$, respectively.

Therefore increasing $\Delta T_u$ reduces the critical value of diamond radius and change in Gibbs free energy ($\Delta G_T^*$). The rate of nucleation ($I$) is given by the equation: $I \sim \exp \frac{-\Delta G_T^*}{kT_r}$. Therefore, with a decrease in the value of $\Delta G_T^*$, the rate of nucleation increases thereby facilitating the formation of diamond. For a 10 nm size nanodiamond, the estimated growth time is about 5-10 ns. This time requirement emphasizes the importance of thermal conductivity of the substrate during rapid pulse laser heating. A rough estimate of $r^*$ for diamond nuclei from equation is ~20 Å, where diamond surface free energy $r_s$ is 0.6 Jm$^{-2}$. $T_m$=4000 K, $\Delta H_m$=1.0 eV/atom, $\Delta T_u$=1000 K, and $\rho = 3.5$ gm/cm$^{-3}$. This is verified experimentally in figure 11.4(d) and (e). Some of the nanodiamonds are marked in figure 11.4(e) and a single nanodiamond is shown in the top right inset of figure 11.4(e).

The value of Gibbs free energy is maximum at the critical radius. Therefore, diamond nuclei having radius greater than 2 nm will be favorable for the further growth of nanodiamonds into microdiamonds. The growth velocity ($v$) is directly related to the undercooling by the following equation: $v = \frac{D_{\infty}f_f}{\lambda_f D^{1 - e^{\frac{(T_m-T_u)\Delta S}{kT}}}}$, where, $D_{\infty}, f, \lambda, f_D, k, T, T_m, T_u$ and $\Delta S$ denote the liquid diffusivity (~$10^{-8}$ m$^2$/sec in liquid state), fraction of the available sites, atomic jump distance,
geometrical factor associated with diffusion, Boltzmann constant, temperature, melting temperature, undercooling temperature, and the change in entropy, respectively. An increase in the value of $T_u$ decreases the value of chemical free energy barrier for graphite to crystalline diamond phase transformation. This also increases the velocity of the melt-front. Therefore, the values of undercooling dictate the conversion of amorphous graphitic phase into diamond via the carbon melt. If the cooling rate is slow (low undercooling and low solidification velocity), crystalline graphite is formed whereas with high cooling rates (large undercooling and large solidification velocity), crystalline diamond is formed.

Therefore, the diamond nucleation from highly super undercooled carbon can occur readily after the PLA technique. Figure 11.1(c) shows the formation of diamond at the tip of a CNF, whereas the base of the CNF is unaltered. There occurs a decrease in volume (volume of diamond=0.65×volume of graphite) after the formation of diamond from graphite and is evident from figure 11.1(c). The formation of diamond preferably occurs at the tip and bends of CNFs and is evident from figure 11.1(d). The bottom right inset in figure 11.1(d) indicates the formation of diamond at the CNF tip. It is interesting to note that these nanodiamond crystallites are surrounded by high-index planes and are not as faceted with low energy planes, as found typically in CVD ("cauliflower") diamond films. The crystallites with high-index planes have been shown to be catalytically more active than low-index ones. The CNFs with diamond tips provide an ideal structure for efficient field electron emission. Therefore, the synthesized nanostructures of diamond onto CNFs using the PLA technique will have immense application in nanocatalysis and field emitting devices. Figure 11.1(e) shows the formation of nanostructures of diamond at a fairly uniform area at the CNF tips and bends. As mentioned above, the heat flow is restricted at the CNF tips and bends, which causes the nucleation of diamond (due to the undercooling process). The
simulation of laser interaction with materials (SLIM) calculations are shown in figure 11.1(f). The temperature vs time plot indicates the onset of melting (of CNF) at ~20 ns. The melting occurs ~4000 K which is ~1000 K below the melting point of graphite. This provides the undercooling necessary to nucleate diamond. The undercooling in CNF depends on the thermal properties and heat flow geometry. Therefore, highest undercooling occurs at the tip of the CNFs and lowest at the base. The inset of figure 11.1(f) illustrates the melt-in and growth regions of the CNF at ~4000 K. The SLIM calculations (for 0.6 J/cm² laser energy density) indicate the solidification velocity of ~2 m/sec and growth time of 15 ns. The solidification velocity and growth time dictate the size of the diamonds nucleated from the highly undercooled state of carbon. The high values of solidification velocity also indicate the liquid-phase growth of diamonds from CNFs after nanosecond pulsed laser annealing. Figure 11.2 indicates high-resolution SEM images of DNFs formed from CNFs after nanosecond pulsed laser annealing with 20 laser pulses. By subsequent laser annealing these diamond regions can be extended to form longer DNFs. The formation of nanostructures of diamond occurs in those CNFs which are aligned perpendicular to the nanosecond laser beam (figure 11.2(a)). The CNFs which are aligned parallel to the laser beam do not convert into diamond. Figure 11.2(b) depicts SEM-EDX of the tip of DNF (formed after PLA). The EDX spectrum (figure 11.2(c)) depicts the presence of only C-Kα peak at 0.277 keV (and no other impurity peaks). This proves that the phase transformation of amorphous CNF into diamond occurs in the absence of a catalyst (at room temperatures and atmospheric pressures). Figure 11.2(d) shows CNF transformation into diamond at the tips and bends after the nanosecond PLA technique (using 20 laser shots). A complete transformation of CNFs into DNFs for smaller diameter CNFs, as compared to larger diameter CNFs after 20 laser shots is seen in figure 11.2(e). The CNFs having diameter less than 50 nm are completely converted into diamond after 20 laser
shots. We have also observed the formation of diamonds on the surface of the CNFs having higher
diameter (50-150 nm) after irradiation with 20 laser shots. The formation of diamond spreads as
the number of laser pulses is increased. As it is evident from figure 11.2(f) that there occurs a
higher electron contrast (due to negative electron affinity) in the diamonds formed at the CNF tips
than that from the graphitic base.

The electron backscatter diffraction (EBSD) by using field-emission scanning electron microscope
is performed to determine the phase (of carbon) at the CNF tip and base after PLA. The EBSD
results are shown in figure 11.3(a)-(n) from the CNF tip, bend, and base showing characteristic
Kikuchi diffraction pattern of diamond (in red) and graphite (in green). The 70 degrees tilted SEM
micrograph (figure 11.3(a)) shows the presence of (laser treated) CNFs. The tip shows the
formation of diamond at the tip of the CNF whereas the base of CNF shows the presence of
graphitic phase. The electron probe size used for EBSD Kikuchi pattern determination is ~10 nm
and is ideal for determination of Kikuchi diffraction patterns in CNFs. The three-dimensional
orientation of diamond and graphite is shown as an inset of figure 11.3(b) and (c). The EBSD
Kikuchi patterns taken from the tip (figure 11.3(b)) and base (figure 11.3(c)) of a CNF and are
shown in figure 11.3(d) and (e), respectively. It should also be noted that, there occurs formation
of diamond just below the tip also (figure 11.3(f) and (g)) up to the point where the undercooling
is large enough (to nucleate and grow diamond). The Kikuchi diffractions (of diamond) are shown
in figure 11.3(i) and (j). It can be clearly seen that there is a minimal change in the crystal
orientation (and Kikuchi diffraction pattern) of the EBSD spots taken at the tip and below the tip.
The highest undercooling occurs at the tip and falls as we move more towards the base (of CNF).
Below the diamond there is formation of crystalline graphite (lowest undercooling). The formation
of crystalline graphite between diamond and amorphous carbon shows that a low undercooling
molten carbon converts into graphite, as shown by Dresselhaus and coworkers.\textsuperscript{26} The amorphous nature of CNF is unaltered close to its base. As mentioned above, there also occurs nucleation of diamond at the bend of CNF and is shown in figure 11.3(h). The characteristic Kikuchi diffraction pattern of diamond from the CNF bend is shown in figure 11.3(h). The dynamical simulations of the diamond Kikuchi patterns and the corresponding crystal orientations are shown in figures 11.3(l-n). The dynamical simulations (by using the Bloch wave approach) of the experimentally acquired Kikuchi patterns reduce the background effect and, therefore, accurate crystal orientations can be calculated. It should be noted that the EBSD technique yields accurate results for smooth samples. In the present case, the EBSD technique was used to identify the phase (diamond and graphite). The details of the crystal orientation are calculated by using high-resolution TEM and FFT analysis.

Figure 11.4 depicts the TEM and SAED analysis of the CNFs and nanostructures of diamond formed on the tip and bends of the CNFs (after the PLA technique). As it is evident from figure 11.4(a) that there is nucleation of diamond at the tip and bend (inset of figure 11.4(a)) of amorphous “solid” CNFs. The formation of diamond at the tip of the CNFs also shows its use as electron field emitters. The amplitude contrast microscopy in TEM reveals that the darker region corresponds to denser diamond structure whereas the lighter contrast denotes amorphous CNFs. Since the degree of undercooling is the highest at the tips (and bends) in CNFs, there is a homogeneous nucleation of nanostructures of diamond (from the undercooled melt of carbon). In the selected area diffraction pattern (figure 11.4(b)) taken from the nanocrystalline diamond region from different rods (in figure 11.4(a)), there was no evidence for the formation of amorphous phase. The SAED pattern shows characteristic diffraction pattern (ring-like and speckled) of nanocrystalline diamond showing the distinct diffractions peaks of 111, 200, 220, 311, 222, 004,
331, and 333 planes. The diffraction profile is overlaid on figure 11.4(b). Figure 11.4(c) shows the amorphous structure of the CNFs (before PLA). The FFT of the amorphous CNF is also shown in the right lower inset in figure 11.4(c). The initial formation of nanodiamonds (NDs) after the PLA technique is depicted in figure 11.4(d). As it is evident that there is formation of NDs closer to the surface on the CNFs than the core (as larger undercooling occurs at the surface than at the core). The FFT analysis of the NDs is shown in the lower left inset of figure 11.4(d). The diffraction pattern shows the presence of 111 diffraction spots (circled in red), corresponding to diamond. This corresponds to <110> cross-section that has two sets of {111} planes of diamond. An inverse FFT of the diffraction pattern (lower right inset in figure 11.4(d)) shows the presence of lattice planes separated by 0.207 nm (interplanar spacing of {111} planes in diamond). A dense formation of nanostructures of diamond occurs at the tip and bend of CNFs and is shown in figure 11.4(e). Figure 11.4(d) and (e) show diamond nuclei in the range of 2-5 nm. It should be mentioned that the nucleation rate is the highest at the tip of the CNFs (where NDs are formed) and with an increase in growth rates, larger diamonds are formed below the nanodiamonds. The top right inset in figure 11.4(e) indicates the presence of {111} diamond planes in the nanodiamonds. Interestingly, some of the nanodiamonds are twinned. The left inset of figure 11.4(e) shows the FFT analysis of a twinned diamond, where multiple diffraction spots are observed. The inverse FFT analysis reveals the presence of twin planes along {111} twin boundary and a <110> twin axis. The details of the nanotwinned diamond structures will be published elsewhere. Below the NDs, single crystalline diamonds having <110> texture is formed (figure 11.4(f)), which is consistent with <110> texture of silicon formed under rapid unseeded crystallization.27 Similar <110> textured growth is found in the diamond structures grown using the PLA of CNFs (figure 11.4(f)). The FFT analysis of the top and bottom portion of TEM micrograph show the presence
of <110> textured diamond, as we can see the presence of 111 and 002 diffraction spots. Previous results also indicate the formation of ~100 nm wide nanocrystalline region in the super undercooled state of Si.\textsuperscript{27-29} In the nanocrystalline region formation of 10 nm size of nanocrystallites Si occurred from the super undercooled state of Si.\textsuperscript{28} The nanocrystallites of Si provided nucleation sites for growth of macrograined polycrystalline Si. The laser parameters and thermal conductivities of the substrate and thin film are shown to be the crucial parameters for achieving the super undercooling process.\textsuperscript{25} Therefore, in the present scenario, the tips and bends of CNF absorbs the laser energy and there occurs high localized temperatures (due to restriction of the heat flow) because of high undercooling. This leads to the nucleation of diamond at the tips (and bends) of CNFs. The conversion of graphitic CNFs into diamonds occur without the intermediate stage of formation of diamond onions.\textsuperscript{8,30} For the case of amorphous Si and Ge (having diamond cubic lattice), the undercooled states are found to occur at 336 and 241 K below their respective melting temperatures.\textsuperscript{31} One of our previous works on nanosecond laser melting (using XeCl Excimer laser having wavelength=308 nm and laser width=45 ns) of carbon implanted copper indicated the formation of diamond (zone-refined on Cu).\textsuperscript{32} Interestingly, it should be noted that the nanosecond laser melting of \textsuperscript{73}Ge\textsuperscript{+} and \textsuperscript{75}As\textsuperscript{+} implanted highly oriented pyrolytic graphite (HOPG) using a ruby laser (energy density=0.6-3.0Jcm\textsuperscript{-2}, wavelength=693nm, pulse duration=30ns) did not form diamond.\textsuperscript{26} This is due to the presence of highly (thermally) conducting HOPG layers, which produced little or no undercooling. In the present case, the amorphous graphitic phase (in CNFs) can be melted at a much lower temperature (1000 K less than the melting point of crystalline graphite) using nanosecond pulsed laser to create a highly undercooled state of liquid carbon. Upon subsequent quenching of this undercooled state, diamond nanofibers are nucleated. At these transition temperatures (~4000 K), Gibbs free energy of
undercooled molten carbon equals that of diamond. This undercooling shift graphite/diamond/liquid carbon triple point from 5000 K/12 GPa to 4000 K/atmospheric pressure. Therefore, the creation of this undercooled state is critical for the nucleation of nanodiamonds. Recently, we have also demonstrated the formation of a new phase of carbon (Q-carbon), nano-, micro-, and large-area diamond on sapphire substrates utilizing the phenomena of undercooling, where the formation of dense Q-carbon (having 75-85% $sp^3$ and rest $sp^2$) phase occurs at the highest degree of undercooling. In the above-mentioned process, amorphous carbon is melted in the super undercooled state (by irradiating with nanosecond ArF pulsed laser), and quenched rapidly to form Q-carbon or diamonds. We have also achieved direct conversion of carbon nanotubes into diamond nanorods by this process which will be reported shortly.

Figure 11.5 depicts TEM image (performed in TEM mode in STEM) and core-loss EELS at 300 K of CNF and diamond formed after the PLA technique. The TEM image clearly shows the formation of crystalline structure of diamond from amorphous CNF after pulsed laser annealing. To prevent the damage of the diamond structure under the intense (concentrated) electron beam, TEM mode in STEM microscope is used, which also has better information limit than the conventional TEM. The inset of figure 11.5(a) shows atomic columns present in the crystalline diamond lattice (after FFT filtering of the atomically resolved STEM image). The room-temperature core-loss EEL spectra (figure 11.5(b)) of CNF and diamond (after PLA) reveal $sp^3$ ($\sigma^*$) and $sp^2$ ($\pi^*$) bonding characteristics. The antibonding electronic states are observed at 285 eV ($\pi^*$) and 292 eV ($\sigma^*$). The EEL spectrum of diamond (after PLA) is considerably different from that of CNF (before PLA). The $\pi^*$ peak is sharp in the case of CNF (predominantly $sp^2$-bonded structure) whereas the $\sigma^*$ peak is prominent in the case of diamond (as compared to CNF). The characteristic fine post-edge structures (at 297, 305, and 326 eV) are also observed in the case
of diamond formed after PLA technique. There also occurs a characteristic drop at 302 eV corresponding to the absolute IIInd band gap in diamond. The long-range periodic structure of crystalline diamond gives rise to modulation to the density-of-states, as it is evident from the $\sigma^*$ region in EELS of diamond (after PLA). The EELS therefore univocally prove the formation of diamond crystallites after PLA of CNF. On the other hand, the amorphous nature of CNF is evident from the broadening of the antibonding states associated with the $\sigma^*$ electronic state. In CNF there is a local electronic effect arising due to interaction of similar electronic $sp^3$ states oriented at different direction (amorphous structure). This is also an indication of a disordered arrangement of the tetrahedrally bonded C atoms ($sp^3$-bonded C) in CNF (before PLA).

Theoretical and experimental results\textsuperscript{34,35} suggest that the local bonding structure of liquid carbon can be varied from a mixture of twofold and threefold coordinated atoms at low density (1.27 g cm$^{-3}$) to fourfold coordinated atoms at high density (3.02 g cm$^{-3}$). The fourfold coordinated liquid structure corresponds to liquid carbon structure at high pressures. The structure of molten super undercooled carbon, which is formed after the PLA process, is similar to the structure of liquid carbon at high pressures, where conversion into diamond phase occurs. Raman spectroscopy is a very powerful technique to determine the bonding characteristics in carbon (especially in graphite and diamond). Figure 11.6 depicts Raman spectroscopy of before and after PLA CNFs. In an area of 2 $\mu$m$^2$, 45 Raman spectra are collected and shown in figure 11.6. As it is evident from figure 11.6(a) there are three distinct Raman peaks centered at 1340, 1570, and 2680 cm$^{-1}$ corresponding to D, G, and 2D vibrational modes, respectively. The stretching of C-C bonds in-plane (E$_{2g}$) in $sp^2$ graphitic materials gives rise to the G vibrational mode.\textsuperscript{8,36} This phonon vibrational mode is highly sensitive to strain (induced by external forces like PLA). Though there is a small red-shift ($\sim$ 4 cm$^{-1}$) of the Raman active vibrational mode (G) after PLA of CNFs, there is a considerable increase
in the FWHM of the mode from 40 to 53 cm\(^{-1}\) (figure 11.6(b)). This indicates a considerable amount of strain in the CNFs after the PLA process due to the formation of nanodiamonds at the tips and bends. The spectral width (of G peak) is also dependent on the creation of electron-hole pair by phonon excitation process (Kohn anomaly).\(^{36}\) Therefore, the increase in FWHM of G vibrational mode in the nanocomposite structure of diamond and CNF can also be due to the change in the Fermi energy level (at the interface) and will provide exciting structures for future optoelectronic devices. The radial breathing modes (RBM), characteristic of carbon nanotubes (single and multi-walled),\(^{37}\) are not present in the Raman spectra of CNFs. There is an insignificant change in spectral width and peak position of the second-order (two-phonon process) vibrational mode (2D) in CNFs before and after PLA. But it should be noted that the intensity of 2D/intensity of G peak is ~50% more in after PLA CNFs as compared to that before PLA CNFs. This indicates a reduction of the sp\(^2\) graphitic entities in CNFs after the PLA process (due to the formation of diamond nanostructures). The most interesting change (after PLA) is in the disorder-induced D band as evident in figures 11.6(c) and (d). As it is evident that the asymmetricity of the D peak increases after the PLA technique. There is a significant change in the Raman spectra between 1250-1450 cm\(^{-1}\) in before and after PLA processed CNFs (shown in figure 11.6(e)). The Raman peak corresponding to nanodiamonds is observed ~1321 cm\(^{-1}\) in the CNF samples after PLA processing. The red-shift of ~11 cm\(^{-1}\) (from 1332 cm\(^{-1}\) in microdiamonds) and spectral broadening are due to phonon confinement\(^{38}\) in nanosized diamonds (formed after PLA). Also, there is an increase in the intensity of D/intensity of G peak in the CNFs after the PLA processing due to the increase in disorderness (destruction of sp\(^2\) entities). Therefore, Raman studies provide a clear evidence for conversion of CNFs into nanodiamonds (due to laser-assisted melting and resolidification) after the PLA technique. Figure 11.7 depicts Raman mapping of CNF before PLA,
after 1 laser shot, and after 20 laser shots. The 532 nm laser was focused on a spot on the sample and the sample was moved by using a motorized stage during the acquisitions of spectra. Figure 11.7(a) shows the Raman spectra acquired from the CNF and the “NO CNF” region. This was done to image both the CNF and without the CNF regions. The D, G, and 2D vibrational modes are present in the CNF region. All the spectral maps are normalized and overlaid in the inset image. The image shows a complete absence of all the modes in the “NO CNF” region. Figure 11.7(b) shows the Raman spectra acquired from the CNF after 1 laser shot and the unaffected (masked) region. This was done to identify the interface between the “before PLA” and “after PLA” regions (figure 11.7(c)). The Raman spectra shown in figure 11.7(b) indicate the formation of diamond (peak ~1320 cm$^{-1}$). The diamond region (from 1310-1332 cm$^{-1}$) was mapped and shown in figure 11.7(c). As it is clearly evident from the Raman map that the diamonds are only formed after the PLA process. Similar Raman acquisitions were performed for the CNFs which were irradiated with 20 laser shots (figure 11.7(d)). The diamond peak is more distinct in the 20 laser shots sample as compared to 1 laser shot sample. This indicates that more diamond transformation was possible after multiple laser shots. The diamond region was also mapped from the 20 laser shots sample (figure 11.7(e)), which shows a complete absence of diamonds in the “Before PLA” region. Figure 11.8 depicts the XPS, XRD, and bonding analysis of CNFs before and after PLA. The XPS survey scan (figure 11.8(a)) shows C 1s and O 1s peaks centered ~ 285 and ~530 eV, respectively in the CNFs (before PLA). The XPS scan also shows the absence of impurity peaks in the CNFs. The high-resolution XPS scans of C 1s for CNFs before and after PLA are shown in figure 11.8(b). In addition to the C-OH (285.7 eV), C=O (286.6 eV), and OH-C=O (288.6 eV) peaks there are sp$^2$ and sp$^3$ carbon peaks present at 284.0 and 285.0 eV, respectively. The CNF (before PLA) do not show the sp$^3$ peak as compared to the 1 and 20 laser shots CNF samples. Therefore, XPS confirms
the conversion of CNF into diamond after the PLA. Figure 11.8(c) depicts the XRD scans for CNF (before PLA) and after 1 and 20 laser shots. The diffraction peaks at 26.0° and 43.9° correspond to graphite (0002) and diamond (111), respectively. There is a considerable broadening of the graphite diffraction peak after the PLA due to a decrease in the crystallite size of graphite (after PLA). The decrease in the crystallite size of graphite after the PLA is also evident from the Raman spectroscopy where there occurs an increase in the intensity of D/intensity of G vibrational mode (after PLA). There is a significant decrease in the FWHM of the diamond peak in the 20 laser shots sample as compared to the 1 laser shot sample. Figure 11.8(d) indicates the Raman spectroscopy and XPS analysis of the before PLA and after PLA (1, 5, 10, and 20 laser shots) CNFs. The sp³% calculated by using the high-resolution XPS indicates a gradual increase in the sp³ content after multiple laser shots. The intensity of diamond/intensity of G vibrational mode calculated from the Raman spectroscopy also increases with multiple laser shots. Interestingly, the intensity of D/intensity of G vibrational mode increases drastically after irradiating the CNF with 1 laser shot. There is a minimal change in the ratio with multiple laser shots. This indicates a decrease in the size of the graphite crystallites after the PLA. But with multiple laser shots there is a minimal change in the graphite crystallite size which also indicates that diamond is formed from the super undercooled state of molten carbon.

11.5. Conclusions

We have synthesized diamond nanofibers from carbon nanofibers by using a highly non-equilibrium technique of pulsed laser annealing. Upon irradiating the CNFs with nanosecond ArF laser, the tips and bends of the CNFs are melted in a highly undercooled state. The highly undercooled state of carbon is a metastable phase and nanodiamonds nucleate from this state. The process (rapid melting, solidification, and growth) is completed in less than 50 ns. Our results
clearly indicate that diamond can be formed at ambient conditions in air from the super undercooled state of carbon without catalyst and atomic hydrogen (CVD process). The nanosecond laser parameters and heat confinement by the one-dimensional CNFs determine the temperature distribution and undercooling and play a critical role in nucleation and growth of nanodiamonds. The nanosecond laser pulses help us to achieve the undercooled state of carbon and upon subsequent quenching leads to the formation of nanodiamonds from CNFs. The nanosecond laser heating and temperature distributions are confined spatially and temporally. Therefore, the tips (and bends) of CNFs melt whereas the underlying areas are unaffected. By subsequent laser pulses, these diamond regions can be extended to form larger diamond nanofibers and nanorods. The formation of DNFs and their heterostructures will have exciting applications ranging from drug delivery to optoelectronics and field emitters. This discovery of conversion of CNF tips into diamond nanofibers at room temperature and atmospheric pressure will open a new frontier for synthesis and processing of diamond nanostructures for a variety of applications.
11.6. Figures:

**Figure 11.1.** High-resolution SEM images of (a) A CNF before PLA technique, (b) and (c) CNF after PLA showing the formation of nanofibers of diamond at the CNF tip, (d) CNF transformation into diamond at the tips and bends after the nanosecond PLA technique with the inset showing the conversion in one CNF, (e) Phase transformation of CNFs into diamond for smaller diameter CNFs, where one-dimensional heat confinement (high undercooling) occurs at the tips and bends of CNFs, and (f) SLIM calculations of the PLA of CNF with the inset showing the melt-in and growth regions.
Figure 11.2. High-resolution SEM images of (a) CNFs after PLA technique (20 laser shots) showing the formation of nanofibers at the CNF tip facing 90 degrees to the nanosecond laser, (b) SEM-EDX of DNFs formed after PLA with the (c) EDX spectra showing the presence of only C-K_α_1 peak at 0.277 keV (and no other impurity peaks), (d) CNF transformation into diamond at the tips and bends after the nanosecond PLA technique (20 laser shots), (e) A complete transformation of CNFs into diamond for smaller diameter CNFs, as compared to larger diameter CNFs after 20 laser shots, and (f) Higher electron contrast (due to negative electron affinity) in the diamonds formed at the CNF tips after the PLA technique.
Figure 11.3. (a) EBSD micrograph showing the formation of diamond at the (b) tip and (c) graphite near the base with the insets showing the three-dimensional crystal orientations, (d) and (e) Kikuchi diffraction patterns of the diamond and graphite, respectively, (f) EBSD micrograph from CNF tip and the corresponding Kikuchi diffraction shown in (i), (g) EBSD micrograph from CNF just below the tip and the corresponding Kikuchi diffraction shown in (j), (h) EBSD micrograph from bend and the corresponding Kikuchi diffraction shown in (k). The dynamical simulations and crystal orientations for the Kikuchi diffractions (i,j,k) are shown in (l,m,n), respectively.
Figure 11.4. TEM images of (a) formation of diamond at the tip of a CNF after PLA with the inset showing diamond formation at the CNF bend, (b) Selected area electron diffraction pattern of nanodiamonds with the overlaid diffraction spectra showing 111, 200, 220, etc. diffraction rings, (c) TEM of CNF before PLA with the inset showing FFT analysis of amorphous CNF, (d) TEM of CNF after PLA showing the nucleation of nanodiamonds at the fiber walls where the undercooling is large with the inset showing FFT analysis showing 111 diffraction spots and the lower right inset showing inverse FFT analysis, (e) TEM image of the nanodiamonds region showing the formation of nanodiamonds (~10 nm) with the top left inset showing the FFT analysis of the nanodiamond showing twin (diffraction) spots, and (f) TEM image of <110> diamonds (inset showing FFT analysis) formed below the nanocrystalline diamond region.
Figure 11.5. (a) TEM image of formation of diamond from CNF after PLA with the inset showing FFT filtered atomically resolved image of single crystalline diamond (formed after PLA of CNF), and (b) EELS at 300 K of diamond and CNF showing the characteristic $\pi^*$ and $\sigma^*$ antibonding electronic states and $\Pi_{nd}$ band gap of diamond.
Figure 11.6. Raman spectroscopy of (a) CNF before PLA, and (b) CNF after PLA in the 1000-2800 cm\(^{-1}\) range, (c) CNF before PLA, and (d) CNF after PLA showing D and G vibrational modes (in the range 1200-1800 cm\(^{-1}\)) with the red window (having same width) showing the asymmetricity in the D vibrational mode, and (e) showing nanodiamond peak centered at 1321 cm\(^{-1}\) in the CNF after PLA.
Figure 11.7. Raman mappings of (a) Before PLA, (b) After 1 laser shot and the corresponding diamond map (spatial distribution) shown in (c), and (d) After 20 laser shots and the corresponding diamond map shown in (e). The diamond map is acquired from the 1310-1332 cm⁻¹ region.
Figure 11.8. (a) XPS survey scan of the CNF before PLA, (b) High-resolution XPS of the C 1s region for CNF before PLA, after 1 laser shot PLA, and after 20 laser shots, (c) XRD of the CNF before PLA, after 1 laser shot, and 20 laser shots, and (d) Intensity of diamond/intensity of G, intensity of D/intensity of G, and sp$^3$% (from XPS) vs various conditions (0, 1, 5, 10, and 20 laser shots).
11.7. References


12. Tunable Charge States of Nitrogen-Vacancy Centers in Diamond for Ultrafast Quantum Devices

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12.1. Abstract

A prerequisite condition for next-generation quantum sensing, communication, and computing is the precise modulation of the charge states of nitrogen-vacancy (NV) centers in diamond. We have achieved tuning of these centers in highly concentrated NV-diamonds using photons, phonons, and electrons. These NV-diamonds are synthesized employing a unique nanosecond laser processing technique which results in ultrafast melting and subsequent quenching of nitrogen-doped carbon films. Substitutional nitrogen atoms and vacancies are incorporated into diamond during rapid liquid-phase growth, where dopant concentrations can exceed thermodynamic solubility limits through solute trapping. This ultrafast synthesis technique generates fewer surface traps thereby forming ~75% NV⁻ centers at room-temperature, which are optically and magnetically distinct as compared to NV⁰ centers. We dramatically increase the NV⁻ concentration
in NV-diamonds by ~53% with decreasing temperature from 300 to 80 K. With negative electrical biasing, the Fermi level in NV-diamond rises and crosses the NV$^0$- level, thereby promoting an exponential conversion of NV$^0$ to NV$^-$ centers. We have also photonically enhanced the photoluminescence signal from NV$^-$ centers, thereby ascertaining the conversion of NV$^0$ into NV$^-$ via absorption of electrons (excited by 532 nm photons) from the valence band in NV-diamond. These NV-centers in diamonds also reveal large excitation lifetime, which ultimately leads to ~65% quantum efficiency at room-temperature. With these results, we believe that the precise tuning of charge states in these uniquely prepared highly concentrated NV-diamonds will lead to superior quantum devices.

12.2. Introduction

Defects such as nitrogen-vacancy (NV) and Si-vacancy (Si-V) color centers in nanostructured diamond and related materials are critical for next-generation solid state devices.\(^1\)\(^-\)\(^3\) The detection and manipulation of NV centers in diamond have gained a tremendous interest as they lead to innovative applications in various domains of high-speed quantum electronic devices.\(^4\)\(^-\)\(^6\) The negatively charged NV$^-$ centers are a potential candidate in state-of-the-art electronic devices owing to their excellent photostability, photon modulated spin transitions, and long coherence time.\(^7\)\(^,\)\(^8\) To enhance the sensitivity of NV-based electronic devices, it is highly desirable to have a high concentration of NV$^-$ centers close to the diamond surface. But in most of the cases, the neutral charge state of NV-centers (NV$^0$) is found closer to the diamond surface,\(^9\) which does not have required spin and optical properties. The fluorescence intensity of NV-centers is relatively low compared with those of organic dyes, quantum dots, and fluorescent proteins.\(^10\) As a result, the absorption cross section of NV$^-$ is about two orders of magnitude smaller than that of organic dyes.\(^11\) These challenges can be addressed by increasing the density of NV$^-$ centers in diamond by
utilizing highly non-equilibrium synthesis technique. The current methods for forming NV-centers in diamond are (a) chemical vapor deposition (CVD),\textsuperscript{12} (b) N\textsuperscript{+} ion implantation,\textsuperscript{13} (c) detonation,\textsuperscript{14} and (d) high pressure high temperature (HPHT)\textsuperscript{15} techniques. The CVD process produces large-grain polycrystalline films with nitrogen concentration limited by thermodynamic solubility limit\textsuperscript{16} and large graphitic content.\textsuperscript{17} Using N-ion implantation technique, Frenkel defects and sp\textsuperscript{2} bonded carbon are formed, which are difficult to anneal. Therefore, post-processing thermal annealing (>1000 °C for 1 hour in a H\textsubscript{2}/Ar atmosphere) is performed to form high-quality NV-centers.\textsuperscript{18} The typical density of N in HPHT diamonds is ~100 ppm. These NV-diamonds have a low conversion efficiency (10\%) of vacancies created by radiation damage to NV\textsuperscript{\textminus}.\textsuperscript{15} The detonated nanodiamonds are contaminated with impurities (Ti, Cr, Fe, Ni, etc.)\textsuperscript{17} which reduces the optical efficiency of NV-centers. Therefore, controlled introduction of N centers exceeding thermodynamic solubility limits is highly desirable for next-generation NV-center based diamond solid-state devices. This process leads to the formation of NV-centers free from impurities and other defects. The charge state manipulation in diamond \textit{p-i-n} diodes\textsuperscript{19,20} and characterization of NV\textsuperscript{\textplus} centers for its application in quantum memory devices\textsuperscript{21} are a significant advancement in NV-based electronic sensing devices. Pulsed laser annealing has been widely used to incorporate dopants in semiconductors (Si, Ge, \textit{etc.}) beyond thermodynamic solubility limits.\textsuperscript{22-25} In this technique, laser-assisted melting of Si to a highly superundercooled state occurs, which is followed by an ultrafast quenching process. This leads to trapping of solute atoms beyond their thermodynamic solubility limits (400 times) by solute trapping.\textsuperscript{26} In the present research, we have uniquely synthesized NV-centers in diamond utilizing a highly non-equilibrium technique. Recently, we have reported conversion of carbon into single-crystal diamond, h-BN into c-BN, synthesis of NV-diamonds,
and formation of B-doped Q-carbon (a high-temperature superconductor) using pulsed laser annealing technique, which is employed in the present study for synthesizing NV-diamonds.\textsuperscript{27-31}

This research represents a fundamental breakthrough in synthesis and manipulation of NV-centers required for quantum devices. These NV-centers are formed by using a highly non-equilibrium pulsed laser annealing technique. Owing to the phenomena of solute trapping during quenching from melt, the concentration of NV-centers (in diamond) can exceed the thermodynamic solubility limits of N in diamond. The diamond growth (in pulsed laser annealing process) occurs from a liquid phase with a solidification velocity of \( \sim 5 \text{ m sec}^{-1} \). Therefore, nano, micro, and large-area NV-diamonds having high NV-concentration and long photoluminescence lifetime can be synthesized. These NV-nanodiamonds can also be arranged periodically in a self-organized fashion, which is a primary requisite for quantum devices. This leads to deterministic placement of NV centers which can be controlled precisely (NV\(^0\) to NV\(^-\) conversion) using electrons, phonons, and photons. The synthesis and charge state manipulation of NV-centers in diamond synthesized by pulsed laser annealing will eventually lead to better design and understanding of quantum nanotechnologies in biological, chemical, and physical sciences.

\textbf{12.3. Experimental}

Carbon thin films (thickness ranging from 50 to 500 nm) are deposited on c-sapphire using pulsed laser deposition technique in laser MBE chamber. Excimer ArF pulsed laser having laser wavelength of 193 nm and pulse width 20 ns is used for thin film deposition. The base pressure of the chamber is maintained at UHV conditions (1.0×10\(^{-9}\) Torr) using a turbomolecular pump in conjunction with a cryogenic pump. These films are doped with nitrogen by bombarding simultaneously with RF (radiofrequency) plasma of \( \text{N}_2^+ \) (0.5-1.0 keV) during the carbon thin film
deposition. The nitrogen concentration is adjusted by controlling the nitrogen ion flux (by changing the accelerating voltage). Subsequently, these N-doped amorphous carbon films are pulsed laser annealed at room temperature and atmospheric pressure with high-power nanosecond laser pulses of ArF having energy density ranging from 0.6-1.0 Jcm\(^{-2}\). The pulsed laser annealing technique (PLA) is completed within 200 ns. In this process, the N-doped amorphous carbon film is melted in the super undercooled state and quenched rapidly to form NV-diamond. By controlling the degree of undercooling, nano, micro and large-area NV-diamonds can be grown. Since PLA technique is an ultrafast process, dislocations (time to nucleate a dislocation=1 \(\mu\)s) or surface defects (graphitic entities) are not formed on the synthesized NV-diamond. The NV-diamonds are characterized by employing photoluminescence spectroscopy (PL), cathodoluminescence spectroscopy (CL), Raman spectroscopy (532 nm excitation laser), field-emission scanning electron microscopy (FESEM), scanning transmission electron microscopy (STEM), electron energy-loss spectroscopy (EELS), electron backscatter diffraction (EBSD), temperature-dependent Hall effect in physical property measurement system (PPMS), time-resolved PL, and electric field-dependent PL. The value of the laser power used during the temperature and electric field-dependent PL measurements is 0.2 mW. This magnitude of laser power was used since at this laser power the laser power dependence concentration of the NV-centers (at temperature range: 300-80 K) is the least. High-resolution SEM with sub-nanometer resolution was carried out using FEI Verios 460L SEM to characterize the NV-diamonds. EBSD HKLNordlys detector (lateral resolution<10 nm) was used to map out the diamond Kikuchi diffraction pattern. Detailed atomic structure and bonding characterization of NV-diamonds are performed using HAADF and EELS techniques in aberration-corrected FEI Titan STEM operated at 200 keV. Collection semiangles 65 and 28 mrad were used for imaging and EELS, respectively. CL/STEM was
conducted in custom-built VG 601HB STEM operated at 60 keV. Thin (<80 nm) cross-sectional specimens for STEM characterization were prepared using Focus Ion Beam (FIB/SEM), FEI Quanta 3D instrument. To clean up the FIB beam induced damage, a low-energy ion beam (5 kV, 10 pA) was also used in FIB/SEM after sample preparation. A Horiba XploRA PLUS confocal Raman microscope having a 0.5 μm spatial resolution and 532 nm laser excitation source is employed to map the Raman active vibrational modes in NV-diamond.

12.4. Results and discussion

Figure 12.1(a) shows the PL spectrum of NV-diamond collected using 532 nm excitation laser at 300 K. The photoluminescence emitted from the NV diamond is collected by the same (as the incident beam) objective (100 X, NA=1.25) after spectrally filtering the residual pump light. The PL spectrum of NV diamond at 300 K shows diamond peak (first-order Raman peak), zero phonon line (ZPL) of NV$^0$, ZPL of NV$^-$ at 570, 575, and 637 nm, respectively. The PL spectrum can be deconvoluted into two spectra belonging to pure NV$^0$ and NV$^-$ centers in diamond. By integrating the (pure NV) curves, the NV$^-%$ (at 300 K) is calculated to be ~75%, which is considerably higher than the previously reported values. The fitted NV curves (for NV$^-$ and NV$^0$) are also shown in Figure 12.1(a). It has been shown earlier that with a decrease in the size of the nanodiamonds there is a decrease in the concentration of NV$^-$ centers. Upon electron irradiation and subsequent annealing, there occurs trapping of vacancy by a substitutitional nitrogen atom thereby creating the NV$^0$ center. To facilitate the formation of NV$^-$ centers, electron donating moieties (substitutional N atoms) are required. Again, due to the presence of surface traps (defect states) the substitutional N atoms can be trapped thereby reducing the density of NV$^-$ centers in nanodiamonds. Therefore, the value of 75% NV$^-$ in our NV diamonds indicates that there exists a higher number of nitrogen atoms than the surface density of electron traps. This is
due to the non-equilibrium technique used in the present case, where the N concentration can exceed thermodynamic solubility limit. The increased NV\(^{-}\) concentration in our samples can be due to: (a) solute trapping during rapid quenching, (b) reduced formation of NV complexes (other than NV\(^{0}\) and NV\(^{-}\)) from substitutional nitrogen (due to ultrafast processing technique) which causes no change in the position of the Fermi energy level, (c) less surface traps (induced defects), and (d) more effective radiative coupling of the NV\(^{-}\) centers as compared to the NV\(^{0}\) centers. The increased concentration of NV centers is consistent with the improvement in the PL intensity and increased lifetime (of the NV centers). Cathodoluminescence (CL) studies in scanning transmission electron microscope (STEM) are performed in NV-diamonds where photoemission from NV\(^{0}\) and NV\(^{-}\) centers is spatially and spectrally resolved. In Figures 12.1(c) and 12.1(d), the CL spectral intensity maps from NV\(^{0}\) and NV\(^{-}\) centers (spectrum between 500-750 nm) are shown from the NV-diamonds region depicted in the annular dark field (ADF) image in figure 12.1(b). The CL intensity is confirmed to result from NV-centers as there are no noticeable signals observed in the spectral range of 660-750 nm (region having no NV-centers). The CL intensity profile (figure 12.1(e)) indicates the presence of NV-centers throughout the cross-section of a NV-diamond with the highest concentration at the core. Previous reports indicate very few NV centers near the surface of a diamond, as most of them are confined near the core.\(^{36,37}\) Figure 12.1(f) shows an atomic resolution ADF image of one of the NV-diamonds from Figure 12.1(b). The single-crystalline structure of diamond (as evident from Figure 12.1(f)) shows the absence of amorphous regions (electron traps) and twins (a commonly observed defect in detonated nanodiamonds (DNDs)).\(^{2}\) These factors result in an increase in the luminescence intensity from the NV-centers. Electron energy-loss spectroscopy (EELS) was also performed on NV-diamond and pure diamond to elucidate the electronic structure modification (due to the N incorporation) at atomic-scale.
Figure 12.1(g) shows the EEL spectra containing C-K edge obtained from NV- and pure-diamond. The core-loss EEL spectra clearly indicate the presence of distinct $\sigma^*$ electronic state (~292 eV) and a minimal $\pi^*$ electronic state (~285 eV). The minimal intensity of the $\pi^*$ core-loss peak indicates the absence of sp$^2$ graphitic regions in nanodiamonds which act as electron traps thereby reducing the formation of NV$^-$ center. Although the edges appear quite identical, the presence of pre-peaks (between 278-286 eV) in NV-diamond are identified (Figure 12.1(h)) by magnifying the above-mentioned energy-range. The presence of these pre-peaks is predicted in NV-diamond by theoretical first principle density functional theory calculations.\textsuperscript{38} As it is evident from the Figure 12.1(h), the two pre-peaks are centered at 281.8 and 284.2 eV. The first peak belongs to NV-centers in diamond.\textsuperscript{38} A higher intensity of the NV-peak is found in the NV-diamond as compared to DNDs, thereby indicating a high concentration of NV-centers in the NV-diamond samples. The high concentration of NV-centers coupled with charge manipulation and long lifetime (of these centers) will ultimately lead to better NV-based multifunctional electronic devices.

Figure 12.2 depicts PL spectra of the NV-diamond at various temperatures (80, 180, and 300 K). Manipulation of the NV-center electron spin states via phonons can give rise to future phonon-mediated quantum networks. The localization of NV centers to a vacancy defect gives rise to a symmetric linear combination of dangling bond orbitals. This leads to the creation of four electronic states: $|a_1\rangle$, $|a_2\rangle$, $|e_x\rangle$, and $|e_y\rangle$. Phonons (and therefore strains) cause displacement of the dangling orbitals thereby modifying the energy levels (of the NV-centers). As it is evident from Figure 12.2(a) that there is a decrease in full width at half-maximum (FWHM) of the ZPL associated with the NV$^0$ and NV$^-$ transitions with a decrease in temperature from 300 to 80 K. The inset in Figure 12.2(a) depicts an exponential increase of NV$^-$/NV$^0$ ratio with a decrease in temperature. Figure 12.2(b) shows a blue shift of the ZPL peaks with a decrease in temperature.
There is a remarkable increase (~53%) in the NV concentration (left inset of figure 12.2(b)) with a decrease in temperature (from 300 to 80 K). The increase in NV\(^-\) concentration was estimated considering the intensity of the PSBs (phonon side bands), as the shape of NV-spectrum changes with temperature. At room temperature, the NV\(^-\) centers do not have adequate fluorescence to be visible. The presence of significant amount of substitutional nitrogen (electron donors) can also cause photoionization during the optical excitation of NV\(^-\) at 300 K. This produces fluctuating electric fields thereby causing an increase in the FWHM of the NV\(^-\) ZPL (at 300 K). Reducing the temperature (to 80 K) leads to a steady state population of NV centers in all spin-projections thereby causing a tremendous increase in the PL signal of the NV\(^-\) ZPL. The inset in Figure 12.2(b) depicts the deconvolution of the ZPL peak of NV\(^-\) center (in diamond) at 80 K. Along with the characteristics ZPL at 637 nm there exists a satellite peak at 639 nm. We observed a blue shift and a decrease in intensity of this satellite peak with a decrease in temperature. The temperature-dependent blue shifts (in NV\(^0\) and NV\(^-\) ZPLs) indicate that these non-linear shifts have a similar origin. Studies reveal that these shifts can also be due to electron-phonon interactions and local expansion of the NV-diamond lattice.\(^{39,40}\)

Figure 12.3 depicts manipulation of NV-centers in diamond using an external electric field. Figure 12.3(a) depicts a schematic of the electric field measurement and scanning electron microscopy image showing the patterned electrode deposited onto NV-diamonds and N-doped DLC for electrical measurements. In the device, the electrons are injected from the \(n\)-type N-doped DLC layer to NV-diamond in the forward-bias condition. This facilitates the capture of an electron by NV\(^0\) centers to form NV\(^-\) centers and cause an increase in the PL intensity. In the reverse-bias conditions, there occur detrapping of electrons from the NV\(^-\) centers thereby forming NV\(^0\) centers. As it is evident from Figure 12.3(b) and (c), there is a tremendous increase in NV\(^-\) concentration.
with an increase in negative voltage (at -7 V). Figure 12.3(b) depicts the PL spectra (both NV⁻ and NV⁰) of NV diamond at various electric fields at 300 K. Figure 12.3(c) shows the remarkable increase in only the NV⁻ concentration at -7 V (from 0 V) in the forward-bias condition. On the other hand, with positive biasing, there occurs an increase in the NV⁰ centers at the expense of NV⁻ centers. The broad peak at ~610 nm is due to the formation of NV⁰ charged states which predominantly occur at positive bias voltage conditions (5 V and 7 V). The inset in Figure 12.3(b) indicates the shifting of Fermi level using an external electric field which ultimately controls the electronic transitions from NV⁺ (non-fluorescent) → NV⁰ → NV⁻ with increasing negative bias. NV⁰⁻ charge transition level is situated 2.9 eV above the VBM, whereas NV⁺⁰ is located below NV⁰⁻. The non-monotonic trend in the NV-centers during the biasing experiments is due to the formation of non-fluorescent NV⁺ centers (in +7V). Therefore, there is a decrease in the PL signal with increasing positive voltage. The formation of these non-fluorescent centers was also reported in earlier studies. Starting from a mixed population of positive, neutral, and negatively charged NV centers, there is an increase in the NV⁻ centers at the expense of the other two centers with increasing negative bias voltage. This is evident from the inset in Figure 12.3(c) which indicates an exponential rise in the NV⁻/NV⁰ ratio with increasing negative bias. The value of NV⁻/NV⁰ is normalized to 1 at 0V. This was done to emphasize the change in NV⁻/NV⁰ ratio with changing electric field (Figure 3c) and laser power (Figure 12.4b). The exponential fit follows the equation (12.1):

\[
\frac{NV^-}{NV^0} = 1.13 \times e^{-0.125V}
\]  

where, \(V\) is the applied voltage in volts. The low exponential growth rate of NV⁻ centers can be attributed to the conversion of these charged states to NV⁰ under laser illumination (optical readout). The increase (or decrease) in NV⁻ centers with an application of negative (or positive)
bias occurs due to trapping (or detrapping) of electrons. When the Fermi level (in NV-diamond) shifts above a charge transitional level, an electron is either trapped or detrapped.\textsuperscript{41,43} The electronic conversion of NV\textsuperscript{0} to NV\textsuperscript{-} follows the equation (12.2):

\[
NV^0 + ne^- \rightleftharpoons NV^-
\]  

(12.2)

Again, the change in free energy, $\Delta G$ (at 300 K) associated with the equation (12.2) can be calculated using the equation (12.3):

\[
\frac{[NV^-]}{[NV^0]} = n \times e^{-\Delta G/0.025}
\]  

(12.3)

where, $[NV^-]$, $[NV^0]$, and $n$ are concentration of NV\textsuperscript{-} and NV\textsuperscript{0} centers and number of electrons associated with the equation (12.2). The values of $n$ and $\Delta G$ are calculated as 1.13 (~1) and 3.125x10\textsuperscript{-3}\times Voltage eV, respectively. The application of an external field controls the Fermi level and causes band bending. The energy difference between the charge transitional level and Fermi level (for an NV-center) is dependent on its distance from the surface.\textsuperscript{43} Since the concentration of the NV-centers is quite high, there is band bending and most of the NV-centers exist as NV\textsuperscript{-} or NV\textsuperscript{0} electronic state. With the application of a negative bias, the Fermi level rises and crosses the NV\textsuperscript{0/-} level thereby promoting the conversion of NV\textsuperscript{0} to NV\textsuperscript{-} centers (inset of Figure 12.3(b)). The average energy difference between NV\textsuperscript{0/-} and $E_F$ in NV-diamond is larger than that in H- or OH-terminated diamond. Therefore, a larger external potential (-7 V) is required to perturb the NV electronic state in NV-diamond as compared to OH-terminated diamond (-0.75 V).\textsuperscript{43} The presence of surface states (defect electronic $sp^2$ states) also causes a change in near-surface band bending, thereby leading to a decrease in external potential and concentration of NV\textsuperscript{-}. The electric field modulation in NV-centers results in band-bending and strong PL modulation (~210% increase in NV\textsuperscript{-} with an application of -7 V). In the NV-diamond electronic device, the electrons are injected from the $n$-type N-doped DLC layer to NV-diamond in the forward-bias condition. This facilitates
the capture of an electron by NV\(^0\) center to form NV\(^-\) center and cause an increase in the PL intensity (near 700 nm). Therefore, there occurs an increase in the concentration of NV\(^-\) centers by applying -7V. In the reverse-bias conditions, detrapping of electrons occurs from the NV\(^-\) centers, thereby forming NV\(^0\) centers (at the expense of NV\(^-\) centers). The broad peak at ~610 nm is due to the formation of NV\(^0\) charged states, which predominantly occurs in reverse bias conditions (5 V and 7 V). Therefore, there is an increase in the concentration of NV\(^0\) centers by applying +7V. All the NV-concentrations are calculated by deconvoluting the NV-PL spectra into pure NV\(^-\) and NV\(^0\) centers, where ZPL and phonon sidebands (of NV\(^-\) and NV\(^0\)) are considered (as shown in Figure 12.1(a)). This strong electric field dependent-PL demonstrates the efficacy of the NV-centers in nanometer-scale optical sensing devices.

Figure 12.4 depicts the modulation of NV-charge centers in diamond using laser (photon wavelength=532 nm) power under isothermal conditions. As it is clearly evident from Figure 12.4, that there is an increase in the concentration of NV\(^-\) centers (in comparison to NV\(^0\) centers) with an increase in laser power. The increase in photoluminescence signal from NV\(^-\) centers ascertains that NV\(^0\) converts to NV\(^-\) via absorption of electrons (excited by 532 nm photons) from the valence band in diamond. This conversion is a two-step procedure. Under laser illumination (energy=2.33 eV), NV\(^0\) and NV\(^-\) are excited from its ground state. The incident photon also excites an electron from the valence band which is captured by NV\(^0\) to form NV\(^-\).\(^{46,47}\) The substitutional nitrogen non-luminescent center (P1), situated closer to the conduction band, can also act as an electron donor to transform NV\(^0\) to NV\(^-\).\(^{48}\) But the increased luminescence signal from our samples suggests that the P1 centers play a minor role in the charge conversion in NV-centers (under laser illumination). Also, since the P1 centers lie ~2.2 eV below the conduction band and therefore 2.33 eV energy
photon will not trigger this transformation. The time-dependent population of the NV\(^{-}\) charged states \(\frac{dP^{-}}{dt}\) can be calculated\(^{32}\) using the equation (12.4):

\[
\frac{dP^{-}}{dt} - \frac{dP^{0}}{dt} = -2r^{0/-} \times P^{-} + 2r^{0/-} \times P^{0}
\] (12.4)

where, \(r^{0/-}\) denotes the rate of conversion from NV\(^{-}\) to NV\(^{0}\) charged state. Therefore, higher values of \(r^{0/-}\) (as compared to \(r^{-/0}\)) leads to \(\frac{dP^{-}}{dt} > \frac{dP^{0}}{dt}\), thereby leading to the formation of NV\(^{-}\) centers. Under the conditions of low to moderate laser power (<15 mW), there is an increase in the concentration of NV centers with increase in laser power due to increase in \(r^{0/-}\). Figure 12.4(b) shows a non-linear dependence of NV\(^{0}\)/NV\(^{-}\) ratio (at lower temperatures: 80 and 100 K) with increasing laser power. This can be explained by using the equation (12.5), where the ratio of concentration of NV-centers can be given by equation (12.5):

\[
\frac{[NV^{0}]}{[NV^{-}]} = \frac{1}{n} \left( 1 + \frac{\Delta G}{kT} + \frac{1}{2} \left( \frac{\Delta G}{kT} \right)^{2} + \frac{1}{6} \left( \frac{\Delta G}{kT} \right)^{3} + \frac{1}{24} \left( \frac{\Delta G}{kT} \right)^{4} + \cdots \right) \) (12.5)

From equation (12.5) it is evident that at higher temperatures the contribution from the higher order terms reduces and NV\(^{0}\)/NV\(^{-}\) ratio assumes a linear dependence with increasing laser power. At lower temperatures (80 and 100 K) there is a significant contribution from the higher order terms. This causes a non-linear dependence of NV\(^{0}\)/NV\(^{-}\) ratio with increasing laser power. The linear and non-linear fits are obtained in Figure 12.4(b) for 125 K and 100 K data, respectively. The values of \(n\) and \(\Delta G\) are calculated as 1.03 (~1) and 7.112\(\times\)10\(^{-4}\)\(\times\)laser power eV, respectively. The NV\(^{-}\) and NV\(^{0}\) defects contain six and five electrons, respectively in \(a_{1}\) and \(e\) orbitals.\(^{49}\) The conversion of NV\(^{0}\) to NV\(^{-}\) (recombination) is schematically represented in the inset of Figure 12.4(a). An electron is excited from \(a_{1}\) to \(e\) orbital (step 1) followed by the excitation of another electron from deep-lying \(a_{1}\) orbital to the \(a_{1}\) in the band gap (step 2). The vacant site in the deep-lying \(a_{1}\) is replenished by valence band electrons (step 3), thereby rendering the electronic structure
as NV$^-$ (having six electrons).\textsuperscript{47} In the case of \textit{ionization} process, NV$^-$ is converted to NV$^0$ by excitation of one electron from the excited state of NV$^-$ centers to the conduction band. To increase the population of the NV$^-$ centers in diamond, \textit{recombination} rates should be greater than \textit{ionization} rates. To increase the population of the NV$^-$ centers in diamond, \textit{recombination} rates should be greater than \textit{ionization} rates. Since the laser powers used in the present experiments are less than 4mW, sample heating is negligible. The photo-induced conversion of NV$^0$ to NV$^-$ is therefore possible with increasing laser power for low to moderate values.

Figure 12.5(a) depicts the time-resolved PL (tr-PL) spectroscopy of NV-diamond using 415 nm and 200 fs laser pulse excitation. These measurements are used to determine the characteristic relaxation dynamics in NV-diamond. The decay times measured in NV-diamond are strongly dependent on the crystal size and local density of electronic states.\textsuperscript{50,51} The tr-PL spectra are collected from the zero phonon lines sidebands as a small fraction of the PL emission is concentrated at the ZPL (due to strong phonon coupling). As it is clearly evident from the spectra that the lifetimes of NV$^-$ centers are more than the NV$^0$ centers in the synthesized NV-diamond. The decay times of the NV centers is determined using the multiexponential decay function equation (12.6):

\[
I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}
\]

where, $I(t)$ is the time-dependent PL intensity, $A_1$, $A_2$, and $A_3$ are pre-exponential factors, and $\tau_1$, $\tau_2$, and $\tau_3$ are the associated lifetimes. The tr-PL spectra indicate a multiexponential decay having a shorter decay component along with primary larger decay times. The additional decay times are due to the presence of bound excitons in the NV center and non-radiative transitions due to the occurrence of intersystem crossing (between the metastable singlet electronic states in NV-diamond: $^3$E to $^3$A and $^1$A to $^3$A).\textsuperscript{52} Figure 12.5(b) and (c) indicate that the lifetimes are dissimilar
throughout the spectrum indicating the presence of distinct electronic states associated with the NV centers. Region I has a shorter lifetime than the other two regions (II and III). There are small lifetime values in region I and II compared to region III, which shows large lifetime values (176 ns in NV$^0$ and 192 ns in NV$^-$). The longest NV$^-$ lifetime in region III is related to the presence of less defects (twins, $sp^2$-entities) in the NV-diamond due to the ultra-fast synthesis technique. The time required to form a dislocation in a crystal is $\sim 1\mu$s. The time required for the completion of PLA process is less than 250 ns. Therefore, owing to the ultrafast processing technique adopted in the present case, single-crystal NV-diamonds are formed. Region II corresponds to the optical transition from $^3E$ to $^3A$ electronic state. The long-lived component has higher PL lifetime than that observed in NV-nanodiamond (25 ns) and NV-bulk diamond (12 ns). This tremendous increase in lifetime is caused by the presence of radiative emission centers in NV-diamond, which ultimately leads to the formation of bound and free excitons. This enhancement in lifetime can also be interpreted as a simple quantum electrodynamics effect. The lifetime of NV$^-$ centers was reported as $13\pm0.5$ ns as compared to a substantial increase up to 192 ns in the present case. This is attributed to a better quality of single crystal NV-diamonds created in the present case by melting and subsequent quenching process. The high concentration of NV$^-$ centers (~75%) in our samples (at 300 K) can lead to an increased lifetime in NV$^-$ color centers as compared to NV$^0$ centers. The mean quantum efficiency ($\eta$) of the NV color centers can also be calculated, which measures the efficacy of NV-diamond for photonic applications. It is well known that the luminescent centers are coupled to nearby defects or “quenchers” which results in an exponential decay of the PL intensity with time. For dipole-dipole interaction coupling, the exponential decay (for the longest lifetime region) of intensity can be well fitted to the following equation (12.7):

$$I(t) = a. N_0. e^{(-a.t)} e^{(-k.(a.t)^{0.5})}$$ (12.7)
where, $a$, $N_0$, and $k$ are intrinsic radiative decay rate, number density of the “quencher” sites, and a dimensional parameter, respectively. The dimensional parameter depends on the concentration of the “quenchers” and the intensity of the resonant coupling. The mean quantum efficiency ($\eta$) is related to the dimensional parameter and is calculated using equation (12.8):

$$\eta(k) = 0.5 \times \left[ 2 + \sqrt{\pi} \cdot k \cdot e^{k^2/4} \left\{ \text{erf} \left( \frac{k}{2} \right) - 1 \right\} \right]$$  \hspace{1cm} (12.8)

Figure 12.5(d) represents the exponential decay fit in the longest lifetime region (III) using the equation (12.7). The goodness of fit for the decay equation (Figure 12.5(d)) is 0.82. The value of $k$ is calculated as 0.487 which corresponds to ~66% quantum efficiency of the NV-centers in diamond. The values of quantum efficiency are considerably larger than that reported (58%) in NV-nanodiamonds synthesized using detonation technique. This increase in quantum efficiency is directly related to the enhanced lifetime in our NV-diamonds. It is well known that substitutional nitrogen defects (and $N_2$ complexes) act as quenchers (non-radiative emitters) for NV$^-$ color centers. The concentration of substitutional nitrogen ($[N_s]$) in P1 centers is also related to the dimensional parameter and is calculated as ~40 ppm as compared to 100 ppm found in type Ib samples (showing a quantum efficiency of ~50%). Therefore, owing to the ultrafast melting and subsequent quenching technique, the synthesized NV-diamonds have low concentration of substitutional nitrogen defects. The results also indicate a dipole-dipole coupling between the color centers and the defects. Region II has moderate lifetimes (13 ns in NV$^0$ and 12 ns in NV$^-$). The shortest decay times (0.50 ns in NV$^0$ and 1.25 ns in NV$^-$) in region I indicate the presence of graphitic ($sp^2$) clusters in diamond nanostructure. These clusters act as additional relaxation channels thereby reducing the decay times in NV-diamond. The ultrafast emission can also be due to the large surface to volume ratio (specific volume) and presence of surface states in the nanodiamonds. It is a well-established fact that the energy levels due to the surface states exist.
inside the band gap (between the conduction and valence band) of diamond. These energy states assist in non-radiative emissions thereby giving rise to short lifetimes.\textsuperscript{60} The lifetime of non-radiative emission is related to number of electrons ($\rho$) occupying the surface states by the relation: 
$$\frac{1}{\tau} \approx \frac{d\rho}{dt}.$$ Therefore, the number of electrons present in the surface states close to NV$^0$ is 2.5 times than that present near NV$. This also indicates that the radiative transitions related to NV$^-$ has larger lifetimes than in NV$^0$ and therefore the synthesized NV color centers in diamond have excellent properties for photonic applications.

The Raman spectra from NV-diamond samples are shown in Figure 12.6. As it is evident from figure 12.6(a), the Raman spectra contain a sharp diamond peak ~1332 cm$^{-1}$ (red region), graphitic (sp$^2$) peak ~ 1550 cm$^{-1}$ (green region), and sapphire peak ~ 500 cm$^{-1}$ (blue region). To analyze distribution of sp$^3$ and sp$^2$ bonded carbon associated with NV-diamond, Raman mapping is performed and is shown in Figure 12.6(b). The mapping is performed on two adjacent diamonds. The smaller diamond on the left shows less graphitic sp$^2$ entities as compared to the right one. The sp$^2$ graphitic related defects formed on the surface of DNDs have been shown to act as electron traps (electron depletion layer), thereby reducing the formation of NV$^-$ centers and leading to a decrease in the photoluminescence intensity.\textsuperscript{35} The intensity of the graphitic region (green region) is ~15 times lower than the intensity of sp$^3$-bonded carbon (red region). The core-loss EEL spectrum (Figure 12.1(g-h)) clearly indicates the presence of distinct $\sigma^*$ electronic state (~292 eV) and a minimal $\pi^*$ electronic state (~285 eV). The minimal intensity of the $\pi^*$ core-loss peak indicates the absence of sp$^2$ graphitic regions in nanodiamonds which act as electron traps thereby reducing the formation of NV$^-$ center. Our ultrafast processing technique (completed in <200 ns) assists in the formation of pristine nano, micro and large-area NV-diamonds having less graphitic related defects (electron traps) on its surface. This promotes better functionalities in the
synthesized NV-centers (large excitation lifetime, manipulation of charge centers using photon, phonon, and electron) thereby rendering them suitable for efficient quantum devices. Generally, repetitive corrosive cleaning with strong acid and prolong oxidation at high temperatures are required to remove the sp$^2$ layers formed on detonated diamonds.\textsuperscript{17,61} In the present case, no such treatments are required as the nano, micro, and large-area diamonds synthesized using our ultrafast laser processing technique (<\!\!\!\!\!\!\!\!\!\!\!\!250 ns) leads to the formation of pure sp$^3$-bonded carbon with less sp$^2$-bonded carbon at the surface. The substitutional nitrogen atoms can also act as electron donors, therefore, forming NV$^-$ centers from NV$^0$ according to equation (12.9):

$$NV^0 + N \rightleftharpoons NV^- + N^+ \quad (12.9)$$

The presence of surface traps (sp$^2$-bonded carbon) captures the electrons provided by the nitrogen substitutional sites and therefore reduces the formation of NV$^-$ charge states (equation 9). Again, the proportion of NV$^-$ centers ($P_{NV^-}$) can also be calculated using equation (12.10):

$$P_{NV^-} = 1 - \frac{1}{1+K\left(\frac{a}{a_t}\right)^{-1}} \quad (12.10)$$

where, $K$, $a$, and $a_t$ denote equilibrium rate constant for the equation (12.9), number of nitrogen atoms, and number of electron traps, respectively. When $a \gg a_t$, $P_{NV^-} \rightarrow 1$. Considering the value of $P_{NV^-}$ as 0.75 and $K$ as 1.4,\textsuperscript{33} the number of nitrogen atoms is calculated to be ~3 times than that of the number of electron traps. It should also be noted that the photoluminescence intensity of NV-defects and lifetime (of charged states) are enhanced with decreasing sp$^2$ content on diamond. A closer analysis of the Raman spectra indicates an increase in FWHM of the T$_{2g}$ peak in NV-diamond. The broadening of Raman peak shows a shortening of phonon lifetime.\textsuperscript{62} The phonon scattering occurs due to the incorporation of nitrogen in carbon substitutional sites in diamond.\textsuperscript{63} There is also a Raman downshift of ~5cm$^{-1}$. It should be mentioned that there is an upshift due to stresses, which is combined with downshift due to reduction in size. After pulsed laser annealing
of the as-deposited nitrogen-doped carbon layers, NV-diamond nanocrystals with an average size of 4-8nm are formed (Figure 12.7(a)). The inset high-resolution SEM in Figure 12.7(a) shows the formation of well-connected NV-diamond nanocrystals, where temperature-dependent Hall effect measurements are performed. Since pulsed laser annealing is an ultrafast synthesis technique, nano, micro, and large-area single-crystal diamonds can be formed by varying the laser parameters. Figure 12.7(b) shows the formation of micro-crystals (2-3 µm) of diamond by pulsed laser annealing technique. This indicates a liquid phase growth, where crystal growth velocities are >5 msec⁻¹. The inset in Figure 12.7(b) shows the characteristic Kikuchi diffraction pattern of diamond (using EBSD technique) from the red dot (in Figure 12.7(b)). The crystal orientation is also simulated from the Kikuchi diffraction pattern and is shown in the lower inset in Figure 12.7(b). Figure 12.7(c) depicts the inverse of temperature dependent carrier concentration in N-doped diamond. It is clearly evident from the plot that the carrier concentration increases with increasing temperature, a characteristic behavior of a doped semiconductor. The carrier density decreases at low temperatures due to incomplete ionization of the dopants (N in this case). The carrier concentration was found to vary from 4.8×10¹⁴ (at 200 K) to 3.0×10²¹ cm⁻³ (at 300 K). The high values of carrier concentration in NV-diamond are a result of dopant (solute) trapping during melting and subsequent rapid quenching of N-doped amorphous carbon (by pulsed laser annealing). The thermodynamic solubility limit of N in single crystal diamond is 2×10¹⁶ cm⁻³.¹⁶ In the present case, this thermodynamic solubility limit can be exceeded (up to 3×10²¹ cm⁻³) utilizing the phenomenon of solute trapping. Laser thermal anneal (LTA) is based upon solid-phase epitaxial growth which is applied to Si and Ge.²⁴ In the case of gas immersion laser doping (GILD), melting of crystalline Si and Ge is involved.⁶⁴ The thermodynamic solubility limit can be exceeded via liquid-phase (GILD) as well as solid-phase (LTA) annealing through solute trapping in Si and
However, in the case of carbon, melting of amorphous pure and doped carbon (pulsed laser annealing) leads to formation of pure and doped diamond \textit{via} solute trapping. A fit to \( N = C \cdot e^{-\Delta E/kT} \) indicates the value of \( \Delta E = 0.73 \text{eV} \). The activation energy of NV-diamonds is extremely large as compared to 0.09 \text{eV} (in \textit{sp}^2-rich N-doped nano- and microdiamonds).\textsuperscript{66} It should also be noted that the electronic states of NV-centers are distinctly different from the N-doped single crystal diamond, as in the latter case the donor activation energy is 1.7 \text{eV}.\textsuperscript{67} The electronic band diagram of NV-diamond is shown as an inset in Figure 12.7(c). The concentration value at 300 K indicates 1 NV in 4 nm diamond. This value is much higher than the thermodynamic solubility limit of N in diamond, thereby indicating that highly non-equilibrium techniques are vital to the synthesis of novel nanostructures.

\textbf{12.5. Conclusions}

This research represents a significant advancement in non-equilibrium synthesis and manipulation of NV-centers in diamond. The NV-diamonds are synthesized using a highly non-equilibrium technique where N-doped amorphous carbon is melted in a super undercooled state and quenched rapidly. Incorporation of nitrogen in excess of its thermodynamic solubility limit is achieved in the non-equilibrium process by solute trapping. This ultrafast technique (completed in <250 ns) assists in the formation of pristine nano, micro and large-area NV-diamonds having less graphitic related defects (electron traps) on its surface. In the present case, no post-processing treatments are required for the removal of the \textit{sp}^2 layer, which quenches PL signal, reduces PL lifetime, and thwarts charge state modulation in NV-diamond. Room-temperature PL spectra indicate as high as 75\% NV\textsuperscript{−} centers (and rest NV\textsuperscript{0}) in the NV-diamond samples. The CL spectrum also indicates a uniform concentration of NV-centers throughout the cross-section of NV-diamond. This demonstrates the efficacy of these centers in quantum processors where a high concentration of
NV-centers close to the surface is desirable. High-resolution EELS depicts the formation of 281.8 eV pre-peak near the C-K edge which conclusively shows the presence of NV-centers. The charge state in NV-centers can be controlled and tuned using phonons, photons, and electrons. There is an exponential increase in the NV\(^-\)/NV\(^0\) ratio with a decrease in temperature (300 to 80 K). With increasing laser power (of 532 nm laser), there is also an increase in PL signal from NV\(^-\) centers ascertaining that NV\(^0\) converts to NV\(^-\) via absorption of electrons (excited by 532 nm photons) from the valence band in diamond. There is a tremendous increase in NV\(^-\) concentration with an increase in forward bias voltage due to trapping of electrons by NV\(^0\)-centers. It is also observed that with positive biasing, NV\(^0\) centers are formed at the expense of NV\(^-\) centers. The trapping and detrapping of electrons are effected by the change in Fermi level above or below a charge transitional level. Quantum photonic devices require large lifetime of NV-centers. The time-resolved PL studies reveal three time-dependent PL regions (I, II, and III) in the NV-diamonds. The region III shows lifetime values of 176 ns in NV\(^0\) and 192 ns in NV\(^-\) which is considerably larger than that observed in NV-diamonds produced by other methods.\(^{54-57}\) This tremendous improvement in lifetime is due the presence of radiative emission centers in NV-diamond. This enhancement in lifetime leads to a remarkable improvement to \(~65\%\) in the mean quantum efficiency of the NV color centers, thereby showing the effectiveness of these centers in photonic applications. The temperature-dependent carrier concentration studies indicate a characteristic behavior of a heavily doped semiconductor (carrier concentration at 300 K = 3.0×10\(^{21}\) cm\(^{-3}\)), where the carrier concentration increases with increasing temperature with activation energy as 0.73 eV. Our results indicate that NV-diamonds synthesized utilizing highly non-equilibrium techniques are a key to high-efficiency multifunctional quantum devices. The formation of NV-diamonds with deterministic placement will lead to novel atomic sensors, biomarkers and quantum computers.
operating at room temperature. These NV structures can lead to quantum computing, sensing and safe data transmission, including the formation of time crystals under periodic non-equilibrium photonic, electronic and thermal excitations.
12.6. Figures:

**Figure 12.1.** (a) PL spectrum of NV diamond at 300 K show diamond peak (first-order Raman peak), zero phonon line (ZPL) of NV$^0$, ZPL of NV$^-$ at 570, 575, and 637 nm, respectively, (b) ADF image of NV-diamonds, (c) CL intensity map of the region shown in (b) for the spectral range 500-750 nm, (d) CL intensity map for the spectral range 660-750 nm, (e) CL intensity (NV-concentration) throughout the cross-section of a NV-diamond with the highest concentration near the core, (f) atomic-resolution single-crystal diamond, (g) Core-loss EELS of NV-diamond and pure diamond, and (h) Core-loss EELS near C-K edge showing the presence of NV peak at 281.8 eV.
Figure 12.2. **Modulation of NV-charge state by phonons:** (a) PL spectrum of NV diamond (at 300, 180, and 80 K) and sapphire (at 300 K) with the inset showing an exponential rise in NV⁻/NV⁰ ratio with decrease in temperature, and (b) A blue-shift and remarkable increase in the intensity and of the ZPL NV⁻ peak with decrease in temperature (300 to 80 K) with the inset showing the satellite peak at 639 nm.
Figure 12.3. Modulation of NV-charge state by electrons: (a) Experimental setup, (b) PL spectrum of NV diamond at various electric field (-7, -5, -2, 0, 5, and 7 V) at 300 K with the inset showing band-bending and shifting of Fermi level with the application of external electric field, and (c) Remarkable increase in the NV- concentration at -7 V with the inset showing an exponential rise in NV-/NV° ratio with increase in negative bias voltage.
**Figure 12.4.** Modulation of NV-charge state by photons: (a) PL spectrum of NV diamond at various 532 nm laser power at 80 K with the inset showing NV\(^0\) to NV\(^-\) conversion, and (b) A decrease in NV\(^0\)/NV\(^-\) ratio with an increase in laser power.
Figure 12.5. (a) Time-resolved PL spectrum of NV$^-$ and NV$^0$ centers using 415 nm, 200 fs laser pulse excitation, (b) Time-resolved PL spectra of NV$^0$ showing regions (I), (II), and (III), (c) Time-resolved PL spectra of NV$^-$ showing regions (I), (II), and (III), (d) Decay fit in the longest lifetime region (III) in NV$^-$ centers to calculate quantum efficiency.
Figure 12.6. (a) Raman spectrum of NV-diamonds showing prominent diamond peak ~1332 cm$^{-1}$, and (b) Raman mapping of (i) Diamond peak, (ii) sp$^2$ graphitic peak on diamond, (iii) Sapphire substrate peak, and (iv) three-dimensional view of diamond, sp$^2$-graphite, and sapphire showing predominant contribution of diamond peak.
Figure 12.7. (a) High-resolution SEM showing the formation of nano- and micro- NV-diamond with the inset showing well-connected NV-diamonds, (b) Large micro-crystals of NV-diamond with the inset showing Kikuchi diffraction and crystal orientation from a NV-diamond (marked by red spot), and (c) Inverse of temperature-dependent Hall carrier concentration in NV-diamond showing the value of activation energy as 0.73 eV with the inset showing the band diagram of NV-diamond showing energy levels of NV-centers.
12.7. References


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13. Conclusions

We have synthesized a novel phase of carbon, Q-carbon, by using a highly non-equilibrium processing technique. This new phase is formed by nanosecond pulsed laser melting and subsequent quenching of a highly undercooled molten state of C. The Q-carbon consists of 75-85% $sp^2$-bonded C and the rest is $sp^3$-bonded C. The undoped Q-carbon phase exhibits novel properties including room-temperature ferromagnetism, extraordinary Hall effect, and electrochromic effect. The field-dependent magnetization plots of Q-carbon indicate finite values of coercivity and saturation magnetization in the temperature range 10-300 K. The temperature-dependent saturation magnetization plots in Q-carbon follow the modified Bloch’s law with the Bloch exponent equal to 2.04, pre-factor of $3.02 \times 10^{-6}$ K$^{-2.04}$, and a Curie temperature of 570 K. The negative values of the ordinary Hall coefficient in the temperature range 10 to 300 K indicate an n-type conductivity in Q-carbon. The extraordinary Hall effect measurements show an exponent value of 1.95 which also suggests a “side-jump mechanism” in Q-carbon. This non-classical electronic scattering mechanism exists in Q-carbon due to the presence of non-conducting centers which distort the wave function and create a local current density thereby indicating potential applications of Q-carbon in spintronics. The origin of intrinsic ferromagnetism and interesting extraordinary Hall effect in Q-carbon are due to the electronic mixing of $sp^2$ and $sp^3$ orbitals during its formation. Some of the unpaired electrons remain in the Q-carbon structure which renders it to be ferromagnetic, which also cause spin-orbit interactions. The EELS analysis indicates a high density of states near the Fermi level in Q-carbon (as compared to DLC and diamond) which renders interesting magnetic, electrical, and optical properties in Q-carbon. We have also shown the electrochromic characteristics of undoped Q-carbon. The excess amount of unpaired electrons near the Fermi energy level in Q-carbon causes a 48% increase in the optical absorption at 265 nm.
with an applied electric field of 10 V. Therefore, in conjunction with standard electrochromic devices (which work in the visible spectral region), Q-carbon electrochromic devices will be an ideal candidate for smart windows having energy-saving applications. By using the Tauc analysis we have also calculated the direct and indirect band gap of Q-carbon to be 3.82 and 2.93 eV, respectively. The KPFM analysis also indicates a negative electron potential (affinity) of Q-carbon as compared to the rest of the film. There occurs an increase in the KPFM contrast with the increase in the tip voltage from 0 to 10 V, which indicates an increased electron concentration and optical absorbance. We have also reported the synthesis and characterization of crystalline diamond phases using the pulsed laser annealing. The multiple laser shots on Q-carbon form nanoneedles, microneedles and single-crystal thin films of diamond. This formation is dependent on the nucleation and growth times which are controlled by laser energy density and thermal conductivities of substrate and as-deposited thin film. The diamond nuclei present in the Q-carbon structure can also be grown into larger sizes by using equilibrium hot filament chemical vapor deposition (HFCVD) process. The texture of diamond crystals is <111> under epitaxial growth and <110> under rapid unseeded crystallization. Therefore, our nanosecond laser processing opens up a roadmap for the fabrication of novel amorphous phases and metastable crystalline phases at room temperature and atmospheric pressure.

Upon B-doping in the Q-carbon, we have observed high-temperature Bardeen-Cooper-Schrieffer (BCS) type-II superconductivity in B-doped Q-carbon thin films. We have synthesized two distinct phases of B-doped Q-carbon which exhibit superconducting transition temperatures ($T_c$) of 36 and 55 K for 17 and 27 at% B-doping, respectively. These novel phases are formed as a result of nanosecond laser melting of boron and carbon layers in a super undercooled state and subsequent rapid quenching. This process of rapid nanosecond melting and quenching have been modeled by
using the simulation of laser interaction with materials (SLIM) program to obtain the detailed temperature distribution, melting, and quenching kinetics. We have also observed extremely high values of diffusion coefficients (~10^{-4} \text{cm}^2/\text{sec}) during the pulsed laser annealing which enhances the dopant concentrations beyond thermodynamic solubility limits (via solute trapping). Therefore, the dopants can also be incorporated into the substitutional sites without affecting their energy levels and the ionization efficiencies. The detailed structure-property correlations indicate that the moderate to high electron-phonon values and increased electronic density of states near the Fermi energy level (as compared to B-doped diamond) result in high-temperature superconductivity in B-doped Q-carbon thin films. The high values of critical current density (~10^8 \text{A/cm}^2) and upper critical field (~10 \text{T}) in the superconducting phases also indicate their immense practical applications in NMR and MRI. The time-dependent magnetic moment measurements in the B-doped Q-carbon follows Anderson-Kim logarithmic decay model with high values of pinning potential near $T_c$. There is also an experimental evidence of three-dimensional (3D) critical fluctuations near $T_c$ in B-doped Q-carbon. The crossover from 2D to 3D critical fluctuations is seen at $T/T_c = 1.01$ and 1.02 for the 36 and 55 K superconductor, respectively as compared to $T/T_c = 1.11$ in other high-temperature superconductors. These critical fluctuations also indicate moderate to strong electron-phonon coupling in B-doped Q-carbon. By increasing the B concentrations, we have also synthesized highly B-doped Q-carbon phase (~50 at % B) which will pave the pathway towards room-temperature superconductivity in carbon-based materials.

We have also used the pulsed laser annealing (ultrafast technique) to synthesize nano- and microstructures of phase-pure cubic boron nitride (c-BN) at room temperature and atmospheric pressure. By using the pulsed laser annealing, nanocrystalline h-BN is directly converted into phase-pure twinned c-BN from a highly undercooled melt state of molten BN. A wide range of
sizes (90 nm to 25 µm) of c-BN can be created by changing the nucleation and growth rates. The electron diffraction patterns indicate the formation of twinned c-BN with [1\bar{1}1] as the twin axis. The twinning density in c-BN can be controlled by the degree of undercooling and quenching rate. The detailed temperature-dependent Raman studies indicate a considerable blue-shift of ~6 cm\(^{-1}\) with decrease in temperature from 300 to 78 K in nano c-BN as compared to micro c-BN. The size-effects of c-BN crystals in Raman spectra were modeled by using the spatial correlation theory. It was also found that the Raman blue-shift in nano c-BN is caused by the anharmonic effects and the decrease in Raman linewidth with decreasing temperature (300 to 78 K) is caused by three- and four-phonon decay processes. Therefore, the formation and characterization of phase-pure twinned c-BN by using the pulsed laser annealing will have a tremendous impact on low-temperature solid-state electrical and mechanical devices. A direct conversion of carbon nanofibers (CNFs) into diamond nanofibers (DNFs) at room temperature and atmospheric pressure was also achieved by irradiating CNFs with nanosecond pulsed laser. We have shown that the nanosecond laser pulses melt the tip of CNFs into a highly undercooled state, and its subsequent quenching resulted in the formation of DNFs. This formation of DNFs is dependent on the degree of undercooling which is controlled by nanosecond laser energy density and one-dimensional heat flow characteristics in CNFs. The CNF to DNF conversion process started at the top and it extended with the number of pulses. We have also achieved the formation of highly concentrated nitrogen-vacancy (NV) centers in diamond by using the pulsed laser annealing. In addition to that, we have also shown the tuning of these NV-centers in diamond by using electrons, photons, and phonons. These NV-diamonds are synthesized by employing the ultrafast melting and subsequent quenching of nitrogen-doped carbon films. This allowed the formation of substitutional nitrogen atoms and vacancies. The nitrogen atoms were incorporated into diamond during rapid liquid-
phase growth, where dopant concentrations can exceed thermodynamic solubility limits through solute trapping. The pulsed laser annealing also generated lower surface defects than obtained in conventional HPHT technique. We have formed ~75% NV\textsuperscript{−} centers at room-temperature, which are optically and magnetically distinct as compared to NV\textsuperscript{0} centers. We have dramatically increased the NV\textsuperscript{−} concentration in NV-diamonds by ~53% with decreasing temperature from 300 to 80 K. We have also shown that with negative electrical biasing, the Fermi level in NV-diamond crossed the NV\textsuperscript{0f} level, thereby promoting an exponential conversion of NV\textsuperscript{0} to NV\textsuperscript{−} centers. The NV\textsuperscript{0} to NV\textsuperscript{−} conversion was also activated photonically \textit{via} the absorption of electrons (excited by 532 nm photons). These NV-centers also revealed large excitation lifetime which ultimately produced ~65% quantum efficiency at room temperature. Therefore, by using the pulsed laser annealing process we have achieved highly concentrated NV-centers in diamond and also their conversion (NV\textsuperscript{0} to NV\textsuperscript{−}) which is a prerequisite condition for next-generation quantum sensing, computing, and communication. Therefore, this research illustrated that highly non-equilibrium nanosecond laser processing opens a new frontier for the synthesis of novel amorphous quenched phases and crystalline metastable phases. Since the pulsed laser annealing is a liquid-phase diffusion process, we have also achieved the incorporation of dopants exceeding their thermodynamic solubility limits thereby forming high-temperature superconductors (B-doped Q-carbon) and NV-centers in diamond for next-generation high-speed electronics.