ABSTRACT

YI-FANG LEE. Fabrication and Properties of Topological and Two-dimensional Thin Film Heterostructures (Under the direction of Prof. Jagdish Narayan and Prof. Justin Schwartz).

Spintronics explores phenomenon that interlink the spin and charge degrees of freedom. It is a field where traditional solid-state physics and materials research have created their strongest bond, with each taking alternate leading roles in a unique, fast paced, technological tango. Such a broad definition implies that the range of subjects that fall under the umbrella of spintronics is inevitably very wide. In order to develop spintronics technology, it is first necessary to fully explore potential materials and their properties; by obtaining a thorough understanding of spintronic phenomena we can effective utilize them to create spin-engineered materials and working devices. However, the spin of the carriers tend to go out of phase (both in time and space) in most of the materials thereby losing the spin coherent current, which is required in order to manipulate and utilize the spin of the moving electrons. Thus, it is of great interest now to identify and engineer the materials so that they retain not only spin coherency, but also are capable of supporting maximum spin polarization. The potential materials systems which are believed to be possessing such characteristics are Room Temperature Ferromagnetic Semiconductors (RTFM) and Topological insulators (TIs).

The primary aim of this research is to (1) integrate emerging defect-induced RTFM material, $\text{Sr}_3\text{SnO}$, with technically important substrate Si (100) using pulsed laser deposition (PLD) technique. The films were grown under different deposition conditions in order to understand the effect of processing parameters on the film properties. The characteristics of the thin films have been investigated in detail using X-ray diffraction, TEM, X-ray photoelectron spectroscopy (XPS), UV- photoelectron spectroscopy (UPS), Physical Property Measurement
System (PPMS) and superconducting quantum interference device (SQUID) in order to establish processing-structure-property correlation. The mechanisms of electrical transport and ferromagnetic properties of Sr$_3$SnO is discussed, and we show the ability to simultaneously control both properties by manipulating the intrinsic defects, presumably oxygen vacancies. The transport mechanism follows the variable-range-hopping (VRH) model, consisting of Efros and Shklovskii (ES) and Mott VRH laws in specific temperature regions; and the ferromagnetism results are explained through the oxygen vacancy constituted bound magnetic polarons (BMP) model. An attempt has been made to elucidate the role of point defects, in controlling the carrier concentration transport and ferromagnetic characteristics of SSO films.

TIs are the other candidates to open up a novel route in spin based electronics where the gapless surface states on TIs are protected from elastic scattering on non-magnetic impurities that makes them promising candidates for low-power electronic applications. On contrary to traditional ferromagnetic materials, where the carrier spin polarization and magnetization are based on the exchange interaction, the spin properties in TIs are based on the coupling of spin- and orbit interaction connected to its momentum.

The secondary aim of this research is to (2) integrate the epitaxial Bi$_2$Se$_3$ thin films on c-sapphire substrates by PLD and demonstrate the existence of topologically protected 2D surface states. Detailed characterization using X-ray diffraction, Raman spectroscopy, XPS, angle-resolved UPS for valence band structure analysis, PPMS for magnetotransport measurements and SUQID for magnetic properties analysis were performed. The different Se% of the samples were prepared to investigate the characteristics and probe the role of defects as a function of processing conditions to establish the correlations between microstructure, strain and physical properties. Furthermore, highly functional hybrid structures
consisting of Bi\textsubscript{2}Se\textsubscript{3} and ferromagnetic insulating materials (FMI) were made to demonstrate the proximity-induced ferromagnetism in Bi\textsubscript{2}Se\textsubscript{3}. Two hybrid structures are studied: Bi\textsubscript{2}Se\textsubscript{3}/Cr\textsubscript{2}O\textsubscript{3}/c-sapphire and Bi\textsubscript{2}Se\textsubscript{3}/MgO/c-sapphire. The insulating behavior is more pronounced due to the additional scattering of the surface states of the Bi\textsubscript{2}Se\textsubscript{3} layer by interfacing with MgO and Cr\textsubscript{2}O\textsubscript{3}. The weak antilocalization effect from the surface states is clearly suppressed, accounting for the presence of magnetic bottom layers. It provides an effective way to study the emergence of a ferromagnetic phase in TIs by the magnetic proximity effect in Bi\textsubscript{2}Se\textsubscript{3}, a step toward unveiling their exotic properties.
Fabrication and Properties of Topological and Two-dimensional Thin Film Heterostructures

by
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DEDICATION

This thesis is dedicated to my family for their love, support, and patience.
BIOGRAPHY

Yi-Fang Lee was born in Taichung, Taiwan in 1982 to Tsung-Sheng and Yu-Shiau. She got admission to National Cheng Kung University in 2000 (Tainan, Taiwan) majoring in Materials Science and Engineering. In 2004, she was admitted to the Master of Science in Materials Science and Engineering Graduate Program, National Cheng Kung University. After earning her Master’s degree in 2006, she started her job in industry as an engineer in the fields of semiconductor process. She came to the US in August, 2011 and joined Prof. Narayan and Prof. Schwartz groups at North Carolina State University in 2011 and took her PhD in Materials Science and engineering in August, 2015
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Chapter 1 Introduction

In traditional semiconductor electronics the elements of device performance, such as rectification in a p-n diode or gain in a transistor, are achieved through control of the spatial motion of carriers through that motion’s sensitive dependence on potential energy variations. These potential energy variations come from applied electric fields or quasi-electric fields (such as heterostructure band offsets). However, shallow channel junction, gate leakage current and heat management\(^1\) are the biggest challenges associated with the physical dimensional shrinkage. The Si industry is searching for new methods and/or materials to achieve performance improvements as an alternative to traditional scaling techniques. Now, physicists are trying to exploit the ‘spin’ of the electron rather than its charge to create a remarkable new generation of 'spintronic' devices which will be smaller, more versatile and more robust than those currently making up silicon chips and circuit elements. The potential market is worth hundreds of billions of dollars a year.

Spin introduces a third element into this mix which couples sensitively to the other two. All spintronic devices act according to the simple scheme: (1) information is stored (written) into spins as a particular spin orientation (up or down), (2) the spins, being attached to mobile electrons, carry the information along a wire, and (3) the information is read at a terminal. Spin orientation of conduction electrons survives for a relatively long time (nanoseconds, compared to tens of femtoseconds during which electron momentum decays), which makes spintronic devices particularly attractive for memory storage and magnetic sensors applications, and, potentially for quantum computing where electron spin would represent a bit (called qubit) of information. Magnetoelectronics, Spin Electronics, and Spintronics are different names for the same thing: the use of electrons' spins (not just their electrical charge) in information circuits.
The fabrication of spintronics devices, which combine both charge and spin functionalities, could revolutionize the technology by providing improved efficiency, reduced power consumption, high boot up speed and data retention in the power-down state. Some devices have already been conceptualized, such as Spin LEDs, Spin FETs, Spin valves, magnetic recorders (based on the Giant Magnetoresistance effect), Non-volatile memories and many ultra-low power devices. Four emerging spintronic subfields are listed here:

1. The first is the currentinduced torque (CIT), also known as the spin-transfer torque. The manipulation of magnetization by CITs has its origin in angular momentum conservation, which twists the layer receiving the angular momentum carried by the spin current. It is a key element for the next-generation magnetic random access memories, logic-in-memory architectures, and high-density memory devices.

2. The second is the spin Hall effect (SHE), which originates from the relativistic spin–orbit coupling (SOC) interaction that turns the electrons perpendicular to the current direction in a spin-dependent way. SHE has now become a standard tool in the detection of spin currents and spin polarization. It has been used to create one of the first spin field-effect transistors (FETs).

3. The third is silicon spintronics. Silicon is not only abundant (its oxide is sand) and the central material for electronics, but it also has very desirable long spin relaxation times. It was a late bloomer in spintronics, mostly because its indirect bandgap and weak SOC have, for decades, precluded spin injection and detection.

4. Finally, the forth entails the spintronic aspects of graphene and topological insulators (TIs), which originate from the band-structure properties and create an effective topological knot.
A significant amount of present solid state research has been devoted in developing and understanding as well as discovering materials for Spintronics. Among all the domains related to spintronics, semiconducting material systems have attracted enormous attention to the industry because they offer not only the possibility of new device functionalities which are not realizable in metallic systems; but also, can be utilized in the existing technology. Equilibrium carrier densities can be varied through a wide range of doping and electronic properties are easily tunable by gate potential compared to metals due to the lower carrier densities. There is, of course, a vast body of knowledge concerning semiconductor materials and processing; these are amongst the most pure materials available commercially. As for the crucial element for the success of spintronics is to find a proper material that combines the desirable properties of ferromagnets and semiconductors. Diluted magnetic semiconductors (DMS) are non-magnetic semiconductors doped with a few percent of magnetic elements, usually transition-metals, such as Ni, Fe or Co; and are expected to be not only easily integrable with existing semiconductors but also highly spin-polarized.

In 1990, special attention was drawn to the possibilities of spin injection in semiconducting systems by the proposal of Datta and Das for a “spin-polarized Feild Effect Transistor (Spin-FET)”. The schematic drawing of Spin-FET device is shown in Fig. 1. Their idea was based upon the manipulation of the spin state of carrier via controlled spin precession. This device is at first glance much like a conventional FET; it has a current source, a current drain, and a channel in between with a tunable conductance. However, the spin-FET was based upon contacts envisaged as spin selective, i.e. capable of injecting and accepting only one spin component of the carrier distribution. There are three fundamental requirements for successful implementation of a spin-FET:
1. Spin injection: The transfer of spins need to across the injection interface without wholesale loss of polarization, i.e. between a magnetic and a non-magnetic material. However, the conductivity mismatch can seriously impair this process for Ohmic contacts between metals and semiconductor. Two solutions offer themselves: The first is replace the ferromagnetic contact with DMS; and the other is use tunnel barriers (MgO or Al₂O₃), so that the spin dependent resistance of the tunnel barrier becomes comparable to the spin independent resistance of the normal metal¹².

2. Spin propagation: Once the “source” interface is traversed, spin polarization must be largely preserved while the spin current undergoes propagation through the device. Here, the TIs materials are the candidates to use as channel for spin precession.

3. Spin collection: It is the implementation of a spin analyzer at the far end of the device, which is capable of collection- i.e. resolving the chemical potential imbalance between spin bands arising from spin injection.

Fig.1. A spin-FET proposed by Datta and Das. Two micromagnets serve as polarizer and analyzer. The prorogation medium between – capable to inducing a gate-controllable net rotation of spin orientation- is a two-dimensional electron gas (2DEG).
This study seeks to discover the new material systems that can be implemented in the spin-FET device and improve the spin injection efficiency. Two material systems are proposed for using in this field, one is DMS and the other is TI. The major challenge for DMS is to create magnetic semiconductors that can work at room temperature. The materials challenge is great because both magnetic and electronic doping is required, and the interaction between magnetic dopant spins and free carriers must be engineered to achieve thermally robust dopant spin-carrier coupling. And the challenges for TIs include: accessing surface conduction channels and preserving them at the room temperature.

The main objective of this thesis includes:

1. Develop the new room temperature DMS material, Sr$_3$SnO, which can be integrated with the Si (100) substrate, and demonstrate the ability to simultaneously control the electrical and magnetic properties by manipulating the intrinsic defects. Investigate the transport and ferromagnetic mechanisms and establish the process - properties - structure correlation to optimize the performance for applications.

2. Demonstrated the existence of topologically protected 2D surface states in epitaxial Bi$_2$Se$_3$ thin films grown on c-sapphire substrate and perform the tunable physical properties and electronic structure through the strain engineering induced by intrinsic defects. The other two templates are studied based on proximity effect: Bi$_2$Se$_3$/Cr$_2$O$_3$/c-sapphire and Bi$_2$Se$_3$/MgO/c-sapphire. Since one major drawback for the implementation of TIs into real electronics devices, is their linear energy spectra, which normally allows incident electrons to pass through a potential barrier via Klein tunneling without reflection, leading to an appreciable off-current and thus a poor on/off current ratio. Therefore, opening a surface energy gap and generating of massive
surface carriers by breaking time reversal symmetry (TRS) is the key for both fundamental physics research and new materials displaying exotic phenomena aimed at technological applications.

Rest of the thesis is organized in the following chapters.

*Chapter 2:* Present the background knowledge pertinent to this thesis, including

- The fundamental understanding of DMS and TIs and their potential applications in spintronics.
- The introduction of each material (ex: substrate, buffer layers, Sr$_3$SnO and Bi$_2$Se$_3$)

*Chapter 3:* Give a brief description of experimental techniques used in the present work.

*Chapter 4:* Study the epitaxial integration of dilute magnetic semiconductor Sr$_3$SnO with Si (001) substrate.

*Chapter 5:* Present the tunable room temperature ferromagnetism in Sr$_3$SnO/c-YSZ/Si (001) heterostructures by controlling the oxygen vacancies concentration using novel post processing techniques.

*Chapter 6:* Present the tunable electronic structure in Sr$_3$SnO/c-YSZ/Si (001) heterostructures, and establish the correlation between the carrier concentrations to physical properties.

*Chapter 7:* Show the evidence for topological surface states in epitaxial Bi$_2$Se$_3$ thin film through magnetotransport measurements and angle-resolved photoemission spectroscopy (ARPES)

*Chapter 8:* Show the controllable magnetotransport properties of Bi$_2$Se$_3$/c-sapphire epitaxial heterostructures by strain engineering through intrinsic defects.
Chapter 9: Demonstrate the new platforms for TIs/ferromagnetic insulator heterostructures (Bi$_2$Se$_3$/Cr$_2$O$_3$/c-sapphire and Bi$_2$Se$_3$/MgO/c-sapphire), indicating the strong suppression of the surface transport channel as well as weaken of WAL effect.

Chapter 10: Summary of the conclusions.
1.1 Reference

10 Jansen, R. Nature Mater. 11, 400–408 (2012)
Chapter 2 Background Knowledge

2.1 Thin Film Epitaxy

Epitaxial growth of thin films with minimal defects is the key for the optimized performance of modern day microelectronic, optical and magnetic devices. Epitaxy means the growth of a single crystal film on top of a single crystal substrate \(^{1-3}\). Traditionally, it was understood that both the film and the substrate would have the same crystal structure and orientation. Homoepitaxy refers to the case where the grown film is made up of the same material as the substrate. In this case, the lattice parameters of the film and the substrate are the same, i.e. no misfit strain exists and there are no missing interfacial bonds. Epitaxial (epi) Si deposited on Si wafers is the most significant example of homoepitaxy. Heteroepitaxy refers to the case where the film and the substrate are composed of different materials. In this case, the properties of films largely depend on the mismatch between the film and substrate lattice parameter, the difference in the film and substrate chemistry and the difference in the thermal expansion coefficient of the film and the substrate. Since the film and the substrate materials are different in heteroepitaxy, the lattice misfit between substrate and film is the key parameter which controls growth, morphology and properties of the film. The lattice misfit is defined as: \( \varepsilon = \frac{a_f}{a_s} - 1 \); where \( a_f \) and \( a_s \) are the lattice constant of the film and the substrate, respectively.

2.1.1 Thin Film Growth Modes

The strain resulting from lattice mismatch contributes to the interface energy which is a key parameter in determining the growth mode. Further, the surface free energies for the substrate and film materials also influence the mode of growth. For heteroepitaxy, in general, thermodynamic understanding has been placed in three categories depending on the resulting film morphology. The surface energy of the substrate (\( \sigma_s \)), the surface energy of the film (\( \sigma_f \))
and the interfacial energy ($\sigma_{sf}$) govern the growth mode for a given system. The three growth modes are illustrated in figure 2.1.1.

1. Frank-van der Merwe (FM):

In this mode, deposition proceeds by two dimensional layer-by-layer growth. Complete wetting of the substrate surface occurs, i.e. the first set of atoms condense to form a monolayer on the substrate, after which the second layer comes in and builds on the first layer to form the film. For this reason the FM growth mode is also referred to as the 2D growth mode. The FM growth mode is illustrated schematically in figure 2.1.1(a). The following condition favors FM growth: $\sigma_f + \sigma_{sf} < \sigma_s$, this equation suggests that the system gains energy when totally covered by the thin-film layer. It is also important to realize that for FM growth to occur, the sum of surface energy of the film ($\sigma_f$) and the interface energy ($\sigma_{sf}$) must be less than the surface energy of the substrate ($\sigma_s$). Alternatively, it becomes easier for layer-by-layer growth to occur as the surface energy ($\sigma_s$) of the substrate increases.

2. Volmer-Weber (VW):

The VW growth mode is associated with the formation of 3D islands. Instead of wetting the surface, individual cluster-like islands are formed. This type of growth is illustrated in figure 2.1.1(b) and it happens when $\sigma_f + \sigma_{sf} > \sigma_s$ is valid, i.e. the surface energy of the substrate is less than sum of the surface energy of the film and the interfacial energy. Here, as shown in the figure 2.1.1(b), the interfacial energy is high and the surface energies of the film and substrate are low. So the system adjusts itself so that the high-energy interface formed is minimal and in doing so 3D islands are formed instead of a continuous wetting layer. It is important to realize that for longer growth times, the islands keep growing in size and finally neighboring islands coalesce to form a continuous thin film.
3. Stranski-Krastanov (SK):

This mode combines the 2D and the 3D growth modes as illustrated in figure 2.1.1(c). Initially, a continuous wetting layer is formed over the substrate. Due to the lattice mismatch, strain accumulates in the 2D film and in order to relieve this strain 3D islands are formed \(^{(5,6)}\). It is important to note that the islands grown in the SK mode are coherently strained and dislocation free, i.e., the accumulated strain that switches the growth mode from 2D to 3D is relieved by forming coherently strained islands rather than by introducing dislocations \(^{(5,6)}\). This type of strain relaxation is called the volume elastic relaxation and it competes with the formation of dislocations \(^{(7)}\). But in the SK case, the interfacial energy and the surface energy of the substrate are high and the surface energy of the film is low which follows: \(\sigma_f + \sigma_{sf} > \sigma_s\)

![Figure 2.1.1. Schematic illustration of the three crystal growth modes](image-url)

Figure 2.1.1. Schematic illustration of the three crystal growth modes \(^{(8)}\).
In fact, the mode of growth in heteroepitaxy depends not only on the various interfacial energies but also on the film/substrate lattice mismatch as well as on the growth temperature. Thus, in general, as the mismatch increases, the mode of growth changes from two-dimensional (layer by layer or FM mode) to three-dimensional (island nucleation and coalescence or VW mode). The SK mode of growth (two-dimensional growth followed by island nucleation) often takes place at intermediate mismatches. In an excellent review of epitaxial growth mechanisms, Markov and Stoyanov summarize the main tendencies in the growth mode as follows: 3-D island formation (VW or SK modes) is favored: (1) when the interfacial bonding is weaker than the bonding in the deposit, (2) at higher substrate temperatures, (3) at lower deposition rates, (4) at larger lattice mismatches, (5) when the film is deposited on less densely-packed substrate surfaces (e.g., \(\{100\}_{\text{fcc}}\) or \(\{100\}_{\text{bcc}}\) planes).

Conversely, layer-by-layer growth is favored in systems (1) for which the interfacial bonding is stronger than the bonding in the film material, (2) in which the lattice mismatch is zero (e.g., homoepitaxy) or very small (<0.01%), (3) at lower substrate temperatures, (4) at higher deposition rates, and (5) when the film is deposited on densely packed substrate surfaces (e.g., \(\{111\}_{\text{fcc}}\) or \(\{110\}_{\text{bcc}}\) planes).

### 2.1.2 Lattice Matching Epitaxy

Lattice matching epitaxy (LME) involves one-to-one matching of lattice parameters across the film substrate interface. Initially, the film grows pseudomorphically, meaning its lattice planes become continuous with those of the substrate and there is a smooth transition across the film/substrate interface. The matching of lattice parameters produces strain in the film (and to some extent in the substrate). In the energy balance approach, when the film thickness, \(d\), is less than the critical thickness, \(d_c\), then the film is strained purely “elastically” in order to fit onto the substrate surface, i.e., the spacing of lattice planes normal to the interface became the
same in the film as in the substrate. Due to the Poisson effect, the unit cell in the film will distort from its bulk shape. The Frank-van der Merwe approach implies that the pseudomorphic growth of the film continues until $d_c$ is reached where the strain energy becomes large enough to trigger the nucleation of dislocations, i.e., the strained film relaxes by “plastic deformation”. These dislocations are nucleated at the film surface and must glide to the interface to partly relax the strained film by misfit dislocations. The burgers vector and planes of the dislocation are governed by the active slip systems and glide planes are determined by the crystal structure of the film. For the low misfit system, the $d_c$ is quite large and strain relaxation may not be possible. Therefore, the obstacles to the glide of dislocations will result in a high threading dislocation density in the film, which is detrimental for devices. The LME mismatch between film and substrate in heteroepitaxy is illustrated in Figure 2.1.2.

![Diagram of lattice matching epitaxy](image)

**Figure 2.1.2 Schematic illustration of lattice matching epitaxy**

### 2.1.3 Domain Matching Epitaxy

Conventional LME is possible as long as the lattice misfit between film and the substrate is less than 7-8%. Above this misfit the epitaxial growth is explained by domain matching epitaxy
(DME), proposed by Narayan et al.\textsuperscript{10}. In DME paradigm, where integral multiples of lattice planes match across the film-substrate interface and the size of the domain equals integral multiples of planar spacing\textsuperscript{10}. It is important to realize that even for the systems that the misfits are slightly off perfect one-to-one domain (integral) matching, the additional misfit can also be accommodated by changing the domain size within the DME framework. Further, by careful examination of grain boundary structure, Narayan et al. showed that the additional tilt in the boundary can be accommodated by changing the periodicity of dislocations in the boundary. This is consistent with the concept of domain size variation. Thus, it is possible to grow epitaxial films with any lattice misfit just as it is possible to have grain boundaries of any tilt. Therefore, by invoking the concept of DME, the misfit can range from being very small to very large. However, if the film and the substrate have similar crystal structure, then the matching of planes becomes equivalent to the matching of lattice constants. Accordingly, for small misfits (< 7% - 8%), the generalized DME is equivalent to the conventional LME.

An important feature of the domain epitaxy concept in that most of the strain is relieved quickly within a couple of monolayers, so that the misfit strain can be engineered and confined near the interface. This makes it possible for the rest of the film to be grown free of defects and lattice strains. This feature of the DME growth process may provide a critical advantage over small-misfit LME systems, where most of the dislocations are generated on the surface, beyond the $h_c$, and then the dislocations glide to the interface as half loops. The half-loop glide process leads to the formation of detrimental threading dislocations throughout the electrically active regions of the film. The nature of dislocations (specifically lattice planes and Burgers vectors) within the DME framework is dictated by geometrical constraints of the growth
process; this is in contrast to contrast to the LME process, where the Burgers vectors and the
planes of the dislocations generated via deformation are normal slip vectors.

2.2 Spintronics

Spintronics is an emerging field of nanoscale electronics involving the detection and
manipulation of electron spin which leads to a new generation of devices based on the flow of
spin in addition to the flow of charge. Electron spin can be detected as a magnetic field having
one of two orientations, known as down and up. This provides an additional two binary states
to the conventional low and high logic values, which are represented by simple currents. With
the addition of the spin state to the mix, a bit can have four possible states ascribe as down-
low, down-high, up-low, and up-high, considering as quantum bits. The higher data transfer
speed, greater processing power and increased memory density is expected due to the existence
of four defined states compared to the traditional logic device, express data as two states (1
and 0)\textsuperscript{11}. Another advantage of spin over charge is that spin can be easily manipulated by
externally applied magnetic fields, a property already in use in magnetic storage technology.
In addition, unlike charge states which are easily destroyed by scattering or collision with
defects, impurity and other charges, the spin of an electron is effectively permanent if
undisturbed. These characteristics open the possibility to develop the non-volatile solid state
devices which does not require the constant application of current to refresh the memory or
high energy efficiency devices that can be manipulated by low-power external magnetic field\textsuperscript{11}.

The major theme in semiconductor spintronics is field-effect spin transistor which is based
on the metal-oxide-semiconductor technology familiar to microelectronics devices, proposed
in 1990 by Datta and Das\textsuperscript{12}. In a conventional field effect transistor (FET), electric charge is
introduced via a source electrode and collected at a drain electrode. A third electrode, the gate,
generates an electric field that changes the size of the channel through where the source-drain current can flow. With respect to the spin transistor, the carrier momentum is introduced in a new way that spin coherence can be scrambled as the carrier propagate from the emitter to collector, i.e. the emitter with their spins oriented along the direction of the electrode’s magnetization while the collector acts as a spin filter and accepts electrons with the same spin only. The concept of a spin transistor is founded upon the assumption that spin polarized electrons can survive traversal over the entire device structure. This involves three distinct fundamental requirements. First, the transfer of spins across the injection interface, i.e. between a magnetic and a non-magnetic material, must be possible without losing the polarization. Second, once the source interface is traversed, spin polarization must be largely preserved while the spin current undergoes propagation through the device. This means that there must be minimal spin relaxation within the paramagnetic channel, i.e. the initially unpolarized electron gas in which the electron propagates from source to drain. Third, the final prerequisite is implementation of a spin analyzer at the end of the device, which is capable of spin-selective collection.

However, it is known that the conductivity mismatch between ordinary ferromagnetic metals and semiconductors would cause the spin injection efficiency negligibly small, leading to undetectable levels of polarized current\textsuperscript{13}. Unlike the case for metal/metal contacts, for metal/semiconductor contacts the ratio of conductivity is huge, and this leads to a large attenuation of the spin signal which yields a strong suppression of spin injection phenomena. Two possible solutions have been proposed to circumvent this limitation: One is to use diluted magnetic semiconductors (DMS) as injectors whose conductivity is similar to that of the nonmagnetic semiconductor, therefore, the ohmic contact between a DMS and a
semiconductor is applicable to spin injection without the conductivity mismatch problem. The other is to use tunnel barriers such as MgO, Al₂O₃ or SiO₂, where the contact resistance of such a tunnel barrier would be spin dependent and become comparable to the spin independent resistance of the normal metal ¹³.

2.3 Diluted Magnetic Semiconductors

Replacing normal ferromagnetic metallic elements with DMS providing a promising approach for improving spin injection efficiency by minimizing the conductivity mismatch issue. The first generation of ferromagnetic semiconductor was attracted attention as early as late 1960 to early 1970 for europium chalcogenides (e.g. EuO) and semiconducting spinels (e.g., ZnCr₂Se₄ and CdCr₂Se₄)¹⁴,¹⁵. This interest gradually waned in the 80’s due to the difficulty associated with the preparation of single crystals and its low ferromagnetic transition temperatures (Tᵥ), which hamper their value in the device application. The second generation of ferromagnetic semiconductor is based on non-magnetic semiconductors doped with small amount of magnetic elements (mostly transition metal ). The common choice of host semiconductor has been II-VI compound (e.g. ZnSe and CdTe), because the valence of cation (s²) is compatible with that of typical magnetic element, e.g. Mn, 3d⁵4s²¹⁶. However, the low Tᵥ and to some extent the difficulty in doping these II-VI-based DMSs p- and n-type made these materials less attractive for applications. Soon after, the discovery of ferromagnetism in III-V based DMS’s, (In,Mn)As and (Ga,Mn)As, has open unique opportunities of introducing ferromagnetism in the semiconductor already used in high speed electronics and optoelectronics devices, which paved the way for a wide range of possibilities for integrating magnetic and spin-based phenomenon with the established fabrication process. In 1989, Munekata et al.¹⁷ first discovered that InAs has the Curie temperature of ~ 50 K by doping
Mn. This material was grown by low temperature (200-300 °C) to prevent the formation of ferromagnetic secondary phases such as MnAs, in the MBE system. In 1996, Ohno and coworkers discovered that Mn doped GaAs was also ferromagnetic with a Curie temperature of 110 K. Recently, Blattner et al. demonstrated a Curie temperature of 333 K for (In,Mn)As grown by metal organic chemical vapor deposition (MOCVD), for which they attributed that ferromagnetic behavior to the formation of small clusters of a few magnetic atoms as proposed by Schilfegaarde.

2.3.1 Theories for Ferromagnetism in Diluted Magnetic Semiconductors

In DMS materials, the delocalized conduction band electrons and valence band holes interact with localized magnetic moments associated with the magnetic atoms. Generally, when 3d transition metal ions are substituted for the cations of the host, the resultant electronic structures is influenced by strong hybridization between the 3d orbitals of the magnetic ion and s or p orbitals of the neighboring host anions in the conduction or valence band, giving rise to the ferromagnetism (FM) through sp-d exchange. In a nutshell, to name a few, the pertinent mechanisms of magnetism in DMS systems are: (1) Indirect superexchange which is accounted for the indirect coupling of spins through the conduction electrons that tend to align the spin of the incomplete d-shells in a ferromagnetic manner; (2) Ruderman-Kittel-Kasuya-Yoshida (RKKY) which is based on the indirect exchange coupling of magnetic moments over relatively large distance via band electrons due to the Coulomb exchange. It becomes efficient when a high concentration of free carriers is present such as in metals; (3) Double-exchange mechanism that is originally described by Zener with reference to mixed-valence manganites can produce large moments by means of the nearest-neighbor interaction, and required mixed cation valence so that $3d^n\leftrightarrow3d^{n+1}$ configuration fluctuation can take place, and
(4) The mean-field Zener model proposed by Dietl \textit{et al.}\textsuperscript{24} which is associated with the original model of Zener and the RKKY interaction. As compared to the RKKY interaction, the mean-field Zener model takes into account the anisotropy of the carrier-mediated exchange interaction related to the spin-orbital coupling in the valence band in determining the magnitude of the $T_c$ as well as the direction of the easy-axis in the p-type ferromagnetic semiconductors. However, on the theoretical side, it is not easy to claim which of the many mechanisms put forth is applicable and in what kind of samples. Moreover, on the experimental side, it is still not crystal clear if the uniformly doped host or some other phase is reasonable for the observed magnetic hysteresis. In contrast to the conventional structurally and chemically homogeneous single-phase ferromagnetic systems involving exchange between neighboring atoms with orbitals overlaps, the doped-DMS system intrinsically places a significant burden on our ability to control dopant distribution, disorder and clustering effects. The concentration between ferromagnetism and the atomistic/electronic state of a material system under such a dilute scenario is too sensitive to allow easy comparisons between works of different groups using different growth techniques and parameter spaces. The picture in wide bandgap semiconductors is complex in that the level splitting and associated hybridization are dopant and doping level dependent.

\textbf{2.3.2 Defect-Related Ferromagnetism - d\textsuperscript{0} Ferromagnetism}

The discovery of room temperature d\textsuperscript{0} Ferromagnetism (FM) in undoped semiconductors, such as TiO\textsubscript{2}, ZnO, HfO\textsubscript{2}, and SnO\textsubscript{2} \textsuperscript{25-30} in low dimensional forms like thin films or nanoparticles has further opened a wider debate as to the origin of ferromagnetic order. All the d\textsuperscript{0} FM materials have small ferromagnetic moments and $T_c$ well above room temperature despite the absence of atoms with partially filled $d$ or $f$ shells. Parasitic ferromagnetic impurity
phases are not a general explanation. The most plausible origin of such ferromagnetic properties in otherwise non-magnetic oxides is defects, such as strain and non-equilibrium point defects inferred to be oxygen vacancies, cation vacancies, and interstitials, which result directly from processing \(^{31-33}\). In TiO\(_2\) and HfO\(_2\), FM has been attributed to the presence of oxygen vacancies, which are presumed to behave as an n-type dopant, and the existing vacancies tailor the physical properties of the films\(^ {34,35}\). In ZnO, FM arises from unpaired electrons of oxygen atoms around the Zn vacancies, whereas carrier concentrations are derived from oxygen vacancies and Zn interstitial complexes \(^{36}\). Further, a pristine SrTiO\(_3\) single crystal is an ideal diamagnetic material due to the absence of unpaired electrons, but it shows the ferromagnetic nature upon KrF (248 nm) laser irradiation under 0.24 J/cm\(^2\) energy density. The energy of this laser is sufficiently high to destabilize the orbital and electronic configuration and thereby to induce FM which is attributed to the spin polarized oxygen vacancies coupled with the localized Ti 3d electrons\(^ {37}\). As for Sr\(_3\)SnO thin films, the FM is interpreted in terms of a bound magnetic polaron (BMP) model, where an impurity band resulting from oxygen vacancies locally trap electrons that occupy an orbital overlapping the surrounding magnetic moments. The FM increases monotonically as the oxygen vacancy concentration increases where the saturation moments \((M_s)\) and coercivities \((H_c)\) were found to be proportional to the oxygen vacancy concentration, confirming vacuum annealing
enhances $M_s$ and $H_c$, while oxygen annealing degrades both properties\textsuperscript{38}. A schematic of the BMPs is shown in Fig. 2.3.1.

Fig. 2.3.1 Schematic of Bound Magnetic Polarons: A donor electron in its hydrogenic orbit couples with its spin antiparallel to impurities with a 3d shell that is half-full or more than half-full. Cation sites are represented by small circles. Oxygen is not shown; the unoccupied oxygen sites are represented by squares\textsuperscript{39}.

There are three possible charge states of an oxygen vacancy: $F^0$ (doubly occupied), $F^+$ (single occupied) and $F^{2+}$ (unoccupied). The $F^0$ center charge are in a singlet ($S=0$) state and form a shallow donor level or lie above the conduction band edge. This can only mediate weak antiferromagnetic exchange between magnetic dopants which will not have any net magnetic moment. However, people have argued that a cluster of $F^0$ with more than three oxygen vacancies is likely to develop a net moment\textsuperscript{39}. When these clusters interact with each other directly or indirectly through isolated oxygen vacancies having paramagnetic moments one can observe some magnetic ordering, which can show its signature as magnetic hysteresis. In contrast to this, isolated $F^+$ centers which were seen in EPR experiments\textsuperscript{40} with spin $\frac{1}{2}$ lie deep
in the gap, can couple antiferromagnetically with vacancies clusters to give a ferrimagnet with a net moment which served as the candidate mechanism to explain room temperature FM in SnO$_2$, a sub category of BMP theory named F-center exchange (FCE)$^{41-43}$.

The FM nature in d$^0$ semiconductors is shaping up to be the most interesting problem to emerge so far. It indicates that the 3d dopants are not the only source of magnetism, instead, the common feature in all systems are associated with the presence of defects. However, in no case has the exact nature of the defects responsible been established, it is plausible that they are point defect-atomic vacancies or interstitials-induced by irradiation, thermal treatments to modify stoichiometry or by lattice mismatch between a thin film and its substrate. Surface, grain boundaries and dislocations might also be implicated. The first mechanism for defect-related FM assumes that defects in a semiconductor or insulator create states in the gap which are sufficiently numerous to form an impurity band. Once the density of states is substantially great, spontaneous spin splitting based on the Stoner criterion $ID(E_F) > 1$ may occur where $D(E_F)$ is the density of states at the Fermi level $D(E_F)$ and I is the value of the exchange energy parameter $^{44}$. The other possible mechanism claims that defect states themselves give rise to magnetic moments associated with molecular orbitals localized in the vicinity of the defects. These states then create the impurity band needed to mediate a long-range ferromagnetic interaction between them $^{45}$. Either the defect states can contribute to the magnetization themselves or through their role in the exchange mechanism, it is essential that the defect ferromagnetic states should be stabilized under device processing conditions and actually be utilized.
2.4 Topological Insulators

Similar to conventional electronics that require switching between high and low current states, spintronics require the control of electron spin states that switch between “up” and “down”. Recent interest has focused on topological insulators (TIs), which can conduct spin-polarised electrons on their surface while their inner bulk acts as an insulator. The experimental discovery of the 2D quantum Hall (QH) effect in 1980s marks the first realization of a topological phase of matter. The QH effect is a quantum version of the Hall Effect, which is achieved by applying strong perpendicular magnetic field in two-dimensional electron systems at low temperatures. Under this condition, the electrons travel only along the edge of the semiconductor, and the two counterflows of electrons are spatially separated into different “lanes” located at the sample’s top and bottom edges (Fig. 2.4.1). Those two basic degrees of freedom are spatially separated in a QH bar, as illustrated by the symbolic equation “2 = 1 + 1.” The upper edge contains only a forward mover and the lower edge has only a backward mover. The states are robust: They will go around an impurity without scattering. Consequences of this order include dissipationless transport and emergent particles with fractional charge and statistics \(^{46}\).
Soon after, the theoretical prediction for a new state of quantum matter— the two-dimensional (2D) topological insulators (TIs) with the quantum spin Hall (QSH) effect was proposed. The general mechanism is owing to the band inversion where the usual ordering of the conduction band (s-orbitals) and valence band (p-orbitals) is inverted by strong spin-orbit coupling (SOC). It was later experimentally observed in the case of HgTe quantum wells, prepared by sandwiching the materials between CdHg which has a similar lattice constant but much weaker SOC. Therefore, increasing the thickness of the HgTe layer increases the strength of SOC for the entire quantum well. It illustrates in Fig. 2.4.2, as for a thin quantum well, the CdHg has the dominant effect and the bands have a normal ordering whereas the thick quantum well, the opposite ordering occurs due to increased thickness of the HgTe layer. The critical thickness for band inversion is predicted to be around 6.3 nm where the TI phase can be observed beyond it. The major difference between QSH and QH states is that, for QH states, it requires an external magnetic field which breaks time-reversal (TR) symmetry whereas for
QSH states, in contrast, TR is invariant and does not require an applied field. In 2D HgTe TI material, the role of magnetic field is assumed by the mechanism of SOC, an intrinsic property of all solids. The QSH state has an insulating gap in the bulk and gapless states at the edge where opposite spin states counter propagate and they are immune to defects, non-magnetic impurities or other perturbing influences in their environment, leading to potential non-dissipative applications\textsuperscript{49}.

Fig.2.4.2. A HgCdTe quantum well structure. As function of layer thickness $d < 6.3$ nm, it is a conventional insulator (left hand side); as $d > 6.3$ nm and the 2D quantum well states cross at a band inversion transition (right hand side)\textsuperscript{50}.

Recently, the three-dimensional (3D) TI were discovered where the surface states consist of single 2D massless Dirac fermions, forming a dispersion Dirac cone crossing at $\Gamma$-point. The hallmark of the topologically surface states (TSS) is the linear energy dispersion where
electrons have a single spin state perpendicular to their moving direction, leading to a helical spin texture inside the Dirac cone (Fig. 2.4.3). Those conductive TSS are protected by the time-reversal symmetry (TRS), meaning the direction of the electron spin is locked perpendicular to electron momentum $\vec{k}$, (i.e., electrons moving in positive $\vec{k}$, have their spins pointing in one direction while those moving in negative $\vec{k}$, having spins pointing in exactly the opposite direction). It shows that TIs could form the basis of an entirely new generation of electronic devices that encode information using both the spin and the charge of an electron based on this unique spin-momentum locking property.

Fig. 2.4.3 (Color online) Edge and surface states of topological insulators with Dirac dispersions. Left: Energy dispersion of the spin non-degenerate edge state of a 2D TI forming a 1D Dirac cone. Right: Schematic real-space picture of the 2D helical surface state of a 3D TI with spin-momentum locking in a perpendicular direction.

The ideal experimental tool to measure the Dirac cone and spin texture is angle-resolved photoemission spectroscopy (ARPES). The electronic structure of Bi$_2$Se$_3$ performed by ARPES is shown in Fig.2.4.4. Band structure along the K-Γ-K direction, where Γ is the center
of the hexagonal surface Brillouin zone (BZ), and the surface states are connected between the bulk conduction band and bulk valence band$^{52-57}$. Apart from ARPES, considerable efforts have focused on magneto-transport studies of various quantum transport phenomenon, including weak anti-localization (WAL)$^{58}$, two-dimensional Shubnikov-de Haas oscillations$^{59,60}$, Aharonov-Bohm oscillations$^{61,62}$, as well as non-saturating linear magneto-resistance$^{63,64}$ associated with these surface states.

Fig. 2.4.4. Electronic band structure of Bi$_2$Se$_3$ measured by ARPES. The bulk conduction band (BCB), bulk valence band (BVB), and surface-state band (SSB) are indicated, along with the Fermi energy ($E_F$), the bottom of the BCB ($E_B$), and the Dirac point ($E_D$)$^{65}$.

Various layered materials including Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Bi$_{1-x}$Sb$_x$ have been identified as 3D TIs. Among all discovered 3D TIs, Bi$_2$Se$_3$ has single Dirac cone in the Brillouin zone with a relatively large bulk bandgap of around 0.3 eV, providing great potential for room-temperature applications$^{66,67}$. Several techniques have effectively prepared Bi$_2$Se$_3$ thin films,
including electrodeposition\textsuperscript{68}, solvo-thermalization\textsuperscript{69} and thermal evaporation\textsuperscript{70}; these approaches produce polycrystalline films suitable for thermoelectric studies but not for TI-based integrated solid state devices. Most high quality epitaxial Bi\textsubscript{2}Se\textsubscript{3} thin films have been grown by molecular beam epitaxy (MBE)\textsuperscript{71}-\textsuperscript{73}. Some groups have also reported epitaxial TI thin films grown by pulsed laser deposition (PLD), including Bi\textsubscript{2}Se\textsubscript{3} on InP (1 1 1)\textsuperscript{A74} and Bi\textsubscript{2}Te\textsubscript{3} on Si (1 1 1) substrates\textsuperscript{75}; but compared with MBE films, most PLD films are polycrystalline\textsuperscript{76-78}.

2.5 Device Applications of Topological Insulators

2.5.1 Detection of Spin Polarized Currents in Topological Insulators

In order to make a spintronic device, the primary requirement is to have a system (spin injector) that can produce a spin-polarized electric current, which has more of its electrons in one spin state than the other. Due to the striking properties of TIs where their spins are locked at right-angle to their momentum, all the surface states conduction should be 100\% spin-polarized in principle once an electric current is passed through a TI film, and this spin polarization can be accordingly reversed by simply flipping the electric current direction. Beyond spin and angle resolved photoemission spectroscopy (spin ARPES) measurements, direct observations of the spin-helical current in TIs through transport measurements have been demonstrated by several groups. Tian \textit{et al.}\textsuperscript{79} reported that based on spin valve devices which consisted of exfoliated thin flakes of Bi\textsubscript{2}Se\textsubscript{3} and ferromagnetic (Ni) contacts, an asymmetry in the hysteretic magnetoresistance (MR) between opposite in-plane magnetic field directions was observed. The polarity of the asymmetry in MR can be reversed by reversing the direction of the DC current which was explained by the spin-valve effect between the current-induced spin polarization on the TI surface and the spin-polarized ferromagnetic contacts. Later, Tang \textit{et al.}\textsuperscript{80} detected the spin-polarized surface states on the TI (Bi\textsubscript{0.53}Sb\textsubscript{0.47})\textsubscript{2}Te\textsubscript{3} device along with
a Co/Al₂O₃ ferromagnetic tunneling contact. The hysteresis loop of resistance was observed when sweeping the magnetic field to change the relative orientation between the Co electrode magnetization and the spin polarization of surface states. Two reversible resistance states were detected by changing the electric current direction, affirming the spin-momentum locking in the TSS.

Another approach is to use circularly polarized light to excite spin-polarized photocurrent in TI surface states. Left- and right-circularly polarized light selectively interacts with opposite spin polarizations with components that are either parallel or antiparallel to the wave vector of the incident light. Since photons in circularly polarized light have a well-defined angular momentum which can couple to the spin-momentum-locking surface states on TIs. This coupling can result in the asymmetrical depopulate of surface states in k-space that converts the pure spin currents from the Dirac cone into a net spin-polarized electrical current. This phenomenon is known as the circular photogalvanic effect. McLver et al. reported that by illuminating 3D TI Bi₂Se₃ with 795 nm circularly polarized laser light which can generate a photocurrent that originates from topological helical Dirac fermions. When the helicity of the light was reversed, the direction of the photocurrent followed the same trend.

2.5.2 Ferromagnetic Contacts Couple with Topological Insulators

Given the intrinsic strong SOC property, TIs are expected to be promising candidates for exploring spin injection or spin-transfer torque-related physics based on coupling its TSS with FM contacts. Jamali et al. demonstrated the successful spin injection by using a spin pumping technique where the magnetization precession in a metallic ferromagnet (CoFeB) is used to inject spin currents into the nonmagnetic 3D TI Bi₂Se₃ layer and the electromotive force is detected by the inverse spin Hall effect (ISHE) at room temperature. The ISHE involves a spin
current inducing a transverse charge current and causing a charge accumulation, which along with the spin Hall Effect (SHE), provides the ability to reversibly convert charge and spin currents.

Similar to electric currents being carried by moving charge, the spin current occurs due to moving spins. The spin current carries angular momentum, which can be transferred to the magnetization, a phenomenon known as spin-transfer torque (STT). In recent years, current-induced magnetization switching based on STT has attracted considerable attention as a scalable means of magnetization reversal in spin devices. Mellnik et al. \(^{86}\) showed that the charge current flowing in-plane in the 3D TI Bi\(_2\)Se\(_3\) thin films can exert a strong STT on an adjacent ferromagnetic permalloy (Ni\(_{81}\)Fe\(_{19}\)) thin film at room temperature, with a direction consistent with that expected from the TSS. Due to the helical locking between spin and momentum on the TSS, it is expected that the flow of charge is accompanied by an enormous non-equilibrium surface spin accumulation with the spin moment. The mechanism behind the STT is associated with the spin-polarized current when coupling to an adjacent ferromagnetic layer, the reorientation of the electron spin on transmission through the ferromagnetic layer will occur. By conservation of angular momentum, a change in the direction of an electron spin angular momentum leads to a torque on the magnetization of the ferromagnetic layer. The STT phenomenon is the fundamental mechanism for magnetoresistive random access memory (MRAM) device where the magnetic state of the free layer can be changed if the torque is sufficiently strong, thus information can be written.

2.5.3 Topological Insulators-Based Field-Effect Transistor

The edge states of TIs have two attributes which are very desirable for classical computing field-effect transistor (FET) channel materials: a high electron mobility and robustness against
defects and impurities. Due to the linear energy spectra the normally incident electrons can pass through a potential barrier via Klein tunneling without reflection, however, it is also a significant drawback for use TI as FET since the Klein tunneling leads to an appreciable off current, and thus a poor on/off current ratio. In the case of graphene, several schemes have been proposed to open an energy gap in linear energy dispersion, such as the use of graphene on SiC, applying electric field to bilayer graphene and use of graphene nanoribbons. Similar to the case of graphene, one way to overcome this problem for TIs is gap generation in the linear energy spectrum, meaning breaking TRS by ferromagnetic perturbation. Zhang et al. fabricated FET device based on magnetically doped TI films with chemical formula $\text{Cr}_{0.15}(\text{Bi}_{0.1}\text{Sb}_{0.9})_{1.85}\text{Te}_3$, and showed the ability to manipulate the magnetic order and magnetotransport simultaneously by means of electric-field-control. Introduction of the ferromagnetic order in TIs is important not only because it is a good platform to study fundamental physical phenomena, such as the quantum anomalous Hall effect, topological magnetoelectric effect, as well as image magnetic monopole; but also it is a precondition for TIs to be applied in spintronics and topological quantum computation. The transport of the Dirac fermions on TI surface shows high selectivity dependence on the direction of the magnetization. Only the perpendicular magnetization induces an energy gap in linear energy spectra while the parallel magnetization will shift the position of the electrons’ Fermi surface, no gap is expected. There are two methods for experimentally introducing ferromagnetic order into the TIs. One is through conventionally doping with some magnetic elements and the other is by ferromagnetic proximity coupling.
2.5.4 Magnetically Doped Topological Insulators

Introducing magnetic dopants (Ex: 3d transition metal ions) into 3D TIs has been proven to be a straightforward way to open a gap of the surface states by breaking TRS. FM has been found in several TI systems doped with 3d transition ions: Fe- and Mn-doped single crystals of $\text{Bi}_2\text{Te}_3$ $^{93-95}$, or Fe-, Mn- and Cr-doped thin films $\text{Bi}_2\text{Se}_3$ $^{96,97}$. Hor et al. $^{98}$ reported using Scanning tunneling microscopy analysis that the Mn randomly substitutes on the Bi sites forming a $\text{Bi}_{2-x}\text{Mn}_x\text{Te}_3$ compound in a single crystal form without any existence of clusters. The system becomes ferromagnetic when the Mn concentration is in the range of $x = 0.04-0.09$. As $x=0.9$, the saturated magnetic moment reached $1.5 \, \mu\text{B}$ per mol Mn at about $12 \, \text{kOe}$ for $\text{H//c}$-axis and $20 \, \text{kOe}$ for $\text{H//c}$-axis at $1.8 \, \text{K}$. Haazen et al. $^{99}$ observed FM in epitaxial thin films of the 3D TIs $\text{Bi}_2\text{Se}_3$ with Cr doping and demonstrated that the Cr substitutes for Bi sites without adding carriers. The crystal quality deteriorates with increasing Cr concentration as confirmed by FWHM of rocking curve. The $T_c$ reached a maximum $\sim 20 \, \text{K}$ for 5.2% Cr doped while the film remains highly textured with a FWHM of $6.8^\circ$. Comparing the in- and out-of-plane magnetization data, Cr-doped $\text{Bi}_2\text{Se}_3$ thin film displayed in-plane easy axis magnetization while Mn- and Cr-doped $\text{Bi}_2\text{Se}_3$ showed perpendicular magnetic anisotropic. Two major mechanisms has been proposed to understand the magnetic origin in TIs: the van Vleck mechanism and the Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling $^{100-102}$. In the former case, the ferromagnetism is independent of the carrier density due to the large spin susceptibility of the valence electrons in the band-inverted TI materials, the magnetic ions can thus be directly coupled through these local valence electrons without the assistance of the itinerant electrons. On the other hand, RKKY is considered as “carrier-mediated” interaction due to the neighboring magnetic ions being coupled through the mediation of the conduction
carriers. However, similar to DMS, there still remains ambiguity regarding to the ferromagnetic mechanisms in 3d transition metal doped-TIs. Therefore, it is important to confirm the absence of other secondary phase formation in the bulk or locally on the surface, clustering or non-uniform distribution of dopants.

2.5.5 Topological Insulators/Ferromagnetic Insulators Heterostructure

Another way of introducing the magnetic order in the surface states is to exchange couple a magnetic layer via the proximity effect. Proximity-induced ferromagnetism in TIs is attainable in TIs/ferromagnet heterostructures by utilizing a thin-film deposition technique. Commonly used ferromagnetic layers are Fe, Co, and Ni, which are metallic. However, there are several drawbacks of using metallic ferromagnetic layers, such as poor crystallinity due to the low surface energy and strong oxidizing nature of tellurium and selenium of the TI materials $^{103,104}$. Most importantly, as a metallic thin-film layer parallel to a TI, these ferromagnetic materials may either overwhelm the TI conduction or form a discontinuous layers which act as magnetic impurities, leading to spin scattering that is detrimental to TSS. Therefore inert and insulating ferromagnetic materials (i.e., ferromagnetic insulators [FMIs]), such as EuS $^{105,106}$, Yttrium iron garnet (YIG) $^{107}$ and GdN $^{108}$ would be highly advantageous. Jiang et al. $^{109}$ reported on the heterostructure of Bi$_2$Se$_3$/YIG grown by molecular beam epitaxy in conjunction with pulsed laser deposition. The presence of the ferrimagnetic insulator YIG causes additional scattering to the TSS, as indicated by the temperature dependence of the resistivity. The surface contribution was greatly reduced through the analysis of two-channel mechanism, collected from the Hall data. Wei et al. $^{110}$ studied the heterostructure based on FMI (EuS) layer combining with TI Bi$_2$Se$_3$ thin films. They observed that for Bi$_2$Se$_3$/EuS samples, each Eu$^{2+}$ ion contributes a saturation magnetic moment that is higher than the $7\mu_B$
upper limit of EuS. It reaches a maximum of 11.3 $\mu B$/Eu$^{2+}$ in the sample with 1 nm EuS, which is 60% larger than the 7 $\mu B$/Eu$^{2+}$ value$^{111}$. Since the excess moment cannot be accounted for by the EuS layer alone, therefore, they claimed that its origin is attributed to the induced moment at the Bi$_2$Se$_3$/EuS interface which is proximity-induced interfacial magnetization. With similar objectives, Yang et al. $^{106}$ and Kandala et al. $^{112}$ investigated the effects on the WAL behavior of the TI in conjunction with an FMI, where the electrons with spin-momentum locking are less likely to encounter backscattering, hence they become localized once the time reversal symmetry is preserved. Generally, all the FMIs have an in-plane easy magnetization axis, although canted magnetization or small perpendicular magnetic hystereses have been reported $^{105,106,108}$. However, the perpendicular magnetic anisotropy can be engineered by choosing a proper interface layer, which is attributed to the hybridization of the electronic states $^{113}$. Thus the proper choice of a FMI and TIs material combination may lead to a strong perpendicular magnetic hysteresis where the symmetry breaking happens right at the interface, rather than affecting the majority bulk states or introducing defects.

2.6 Material Systems

2.6.1 Strontium Tin Oxide (Sr$_3$SnO)

In the Ural Mountains in 1839 the geologist Gustav Rose has discovered the mineral CaTiO$_3$ and given the name perovskite in honor of the eminent Russian mineralogist, Count Lev Alexevich von Perovski$^{114}$. The ideal perovskite with the general formula ABX$_3$ has full or nearly cubic symmetry in which the body center position is occupied by B atoms, which is surrounded by an octahedron, the edges by A atoms and the face centers by X atoms in Pm3m space group$^{114,115}$. In addition, where A is a monovalent or divalent cation, B is penta- or tetravalent transition-metal atom and X represents anions such as those of oxygen, nitrogen and
fluorine, display a wide range of interesting physical properties and have numerous technological applications because of the enormous variety of solid state phenomena they exhibit. Soon after, the new category, called “anti-perovskite” structure (A$_3$BO) where A= Ca, Sr, Ba and B= Sn, Pb have been synthetized for the first time in 1980 by Widera and Schaefer. The A, Sn, and O are filled 3c (0, 0.5, 0.5), 1a (0, 0, 0) and 1b (0.5, 0.5, 0.5) Wyckoff positions, respectively, and that is based on the reverse occupancy of metal and nonmetal elements in cubic corner and body center positions. Recently, Klintenberg has identified 17 compounds as new potential TIs using massive computing and data-mining of electronic structures, the results are listed in Table 2.6.1. Oxides with the anti-perovskite structure were predicted having the band-inversion at the Γ-point in the presence of strong spin-orbit coupling (SOC); one such oxide is Sr$_3$SnO (SSO). The strong SOC interaction could induce band inversion, which is a key ingredient of a topologically nontrivial material, characterizing as band insulators with gapless linear energy dispersion surface states. More recently, Hsieh et al. reported first principles calculations of the SSO band structure and found that it lies very close to the topological phase transition point and not belonging to the inverted regime with opposite orderings of the d and p orbitals. According to theoretical calculations, SSO crystallizes in the cubic system with space group Pm-3m and a theoretical unit cell of 5.12 Å where the crystal structure is displayed in Fig. 2.6.1. SSO has an indirect local density approximation (LDA) band gap of 0.1 eV throughout the Brillouin zone.
Table 2.6.1: Results of the mining algorithm for second generation non-trivial topological insulators. 17 compounds are identified as new potential topological insulators.

<table>
<thead>
<tr>
<th>Material</th>
<th>Spgrp</th>
<th>Struct. type</th>
<th>LDA band gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
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<td>P m -3 m</td>
<td>CaTiO₃</td>
<td>0.2</td>
</tr>
<tr>
<td>Sr₃PbO</td>
<td>P m -3 m</td>
<td>CaTiO₃</td>
<td>0.1</td>
</tr>
<tr>
<td>Ba₃PbO</td>
<td>P m -3 m</td>
<td>CaTiO₃</td>
<td>0.1</td>
</tr>
<tr>
<td>Yb₃PbO</td>
<td>P m -3 m</td>
<td>CaTiO₃</td>
<td>0.2</td>
</tr>
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<td>Ca₃SnO</td>
<td>P m -3 m</td>
<td>CaTiO₃</td>
<td>0.2</td>
</tr>
<tr>
<td>Sr₃SnO</td>
<td>P m -3 m</td>
<td>CaTiO₃</td>
<td>0.1</td>
</tr>
<tr>
<td>Yb₃SnO</td>
<td>P m -3 m</td>
<td>CaTiO₃</td>
<td>0.1</td>
</tr>
<tr>
<td>GdPtSb</td>
<td>F -4 3 m</td>
<td>AlLiSi</td>
<td>0.2</td>
</tr>
<tr>
<td>Bi₂SeTe₂</td>
<td>R -3 m H</td>
<td>Bi₂Te₃</td>
<td>0.3</td>
</tr>
<tr>
<td>Bi₂SbTe₂</td>
<td>R -3 m H</td>
<td>Bi₂Te₃</td>
<td>0.3</td>
</tr>
<tr>
<td>PbTl₃Te₃</td>
<td>I 4/m c m</td>
<td>In₅Bi₃</td>
<td>0.1</td>
</tr>
<tr>
<td>BiTl₄Te₆</td>
<td>I 4/m c m</td>
<td>In₅Bi₃</td>
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</tr>
<tr>
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<tr>
<td>HgKSb</td>
<td>P 63/m m c</td>
<td>KZnAs</td>
<td>0.2</td>
</tr>
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</table>

⁹The material has small hole pockets.

Fig. 2.6.1 Crystal structure of Sr₃SnO.
2.6.2 Bismuth Selenide (Bi$_2$Se$_3$)

Bi$_2$Se$_3$ is a narrow gap semiconductor, which crystallizes in a rhombohedral structure (a=4.14 Å, c=28.7 Å) belonging to the R-3m space group. The primitive lattice vectors $t_1$, $t_2$, and $t_3$ and rhombohedral primitive unit cell are shown in the Fig 2.6.2 (a). The crystal has the three-fold rotation symmetry with the trigonal axis defines as the z-axis, the two-fold rotation symmetry with the binary axis defined as the x-axis, and the reflection symmetry with a bisectrix axis in the reflection plane, defined as the y-axis. It consists of a layered structure where one individual layer forms a triangular lattice. Five-atom layers, named as a quintuple layer (QL), are stacked along the z direction. There are five atoms in one unit cell with two equivalent Se atoms denoted by Se1 and Se1', two equivalent Bi atoms denoted by Bi1 and Bi1', and the third Se atom denoted by Se2, as shown in Fig. 2.6.2 (b). The inter-layer bonding within the QLs is strong because of the dominant covalent character, but the bonding between the QLs is much weaker due to the van der Walls-type interaction. Traditionally it is an important material for thermoelectric applications. Very recently, it regenerates great interest by being predicted to be a 3D TI, a new state of quantum matter. According to the theory, it has a large bulk energy gap and its topological surface states can be described by a single Dirac cone at the Γ point.
Fig. 2.6.2 (a) Crystal structure of Bi$_2$Se$_3$ with three primitive lattice vectors denoted as $t_{1,2,3}$; (b) Side view of the quintuple layer structure. Along the $z$-direction, the stacking order of Se and Bi atomic layers is……- C(Se1')-A(Se1)-B(Bi1)-C(Se2)-A(Bi1')-B(Se1')-C(Se1)-…..
2.7 Substrates and buffer layers

2.7.1 Silicon

Silicon is a group IV elemental semiconductor. Most of the commercial electronic devices are currently based on silicon. Owing to its natural abundance and large scale industrial use, silicon substrates are widely and cheaply available. Hence the integration of new functional materials with silicon substrate offers unique technological advantage. Silicon has a diamond-cubic crystal structure (Fig. 2.7.1) with lattice constant of 5.431 Å. The thermal expansion coefficient of Silicon is \( \sim 2.6 \times 10^{-6} \text{ K}^{-1} \). The band gap of silicon is \( \sim 1.12 \text{ eV} \) at room temperature. Silicon substrates are available in large sizes (up to 400 mm diameter). Both n-type and p-type silicon substrates with different doping concentration are available. One of the biggest challenges in integrating oxide materials with silicon is the tendency of silicon to readily form an amorphous silicon dioxide oxide (SiO\(_2\)) layer.

![Fig. 2.7.1 Diamond cubic crystal structure of Silicon](image)

Fig. 2.7.1 Diamond cubic crystal structure of Silicon
2.7.2 Aluminum Oxide (Al₂O₃)

Al₂O₃ (sapphire) is composed of ionic bonds and has rhombohedral/hexagonal crystal structure, which belongs to the space group of R-3c. The lattice structure of the hexagonal unit cell consists of close packed planes of oxygen, alternating with a hexagonal array of aluminum planes. The aluminum planes are in hexagonal close packed arrangement, with one third of the sites vacant. The vacant sites produce the 2/3 stoichiometric ratio of Al/O in sapphire. The Al planes are arranged with the Al vacancies ordered with a three-fold symmetry axis along the [0001] direction. The lattice constant of Al₂O₃ hexagonal unit cell are a=4.7587 Å and c=12.9929 Å. Sapphire is an insulator with a band gap of 9 eV at room temperature. The thermal expansion coefficients of sapphire are 6.2×10⁻⁶ and 7.07×10⁻⁶ K⁻¹ along a- and c-axes, respectively.

Fig. 2.7.2 (Left) Lattice structure of sapphire. (Right) Sapphire planes used in growth of thin films. There are four most common face terminations of hexagonal Al₂O₃ used for fabrication of thin films. They are (0006) (c-plane), (1-102) (r-plane), (1-100) (m-plane), and (2-1-10) (a-plane). The lattice structure of sapphire and important crystallographic planes in Al₂O₃ are shown in Fig. 2.7.2.
2.7.3 Yttria Stabilized Zirconia (YSZ)

Yttria-stabilized zirconia (YSZ) is an attractive buffer layer for the subsequent growth of numerous oxide materials on non-oxide substrates. YSZ has a high dielectric constant (≈25) and large bandgap (4.2 eV)\textsuperscript{131}. YSZ has excellent chemical stability on silicon. The free energy of formation of ZrO\textsubscript{2} (ΔG (800 K) = −941.6 kJ kmol\textsuperscript{-1}) is smaller than that of SiO\textsubscript{2} (ΔG (800 K) = −734.2 kJ kmol\textsuperscript{-1}). The thermal expansion coefficient of YSZ is ≈ 8-9 x 10\textsuperscript{-6} K\textsuperscript{-1}. Crystal structure of YSZ is dependent on the yttria content. Pure zirconia (ZrO\textsubscript{2}) is monoclinic. When doped with 3-5 mol % yttria, the tetragonal phase of zirconia is stabilized at room temperature. Lattice parameters of tetragonal YSZ (space group P42/nmc) are a = 3.6067 Å, c= 5.1758 Å (for 3 mol % Y\textsubscript{2}O\textsubscript{3} doped ZrO\textsubscript{2}). A unit cell of tetragonal YSZ is shown in Fig. 2.7.3 (left). Yttria content of 8 mol % or higher makes the cubic phase of zirconia stable at room temperature. Cubic YSZ crystallizes in a fluorite-type structure (space group: Fm-3m) with a lattice parameter ~5.1289 Å (for 15 mol % Y\textsubscript{2}O\textsubscript{3} doped ZrO\textsubscript{2}). A unit cell of tetragonal YSZ is shown in Fig. 2.7.3 (right).
Fig. 2.7.3 Crystal structure of tetragonal (left) and cubic (right) YSZ. Oxygen atoms are shown in red color while (Zr, Y) atoms are shown in green color.

2.8 Thin Film Ferromagnetic Insulator

2.8.1 Chromium Oxide (Cr$_2$O$_3$)

Chromium (III) oxide is one of the principal oxides of chromium. Cr$_2$O$_3$ has the corundum structure (space group: R-3C), with hexagonal-close-packed (001) layers of O atoms with 2/3 of the octahedral holes filled by Cr atoms (shown in Figure 2.8.1)\textsuperscript{132}. The lattice constants of Cr$_2$O$_3$ are 4.95 and 13.59 Å for a- and c-axes, respectively\textsuperscript{133}. Cr$_2$O$_3$ is a representative magnetoelectric (ME) insulating material\textsuperscript{134-135} where magnetization cab be induced by applying an external electric field. Below the Néel temperature, 307.8 K, Cr$_2$O$_3$ presents as an anti-ferromagnetic (AFM) material\textsuperscript{136}. The high insulating nature of Cr$_2$O$_3$ makes it a suitable candidate to be employed as a tunnel barrier in magnetic tunnel junctions\textsuperscript{138}. Furthermore, Punugupati et al. showed that the PLD grown-Cr$_2$O$_3$ thin films exhibit ferromagnetic-like hysteresis loops with high saturation and finite coercivity up to 400 K due to oxygen related
defects whose concentration is controlled by the strain present in the films. Therefore, due to its ferromagnetic insulator properties, it becomes a potential candidate to integrate with TIs to study the TRS breaking induced by proximity effect.

Fig. 2.8.1 Crystal structure of corundum structure for Cr₂O₃ (Cr atoms are label as gray while O is red). Left: The rhombohedral primitive cell and right: the hexagonal representation

2.8.2 Magnesium oxide (MgO)

MgO crystallizes in a cubic cell which has a six-coordinated rocksalt (B1) structure with a lattice constant a= 4.21 Å. The crystal structure (shown in Figure 2.8.2) can be described as a face-centered cubic lattice of Mg ions with O ions occupying all the octahedral holes or vice versa. There is an increasing interest in the growth of high quality MgO films because of their unique physical properties which allow the fabrication of buffered epitaxial layers of ferroelectric materials and superconductors, as well as wide-band-gap semiconductors for many optoelectronic applications. Moreover, the MgO thin film with (001) orientation was confirmed as a new type of magnetic tunnel barrier that exhibits a large magnetoresistive effect.
at room temperature. For example, recent experiments at room temperature have demonstrated giant tunnel magnetoresistance (TMR) ratios of up to 180 % in single-crystal Fe/MgO/Fe magnetic tunnel junctions (MTJs) \(^{140,141}\), 220 % in highly oriented (001) CoFe/MgO/CoFe MTJs \(^{142}\), and 230 % in sputtered CoFeB/MgO/CoFeB MTJs \(^{143}\). Recently, Li et al. \(^{144}\) showed that the undoped MgO thin films grown by pulsed laser deposition (PLD) have the RTFM signature and that the ferromagnetism exhibits strong correlation between magnesium vacancies (\(V_{\text{Mg}}\)) and the crystallinity. Therefore, due to the existence of ferromagnetism and its high insulating nature of the MgO thin film, it becomes an interesting platform for exploring the magnetic proximity effect between a ferromagnetic insulator and a TI.

Fig. 2.8.2 Crystal structure of MgO
2.9 Reference

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Chapter 3 Experimental Techniques

Sample growth, preparation techniques and physical property analysis are described in this chapter. All the thin films in the present study were fabricated using pulsed laser deposition technique. Si (100) and sapphire (0001) were used for Sr$_3$SnO and Bi$_2$Se$_3$ thin films deposition, respectively.

3.1 Pulsed Laser Deposition

The use of laser energy in the form of monochromatic and coherent photons has gained wide spread momentum in the processing and characterization of materials. In the world of materials science, lasers have been in constant use over a broad range of applications ranging from process monitoring, localized melting, surface cleaning, to more diverse applications involving laser-induced rapid quenching to improve surface hardness, laser annealing of semiconductors, and pulsed laser deposition (PLD) for growing thin films.$^{1,2}$

PLD is one of the most convenient thin film growth techniques that uses a high intensity pulsed laser beam as an external energy source to ablate a target, form a plume, and deposit thin films onto a substrate. In this case, both the target material and the substrate are housed in a vacuum chamber. Though several models have been proposed to explain the dynamics of laser-target interaction, none of them are effective in accounting for all of the observations. However, a consensus between these models results in three types of absorptions that ought to be taken into account: (1) Energy absorbed by carriers at the surface of the target. (2) Energy absorbed by lattice phonons and electrons in the lattice of the target. (3) Absorption by the plume. The mechanism of laser ablation depends on the optical, topological and thermodynamical properties of the target material in addition to the laser characteristics. As an example, metallic surfaces absorb by free carriers, dielectric surfaces absorb by below bandgap
radiation inside the lattice as free carriers are absent and in semiconductors it is a mixed mechanism. However, the ultraviolet radiation of the laser beam is absorbed by most surfaces to a depth of about 1000 Å. At the incidence of laser radiation, electromagnetic energy is initially converted into electronic excitation and then into thermal, chemical and mechanical energy to result in evaporation, ablation, excitation, plasma formation and exfoliation.¹

The laser pulses are extremely short in the range of about 25 ns and increase the surface temperature rapidly to a few thousands of degrees Celsius as photons are absorbed on the surface, forming a molten layer also termed the Knudsen layer. However, the rest of the target volume remains virtually at room temperature. This vaporization process takes place in a short duration but with considerable mass transport resulting in a flash of evaporants that are deposited onto the substrate, producing a thin film with a composition identical to that of the target surface. The evaporants form a plume that consists of a mixture of several energetic species including atoms, molecules, electrons, ions, clusters, micron sized solid particulates and molten globules. The collision mean free path inside the plume is so short that the plume rapidly expands away from the target surface to form a nozzle jet with hydrodynamical flow characteristics. This results in a highly forward-directed velocity distribution and confined plume of materials that condenses on the substrate with very little contamination.

Another aspect to be considered is the secondary interaction between the plume and the laser beam. This high-order interaction is bound to increase the plasma temperature and make the evaporants more energetic thus, increasing the adatom surface mobility and resulting in better quality films. The ability to replicate the exact composition of the target material in the deposited film is one of the incredible benefits of PLD compared to other thin film deposition techniques. This is similar to unconfined plasma in a sputter process. However, PLD does not
require a constant glow discharge as compared sputtering in which independent control of process parameters is limited. PLD also scores over thermal evaporation, which produces a vapor composition dependent on the vapor pressures of elements in the target material, while the laser-induced expulsion produces a plume of a material with stoichiometry similar to the target. It is usually easier to obtain the desired film stoichiometry for multi-element materials using PLD than with other deposition technologies. PLD has been applied to the deposition of thin films of many compounds such as oxides, semiconductors, ferroelectrics, and even polymers and ceramics.\textsuperscript{3-7}

The advantages of using pulsed laser deposition can be summed up as follows: (1) The use of an evaporation power source that is independent of vacuum hardware makes the technique extremely flexible and adaptable to different modes of operation even though the laser-target interaction is a complex phenomenon. (2) A dynamic range of deposition pressures can be reached and are considered to be the greatest compared to other deposition processes. (3) PLD has the ability to reproduce the target composition with relative ease even in the case of complex materials. (4) At wavelengths of 250 nm and below, most of the materials absorb laser energy via linear or non-linear processes, and hence, coupling of energy is possible to most surfaces.\textsuperscript{8} (5) PLD has the ability to fabricate films in high partial pressures of reactive gas, such as oxygen. In the deposition of many oxide films, it is critical to maintain the proper oxygen content in the chamber. The presence of reactive gas can help bind volatile species to a substrate and aid in preserving the film stoichiometry. (6) Well-oriented and crystalline films can be obtained using PLD owing to the high surface adatom mobility while working at room temperature. (7) Other advantages of PLD result from its minimal vacuum requirements, lack of a stringent need for specialized targets, and ability to deposit films of many different
materials in situ for multilayer structures. Smaller targets can be used for deposition, making the process more economical.

The most important process parameters in PLD system are; laser wavelength, pulse duration, target-substrate distance, laser energy, laser spot size, pulse frequency, substrate temperature, and background gas and pressure. In this dissertation work, a Lambda LPX 100 KrF pulsed excimer laser of 248 nm, pulse width of 25 ns and the 4.5 cm working distance (target-substrate distance) were fixed for all the depositions. As for the energy density, repetition rate, substrate temperature and the deposition ambient (Ar or O₂) were optimized for each material to obtain high quality and epitaxial thin films.

3.2 Structural Characterization Techniques

3.2.1 X-ray Diffraction

The atomic planes of a crystal reflect incident x-ray beams that interfere with one another as they leave the crystal, provided the wavelength is closer to the magnitude of the inter-atomic spacing. This phenomenon is called x-ray diffraction. Diffraction arises from the constructive or destructive interference between two or more waves and can be observed whenever Bragg’s law is satisfied. Bragg's law refers to the simple equation⁹: \( n \lambda = 2d \sin \theta \), where \( \theta \) is the angle of incidence, \( d \) is the distance between atomic layers in a crystal, \( \lambda \) is the wavelength of the incident x-ray beam and \( n \) is an integer. In the present work \( \theta-2\theta \) scans were performed using Rigaku D-MAX/A diffractometer with Cu Kα radiation. This instrument is a two-circle diffractometer in which the sample can be rotated along one of the axis (\( \theta \)-axis) and also the detector can be rotated independently (\( 2\theta \)-axis). A schematic diagram for this diffractometer (\( \theta-2\theta \) scan) is shown in Figure 3.2.1 (a). Bragg’s law can also be used to explain the interference pattern of ions, electrons, neutrons, and protons that have a wavelength similar to the distance
between the atomic or molecular structures of interest. As a x-ray beam traverses through a material, its intensity decreases with the distance traveled and a x-ray diffractometer is used to measure the intensities of reflected beams from small areas. These results provide direct evidence of atomic-level spacing within the crystal lattice of the specimen. It also yields details of the crystal structure for the different phases present in the specimen. Moreover, finer details of the crystal structure, such as the state of atomic order, also can be derived. It is important to realize that in the XRD technique only the planes parallel to sample surface contribute to the signal. For a single crystalline sample only one set of planes are parallel to the surface. So an XRD scan of a single crystal should have only one peak and higher order peaks of the same family. In the case of a poly crystalline film, several planes belonging to different grains will be parallel to the sample surface. Hence the XRD scan of a poly sample will have numerous peaks representing various planes.

Though two-circle diffractometer gives information about the growth orientation, it does not give any information on in-plane orientation of thin film. Knowing in-plane orientation is important to establish epitaxy. The in-plane orientation of thin films can be accessed by four-circle Diffractometer, shown in Figure 3.2.1 (b). In addition to rotation along θ-axis and 2θ-axis, in four-circle diffractometer the sample can be tilted with respect to the incident beam (ψ-axis) and also rotated 360 degrees around the surface normal (φ-axis). The in-plane epitaxial details can be established by φ-scans. To perform a φ-scan an appropriate crystallographic plane (hkl), which is inclined to the growth plane (sample surface) is identified. The θ and 2θ angles are set to corresponding to Bragg angle for the identified plane. The sample tilt, ψ is set equal to the crystallographic angle between the growth plane (sample surface) and the (hkl) plane
identified for the $\phi$-scan. The diffraction intensity is then recorded as a function of sample rotation along $\phi$-axis. If the film is epitaxial, the $\phi$-scan exhibits sharp peaks at certain $\phi$-angles. On the other hand if the in-plane orientation of the film is random, there is no appreciable variation in the diffraction intensity in the $\phi$-scan.

Fig. 3.2.1 (a) Schematic illustration of the XRD $\theta$-2$\theta$ scan; (b) Schematic diagram of the Philips X’Pert diffractometer used for $\phi$-scan. IBO: Incident beam optics, DBO: Diffracted beam optics.
3.2.2. X-Ray Photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is based on the photoelectric effect where a photon incident on a sample in which an electron is bound with a binding energy (BE) and emits an photoelectron with kinetic energy (KE). Fig. 3.2.2 shows a schematic for the emission of electrons from the core orbital of the surface elements. The process can be explained based on the equation: $KE = h\nu - \phi_s - BE$ (where $h\nu$ is the energy of the incident radiation, KE is the kinetic energy of the photoelectron, $\phi_s$ is the work function of the instrument and BE is the binding energy of the orbital from which the electron is ejected). A typical XPS consists of an x-ray source and an electron energy analyzer to measure the KE of the emitted photoelectrons. Thus, from the measurement of the photoelectron KE, one can determine the electron BE, which is characteristic to the particular atom, and thus the corresponding atom can be identified. Furthermore, the BE gives the local chemical environment information of the specific surface elements. Any shift observed in the peak position reflects a change in electron valence state of elements. The intensity can be correlated with the concentration of electrons corresponding to the specific elements on the surface, such as the C 1s peak which was used as a reference for the spectrum analysis.

3.2.3 UV-Photoelectron spectroscopy (UPS)

In its principle of operation, the UV-Photoelectron spectroscopy (UPS) is similar to XPS, in that a surface is irradiated with the photons and the energies of the ejected photoelectrons are analyzed. The physical relationship involved is the same as XPS, but in UPS the energy $h\nu$ of the exciting photons is much lower, because the photons are derived from a gaseous discharge that produces hard UV radiation. The gas normally used is helium, which, depending on pressure conditions in the discharge, will provide line source of energy 21.21 eV (He I) or
40.82 eV (He II) with very narrow line-widths (~20 meV). In this research, the He I (21.21 eV) was used. Because of these low exciting energies, the BE do not refer to core levels, as in XPS, but to shallow valence-band levels and to other shallow levels, such as those for adsorbates, near the valence bands.

Because only the photoelectrons whose kinetic energy is higher than the work function Φ of a sample can escape from the surface, consequently, Φ can be determined in photoemission by the difference between the photon energy and the width of the spectrum. The width of the photoemission spectrum is given by the energetic separation of the high binding energy (secondary electron) cutoff and the Fermi energy. In this context, possible shifts of the cutoff and thus of the vacuum level suggest the formation of an interfacial dipole layer Δ. In photoemission spectroscopy, electrons from occupied states are excited above the vacuum level and can thus escape from the sample. In a first approximation, the measured kinetic energy ($E_{kin}$) allows the determination of the binding energy ($E_B$) of the photoelectron via a simple equation: $E_B = h\nu - E_{kin} - \phi_{SP}$ where $h\nu$ is the photon energy and $\phi_{SP}$ is a spectrometer specific constant, the work function of the spectrometer. The spectrum is calibrated in a way that the Fermi level is located at 0 eV binding energy. The Fermi level (or “edge”) manifests itself as a step, since it separates occupied and empty states (photoemission spectroscopy works only with occupied states, since there need to be electron that can be photoemitted, i.e. states above the Fermi level do not emit electrons). Then there is the high binding energy cutoff (or “secondary edge”), where the spectrum ends. Since we know the binding energy of the electrons right at the secondary edge, we can determine the work function, which is just the difference between the energy of the UV photons (21.2 eV for He I radiation) and the binding energy of the secondary edge.
Angle-resolved photoemission spectroscopy (ARPES), also known as ARUPS (angle-resolved ultraviolet photoemission spectroscopy), is a direct experimental technique to observe the distribution of the electrons (more precisely, the density of single-particle electronic excitations) in the reciprocal space of solids. ARPES is one of the most direct methods of studying the electronic structure of the surface of solids where it provides the information on the direction, speed and scattering process of valence electrons in the sample being studied (usually a solid). The photoelectrons are stimulated by incident photons and escape into the vacuum, where they are counted by an angle-resolved electron energy analyzer. Collected photoelectron energies are characterized by a finite acceptance angle, allowing one to measure kinetic energy of the emitted electrons for a given emission angle. This means that information can be gained on both the energy and momentum of an electron, resulting in detailed information on band dispersion and Fermi surface. This technique is a refinement of ordinary photoemission spectroscopy.

![Diagram of photoemission process](image)

Fig. 3.2.2 The discs represent electrons and the bars represent energy levels within the material being analyzed [11].
3.2.4 Scanning/Transmission Electron Microscopy (STEM/TEM)

The principle of electron microscopy is based on the fact that electron wavelengths in the order of atomic dimensions can be used to observe microscopic features with a very high resolution. For atomic scale characterization and exact orientation relationship, Transmission Electron Microscopy (TEM) is the most effective and direct technique available. TEM can also be used to investigate defects such as dislocations and their burgers vectors, stacking faults, twins and precipitates. For this purpose, we used a JEOL 2010F transmission electron microscope with a point-to-point resolution of 1.8 Å. A Gatan imaging filtering system was used for HRTEM. The image resolution of TEM can be related to the Rayleigh criterion for light microscopy. It states that the smallest distance that can be resolved, δ, is given approximately by the equation δ = 0.61λ/μsinβ, where λ is the wavelength of the radiation, μ is the refractive index of the medium, and β is the semi-angle of collection the magnifying lens. The smaller the wavelength the better is the resolution. Hence resolution obtained in a TEM is in the order of few angstroms, i.e. atomic level resolution. Further, from DeBroglie’s equation, λ ~ 1.22/E^{1/2}, where E is the energy of the electron in eV, the λ is wavelength in nm. Hence, we can obtain electrons with very small wavelengths by increasing the energy. Essentially, a TEM consists of two main components; the illumination system and the imaging system. The illumination system consists of the electron gun and electromagnetic lenses that focus the beam onto the sample.\textsuperscript{10, 11} The electron beam interacts with the specimen. The imaging system detects the scattered electrons to form the image/diffraction pattern. The important TEM techniques used in this study were; diffraction, bright field imaging and high resolution TEM.

Diffraction: The TEM operates in two modes; the diffraction mode and the image mode. Diffraction patterns can be formed on the screen by placing the back focal plane on the
objective plane of the intermediate and projector lens. For thin samples information obtained in the diffraction mode is mainly from elastically scattered electrons. Since the electron wavelength is small, the Ewald sphere will have a large radius. Consequently, almost a plane section of the reciprocal lattice (zero order Laue zone) is observed during electron diffraction. Generally, a parallel beam of electrons is used for diffraction (selected area diffraction). Single crystal samples scatter the electron coherently and thus produce a spot diffraction pattern. Polycrystalline samples produce ring-like patterns. Sample with nano-sized grains produce spotty discontinuous rings. The diffraction pattern of an amorphous sample will show a diffused ring.

Imaging: Bright field imaging is done using the transmitted beam of electrons. This is done by inserting the objective aperture in the back focal plane (the plane where the diffracted image is formed). The objective aperture then allows only the transmitted beam through for bright field imaging. The dark field imaging is done when the diffracted beam is allowed to pass and the transmitted beam is blocked. The best contrast is obtained in a two beam condition. In this condition, the sample is titled such that only one diffracted beam is strong enough to remain. Essentially, two spots remain in the diffraction pattern: the central transmitted spot and another strong diffraction spot with a known g-vector. If the objective aperture is placed on the central spot, we obtain a bright field image. If the sample is tilted such that the diffracted beam passes through the aperture, then we obtain a dark field image.

HRTEM: This technique allows lattice imaging of the sample. Here, atomic level resolution is obtained by allowing many beams to pass through the objective aperture. The diffracted beams interfere with the direct beam resulting in a phase contrast. This phase contrast contributes to a high resolution TEM image. For proper analysis of a HRTEM image the
sample should tilted to an exact zone. Choosing the proper defocus condition (based on the contrast transfer condition) is also of prime importance for good resolution of a HRTEM image. A first Scherzer defocus condition with minimal objective lens astigmatism is used to obtain a good HRTEM image.

The STEM high-angle annular dark-field (HAADF) images are taken by using an aberration-corrected FEI Titan G2 microscope operated at 200 kV. The image contrast in HAADF is proportional to the atomic number ($Z$), the material density or the sample thickness, enabling us to detect different phases in the microstructure. The probe size, the convergence angle and the collection inner semi-angel are 0.1 nm, 21 mrad and 77 mrad, respectively.

### 3.3 Magnetic, Electric and Magneto-transport Characterization Techniques

#### 3.3.1 Superconducting Quantum Interference Device (SQUID)

Several methods are used to measure the magnetic behavior of materials. Among the measurement tools, vibrating-sample magnetometer (VSM) and superconducting quantum interference devices (SQUID) are most commonly used due to their high precision and sensitivity to measure the magnetization of the very small mass specimens and weak magnetic behavior. A SQUID is capable of measuring very small changes in magnetic field with higher sensitivity than VSM; as low as $10^{-7}$ emu. In a SQUID devices, the work mechanism is based on the tunneling of superconducting electrons across the insulating gap (Josephson junction). The great sensitivity of a SQUID is associated with change of flux when a sample moves through superconducting magnetic coils. A measurement is performed by moving the sample through the superconducting detection coils using a vibrating sample magnetometer. This will induce a flux change in the Josephson junction, which acts as a detection coil. As the Josephson junction is under constant current bias, an induced flux change will induce a change of the persistent current proportional to the change in flux. Due to the quantization of flux, this
relationship is very linear, allowing for great accuracy of the measurement\textsuperscript{12-14}. In this research, the SQUID is operated at the temperature range between 5 K and 300 K, and the magnetic fields is up to 1 Tesla.

### 3.3.2 Physical Properties Measurement System (PPMS)

Physical Property Measurement System (PPMS) is a versatile instrument offering the options for measuring a large variety of physical properties, which is manufactured by Quantum Design. The PPMS is a liquid helium cooled, temperature and field variable system capable of doing a number of thermal and electrical measurements. The system can generate magnetic fields between ±9 Tesla and temperatures between 1.9 and 400K. It is computer controlled and data can be viewed via a computer in real-time. The PPMS is composed of a standard dewar with a liquid helium bath in which a probe is immersed. The probe is capable of temperature control and is composed of a superconducting magnet, a sample puck connector and electrical connections. The sample chamber is inside a vacuum tube base has 12-pin connector that connects to sample puck and a vacuum pump continuously pumps sample chamber. Resistivity, Hall Effect and magnetotransport measurements were performed in the PPMS for this research.
3.4 References

Chapter 4 Epitaxial integration of dilute magnetic semiconductor Sr3SnO with Si (001)

In this chapter, we report the epitaxial thin films heterostructures of topological insulator candidate Sr3SnO (SSO) are grown on a cubic yttria-stabilized zirconia (c-YSZ) / Si (001) platform by pulsed laser deposition. X-ray and electron diffraction patterns confirm the epitaxial nature of the layers with cube-on-cube orientation relationship: (001)[100]SSO∥(001)[100]c-YSZ∥(001)[100]Si. The temperature dependent electrical resistivity shows semiconductor behavior with a transport mechanism following the variable-range-hopping model. The SSO films show room-temperature ferromagnetism with a high saturation magnetization, and a finite non-zero coercivity persisting up to room temperature. These results indicate that SSO is a potential dilute magnetic semiconductor, presumably obtained by controlled introduction of intrinsic defects.
4.1 Introduction

Topological insulators (TIs) are an exciting class of materials with unique properties making them potentially useful in high speed, low power digital devices, quantum computing and spintronics. The primary defining characteristic of a TI is that while its bulk is insulating, its surfaces are highly conductive, owing to the presence of a finite energy band gap\textsuperscript{1-4} and gapless surface states that result from strong spin-orbit coupling (SOC). The exciting feature is that these surface states are immune to non-magnetic defects, which makes their transport efficient and robust. Angle-resolved photoemission spectroscopy (ARPES) measurements on bulk single crystals of Bi\textsubscript{x}Sb\textsubscript{1-x}, Bi\textsubscript{2}Se\textsubscript{3}, and Bi\textsubscript{2}Te\textsubscript{3} have verified the existence of the 3D TI phase, which resulted in a tremendous surge of interest\textsuperscript{5-9}. Identification of candidate TI materials is one of the most critical issues of this field. Materials with heavy elements produce large SOC which result in the semi-metallic topologically protected surface states.

Using massive computing and data-mining of electronic structures, Klintenberg has identified a number of oxides with the required band-inversion at the \textGamma-point in the presence of SOC\textsuperscript{[10]}. One group of oxides identified belongs to the CaTiO\textsubscript{3} (perovskite) structure type from a class of inverse perovskites; Sr\textsubscript{3}SnO (SSO) is one such oxide. According to theoretical calculations, SSO crystallizes in the cubic system with space group Pm3m and a theoretical unit cell of 5.12 Ǻ. SSO has an indirect local density approximation (LDA) band gap of 0.1 eV throughout the Brillouin zone\textsuperscript{10}.

The focus of the current work is the epitaxial integration of SSO with the technologically important substrate Si (001), and exploring the electrical and magnetic properties of SSO for possible spintronics applications. In this letter, epitaxial c-YSZ buffer layers are used to enable integration of high-quality epitaxial SSO thin films with Si (001) through pulsed laser
deposition (PLD). The SSO/c-YSZ/Si (100) heterostructure is found to be an intrinsic semiconductor with ferromagnetism at room temperature, resulting from intrinsic defects without the presence of extrinsic magnetic elements.

4.2 Experimental Details

The SSO/c-YSZ/Si (001) thin film heterostructures were grown in a multitarget PLD deposition chamber (base pressure= 1×10^{-6}) by sequentially ablating YSZ (5 mole% Y_{2}O_{3}), SnO_{2} and SrO targets using LPX 100 KrF excimer laser (λ= 248nm, τ= 25ns). The energy density and repetition rate were kept at 3–3.5 J/cm^{2} and 5 Hz, respectively, and the target-substrate distance was maintained at 40mm during deposition. The Si (001) substrates were cleaned ultrasonically in acetone and methanol. First, the c-YSZ buffer layer is deposited at a substrate temperature of 750 °C; using 500 pulses under a base pressure and subsequently 1000 pulses in a 5.5×10^{-4} Torr oxygen partial pressure. A c-YSZ thin film can be grown on Si (001) even without etching the native oxide layer with hydrofluoric acid. This layer of native oxide is etched away and removed by a zirconium-rich flux during early stages of deposition. This is explained on the basis of following reaction: Zr + 2SiO_{2} → ZrO_{2} + 2SiOx. The SiO_{x} that formed is quite volatile and evaporates at the deposition temperature used in the present study (750°C). Subsequently, the temperature of the grown c-YSZ platform is set at the SSO deposition temperature, the oxygen partial pressure is increased to 5×10^{-3} Torr, and the SSO deposition begins. Stoichiometry control requires alternating laser pulses, for example, 15 pulses of the SrO target and 3 pulses of the SnO_{2} target, for a 5:1 ratio. 100 repetitions of the cycles are carried out to complete the deposition. This pulse ratio provides in-situ control of the desired phase formation and stoichiometry. The pulse ratio and oxygen partial pressure are optimized to obtain stoichiometric single crystal SSO films. The films are then annealed inside
the PLD chamber at 750 °C under 1×10^{-1} Torr oxygen pressure for 3 hours, facilitating the diffusion and reaction of each layer and the formation, of high quality SSO films.

The structure of the films is characterized by XRD θ-2θ scans at room temperature using a Rigaku x-ray diffractometer with Cu Ka radiation (λ= 1.5418Å) to examine the out-of-plane orientation. The in-plane orientation is evaluated by φ-scanning XRD in a Panalytical Empyrean X-ray diffractometer with a Xe-proportional counter as detector. Microstructural analysis is performed using a JEOL-2000 FX transmission electron microscope (TEM). Selected area electron diffraction (SAED) from cross-section samples is used to confirm the single crystalline growth and the epitaxial relationships. The temperature dependent electrical resistivity is measured by the four-probe dc method using a Keithley 6221 current source and 2182A nano-voltmeter in the temperature range of 5K-285K. Magnetic hysteresis measurements are performed by sweeping the magnetic field from -10 to +10 kOe at temperatures ranging from 5K to 300K using a Quantum Design superconducting quantum interference device (SQUID) magnetometer.

**4.3 Results and Discussions**

Fig. 4.1 (a) shows the θ-2θ XRD patterns of the SSO/c-YSZ/Si (001) heterostructure SrO to SnO₂ pulse ratios of 3:1, 4:1 and 5:1 under the oxygen partial pressure of 1×10^{-4} Torr. When the SrO to SnO₂ pulse ratio is 3:1, the observed peaks are attributed to Sr₂SnO₄ in the XRD pattern and the Sr₂SnO₄ phase is in a single orientation such that Sr₂SnO₄ (110) [ICSD Number: 27114] planes are orientated parallel to c-YSZ (001) planes. When the SrO to SnO₂ pulse ratio is increased to 4:1, the Sr₂SnO₄ (110) orientation is diminished as the (200) orientation appears and grows. As the ratio is increased to 5:1, the Sr₂SnO₄ (110) orientation disappears while a weak (200) peak remains. This shows a high degree of out-of-plane preferential growth of SSO.
in the [001] direction based on the c-YSZ/Si (001) platform. This is understood as a result of the significant boiling point difference between metallic Sr and Sn. It is generally accepted that the fast heating of the target surface by the intense laser results in temperatures greater than 5000 K within a few ns.\textsuperscript{14-15} The boiling point of Sr is only half of that of Sn, so during the ablation process most of the Sr will evaporate due to its low boiling point. Furthermore, if there is insufficient oxygen during deposition, then metallic Sr is presumably lost.

Fig. 4.1(b) shows the effect of oxygen partial pressure for the 5:1 pulse ratio. As the oxygen partial pressure increases, the Sr\textsubscript{2}SnO\textsubscript{4} (200) orientations decrease. For an oxygen partial pressure of 5×10\textsuperscript{-3} Torr, only the SSO phase is found and both c-YSZ and SSO exhibit single crystallographic peaks, suggesting single-phase epitaxial growth on the (001) plane Si substrates. The effect of oxygen partial pressure on the Sr\textsubscript{2}SnO\textsubscript{4} (200) diffraction peak is clearly seen in Fig. 4.1(c) supporting the key role of oxygen as an oxidizing agent to help form and stabilize the desired crystalline phase at the deposition temperature.
Fig. 4.1 θ-2θ XRD pattern of SSO on a c-YSZ/Si(001) heterostructure (a) under different pulse ratio; (b) under different oxygen partial pressure and (c) Sr$_2$SnO$_4$ (200) peak under different oxygen partial pressure.

Fig. 4.2 displays the θ-2θ XRD pattern of the SSO/c-YSZ/Si (001) heterostructure; the SSO is grown at 750°C, the SrO to SnO$_2$ pulse ratio is 15:3, the oxygen partial pressure is 5×10$^{-3}$
Torr and the film is annealed inside the PLD chamber at the same temperature under $1 \times 10^{-1}$ Torr oxygen pressure for 3 hours after deposition. The films are highly textured or epitaxial with [001] as the preferred orientation. No additional peaks are observed, excluding the possibility of the formation of other phases. The intense peak at the diffraction angle of about $34.5^\circ$ is assigned to c-YSZ (002) and the SSO (002) reflections owing to their virtually the same $2\theta$ values ($34.76^\circ$ or c-YSZ and $34.88^\circ$ for SSO). The high resolution XRD scan, seen in the inset of Fig. 4.2, delineates the two separate peaks which are identified as c-YSZ (002) and SSO (002) planes. In addition, second-order (004) c-YSZ and (004) SSO peaks are observed. These symmetry peaks are aligned with (004) silicon diffraction, suggesting that both c-YSZ and SSO are highly textured or epitaxial films. The calculated d spacing from the XRD pattern for SSO (002) and c-YSZ (002) are 0.2572 and 0.2580 nm, respectively, so the lattice mismatch is about 0.311%. The d spacing for the Si (002) substrate is 0.2714 nm, so the lattice misfit between c-YSZ and the Si substrate is about 5.042%.
Fig. 4.2 XRD pattern of the epitaxial SSO film grown on c-YSZ/Si(001) at 750 °C, O₂ pressure of 5×10⁻³ Torr, SrO to SnO₂ pulses ratio 15:3 and annealed inside the PLD chamber at the same temperature under 1×10⁻¹ oxygen pressure for 3 hours (inset: the high resolution XRD scan)

Fig. 4.3(a) shows a high resolution cross-sectional image of the SrO/SnO₂ multi-layered structure on a c-YSZ substrate. Here we observe distinct SrO and SnO₂ layers as-deposited; the layers are distinct due to the lack of an in-situ annealing process. The thicker (~4 nm) and thinner (~2.5 nm) layers correspond to SrO and SnO₂, respectively. Note that the bright contrast is due to differences in the atomic number, i.e. high atomic number produces a darker contrast. Here a 5:1 ratio of SrO:SnO₂ pulses was used at 750 °C under 5×10⁻³ torr oxygen pressure. This is understood as a result of the significant boiling point difference between metallic Sr and Sn. The boiling point of Sr is half of that of Sn (Sr= 1382 °C and Sn= 2603 °C), so during the ablation process most of the Sr will evaporate. Therefore, more SrO pulses are
required to compensate for the loss of Sr, and high oxygen partial pressure is needed as an oxidizing agent to help form and stabilize the desired crystalline phase at the deposition temperature. Fig. 4.3(b) shows a high resolution image of the films after annealing in the PLD chamber at 750 °C under $1 \times 10^{-1}$ torr oxygen pressure for 3 h. The annealing process facilitates the diffusion between each layer and thus the formation of high quality SSO films. The SSO/YSZ interface is sharp; no evidence of interfacial reaction is observed.

Fig. 4.3 (a) Cross-sectional HRTEM image of multi-layered SrO/SnO$_2$ on a c-YSZ substrate; (b) cross-sectional HRTEM image of SSO/c-YSZ interface (inset: SAED pattern of the heterostructure).

XRD φ-scans were performed in order to obtain information about in-plane orientation for the SSO/c-YSZ/Si (001) heterostructure (Fig.4.4). The φ-scan is for the SSO (111) reflection ($2\theta=30.19^\circ$, $\psi=54.73^\circ$), the c-YSZ (111) reflection ($2\theta=30.07^\circ$, $\psi=54.73^\circ$), and the Si substrate (111) reflection ($2\theta=28.39^\circ$, $\psi=54.73^\circ$). The only growth orientations for the SSO, c-YSZ, and Si are (002), (002) and (004), respectively. The four-fold symmetry of the sharp
(111) reflections and coincidence with Si (111) peak φ-positions confirms the epitaxial growth of c-YSZ. The SSO (111) reflection peaks occurring at every 90° correspond to good alignment of a and b axes of the c-YSZ buffer for cube-on-cube orientation. Fig. 4.5 shows a low-magnification <110> bright-field cross-section TEM image of the epitaxial SSO (125nm) /c-YSZ (50nm) /Si (100) heterostructure. The corresponding growth rates of c-YSZ and SSO are found to be 0.4 Å and 0.6 Å per laser pulse. The SSO/c-YSZ interface is sharp; no evidence of any interfacial reaction is observed. The selected area electron diffraction (SAED) pattern (Fig. 4.5 inset) shows the diffraction spots from the Si [110] zone axis, indicating epitaxial growth, with an epitaxial relation described as SSO<110>∥c-YSZ<110>∥Si<110>. Only high-order diffractions from SSO and c-YSZ are distinguished due to the small difference in d-spacing, 0.2572 nm for SSO (002) and 0.2580 nm for c-YSZ (002). These results are consistent with details of the epitaxial relationship between c-YSZ and SSO obtained from φ-scan results.
Fig. 4.4 X-ray diffraction φ scans for SSO (111), c-YSZ (111) and Si (111) reflections.
Fig. 4.5 Low magnification cross-section of the complete heterostructure thin film. Dotted red line marks the interface between SSO and c-YSZ (inset: selected-area-diffraction pattern of SSO and c-YSZ films on Si (001), cross section of SSO[110]/c-YSZ[110] and Si [110] zone axis

The temperature dependent resistivity in the temperature range of 5 K-285 K is shown in Fig. 4.6. This figure clearly reveals that the resistivity increases gradually with decreasing temperature followed by a sharp rise as the sample is cooled further, suggesting typical semiconducting behavior. These results are analyzed using the variable range hopping (VRH) model, which best describes the conduction mechanism of SSO thin films. In the VRH model, \( \rho(T) = \rho_{\infty} \exp \left( \frac{T_0}{T} \right)^{s} \), where \( \rho_{\infty} \) depends on the phonon frequency and density, and, \( T_0 \) is the
characteristic temperature. The value of the exponent $s$ depends critically on the nature of hopping process.$^{16-17}$ The plot suggests that there are two types of transport mechanisms contributing to the resistivity. It is possible to separately find the best-fitting functions for the lower (up to 10 K) and higher (170 K – 285 K) temperature regions.

The low-temperature (LT) region displayed in the bottom left inset in Fig. 4.6 (a) is well fitted by the Efros and Shklovskii (ES) VRH law$^{18}$ shown as a straight line. It has been attributed to an electrostatic blockade of charge carriers between the grains with a grain charging energy $E_c$. The ES-VRH resistivity model is expressed as $\rho(T) = \exp\left[2(C/k_B T)^{1/2}\right]$, where $C \equiv E_c [13,14]$. The LT resistivity gives a satisfactory fit with a slope of 7.79 K$^{1/2}$ and the estimated $E_c$ is found to be 1.30 meV, comparable to values of 1.37 meV and 0.6 meV - 3.87 meV reported for other semiconducting oxides, such as SnO$_2$ and ZnO, respectively.$^{19-20}$

The high-temperature (HT) region shown in the top right inset Fig. 4.6 (b), reveals that the best fit is obtained for $s$ in the vicinity of 1/4, obeying the $\ln \rho \propto (1/T)^{1/4}$ relation, a signature of the Mott VRH law.$^{16}$ In the Mott VRH conduction theory, the characteristic temperature is defined by$^{21-23}$

$$T_0 = \frac{18}{k_B N_0(E_F) \xi^3}$$

(1)

where $N_0(E_F)$ is the electronic density of states (DOS) at the Fermi level in the absence of electron-electron interactions, and $\xi$ is the localization length of the relevant electronic wave function. The most probable hopping distance and the average hopping energy are, respectively, given by$^{21-23}$
\[
\overline{R}_{\text{hop,Mott}} = \frac{3}{8} \xi \left( \frac{T_0}{T} \right)^{\frac{1}{4}}
\]  

(2)

and

\[
\overline{W}_{\text{hop,Mott}} = \frac{1}{4} k_B T \left( \frac{T_0}{T} \right)^{\frac{1}{4}}
\]  

(3)

where \( \xi \sim 10^{-9} \text{m} \). Using the measured values of \( T_0 \), Mott hopping parameters, \( N_0(E_F) \), \( \overline{R}_{\text{hop,Mott}} \), \( \overline{W}_{\text{hop,Mott}} \) are calculated at 285 K as listed in Table I. Inspection of Table I reveals that the criteria for Mott VRH conduction, \( \overline{R}_{\text{hop,Mott}} \xi > 1 \) and \( \overline{W}_{\text{hop,Mott}} > kT \), are satisfied by the SSO thin films over the temperature range of 170 K - 285 K. This suggests that the temperature dependence of VRH conduction, which is a phonon-assisted quantum-mechanical tunneling process, governs the charge transport properties of SSO thin films.
Fig. 4.6 Resistivity as a function of temperature (5 K - 285 K). Bottom left inset (a): lnρ vs. $T^{-\frac{1}{2}}$ at low temperature (5 K - 10 K). Top right inset (b): lnρ vs. $T^{-\frac{1}{4}}$ at high temperature (170 K - 285 K) along with best fit results obtained by least-square fitting.
Table 4.7. Values of resistivity, and value of the Mott VRH conduction parameters obtained at 285 K

<table>
<thead>
<tr>
<th>$\rho_{RT}$ ($\Omega$-cm)</th>
<th>$T_0$ (K)</th>
<th>$N_0(E_F)$ m$^3$eV$^{-1}$</th>
<th>$R_{hop,Mott}$ (nm)</th>
<th>$W_{hop,Mott}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3x10$^{-2}$</td>
<td>9.31x10$^4$</td>
<td>2.24x10$^{27}$</td>
<td>1.59</td>
<td>26.1</td>
</tr>
</tbody>
</table>

Fig. 4.7 shows the magnetic hysteresis from -10 to +10 k Oe as a function of temperature. The diamagnetic contribution of the substrate and buffer has been subtracted and the magnetization starts to saturate at about 3500 Oe. The room temperature values of saturated magnetic moment and coercivity for SSO thin films are ~7.3 emu/cm$^3$ and 75 Oe, respectively. Plotted in the bottom inset are the enlarged M vs. H loops at low field (from -400 to +400 Oe) to decipher the presence of ferromagnetic behavior up to 300 K. The coercivity has decreased from ~180 Oe at 5 K to ~75 Oe at 300 K while the saturation moment shows the same trend, consistent with typical ferromagnetic behavior. The impurities were surveyed for in the time-of-flight secondary ion mass spectrometer (ToF-SIMS) analysis in these SSO samples are at too low concentration to account for the observed magnetic moment.

The combination of room temperature semiconducting and ferromagnetic features implies, that SSO is a potential dilute magnetic semiconductor (DMS). The room-temperature ferromagnetism (RTFM) and observed magnetic properties in the SSO system are attributed primarily to the intrinsic defects, and the observed ferromagnetic behavior might be interpreted using the framework involving defect-mediated long-range ferromagnetic ordering.$^{25}$ Due to this interaction, pure metal oxides with non-stoichiometric defects have been reported to show
the RTFM properties in, for example, ZnO and MgO systems\textsuperscript{,25} similar to the behavior observed in SSO.

Fig. 4.7 Isothermal field-dependent magnetization curves up to 10,000 Oe for the SSO thin film samples in the range 10 K – 300 K. For clarity, the bottom right inset plots the enlarged M-H loops in the range ± 400 Oe to show the hysteresis and coercivity in a more discernible way.

4.4 Conclusion

In summary, single-crystal TI candidate SSO films have been grown on silicon (001) substrates with c-YSZ as a template buffer layer using pulsed laser deposition. X-ray φ-scans demonstrated the heteroepitaxial relationship of deposited film as (001)[100]SSO∥(001)[100]c-YSZ∥(001)[100]Si. SAED from cross-sectional bright field
imaging of SSO/c-YSZ/Si (001) samples confirm these results. The resistivity as a function of temperature suggests that SSO is a semiconductor with charge transport governed by the VRH conduction mechanism. Moreover, the RTFM in SSO epitaxial films, possess a high saturation magnetization, and finite non-zero coercivity persisting up to room temperature. These results infer that SSO is not only a possible TI candidate, but also a potential DMS with tremendous potential in multifunctional device applications, related to spintronics.
4.5 Reference

Chapter 5 Oxygen vacancy enhanced room-temperature ferromagnetism in Sr$_3$SnO/c-YSZ/Si (001) heterostructures

The magnetic properties of Sr$_3$SnO (SSO) epitaxial thin films prepared under various post-growth annealing treatments are reported. The SSO films are grown on cubic yttria-stabilized zirconia Si (001) platform by pulsed laser deposition. Post-growth vacuum annealing is found to enhance the room-temperature ferromagnetism (RTFM), whereas oxygen annealing reduces it. The results are explained through the oxygen vacancy constituted bound magnetic polarons (BMP) model. An empirical relationship between the extracted BMP concentration and the oxygen vacancy concentration is shown using X-ray photoelectron spectroscopy data. The results indicate a promising way to tune RTFM by manipulating oxygen vacancies and related defects.
5.1 Introduction

The discovered TIs in three dimensions (3D) are non-magnetic insulators with time-reversal symmetry (TRS) protected by gapless surface states.\(^1\) It is important to break the TRS of TIs by combining external perpendicular ferromagnetic coupling envisaged for practical applications.\(^2\) A natural strategy to achieve this is through doping of transition metal (TM) elements with spin orientation out of the surface plane, as demonstrated by the success of dilute magnetic semiconductors (DMSs).\(^3\)

Introducing magnetic ions into TI materials is an effective way to generate robust magnetism and open a surface energy gap resulting in the emergence of massive Dirac fermions. Furthermore, precise, simultaneous control of magnetic, and charge doping can alter the Fermi-energy \((E_F)\) level inside the Dirac gap.\(^4\)\(^-\)\(^5\) By using TM elements, such as Cr and Fe, the 3D TIs Bi\(_2\)Te\(_3\), Bi\(_2\)Se\(_3\), and Sb\(_2\)Te\(_3\) have become magnetically ordered insulators. The ferromagnetic moments resulting from TM-doped TI systems has been theoretically proposed through the van Vleck mechanism and the Ruderman–Kittel–Kasuya–Yosida mechanism.\(^6\)

Based on these peculiar properties and interesting phenomenon, the intricate interplay between topological order and ferromagnetism (FM) is expected to give rise to a variety of unconventional effects that may lead to new device paradigms.\(^4\)\(^-\)\(^7\)

Recently, many undoped oxides, such as ZnO, TiO\(_2\), In\(_2\)O\(_3\), SnO\(_2\), and HfO\(_2\), have been reported to show FM features, although the origin of such FM is not well understood. The most plausible origin of such FM properties in otherwise non-magnetic oxides is defects, such as strain and non-equilibrium point defects inferred to be oxygen vacancies, cation vacancies and interstitials, which result directly from processing.\(^8\)\(^-\)\(^10\) In TiO\(_2\) and HfO\(_2\), FM has been attributed to the presence of oxygen vacancies, which are presumed to behave as an n-type
dopant, and the existing vacancies tailor the physical properties of the films.\textsuperscript{11-12} In ZnO, RTFM arises from unpaired electrons of oxygen atoms around the Zn vacancies, whereas carrier concentrations are derived from oxygen vacancies and Zn interstitial complexes.\textsuperscript{13}

Sr\textsubscript{3}SnO (SSO) has been identified by Klintenberg as a potential TI material with the required band-inversion at the $\Gamma$-point in the presence of spin orbital coupling (SOC).\textsuperscript{14} Recently, we reported that, even in the absence of TM ions, single crystal SSO thin films are DMSs with RTFM.\textsuperscript{15} In the current work, we unravel the origin of RTFM in SSO and show a clear relationship between RTFM and oxygen vacancies. In particular, we find that post-growth vacuum annealing (VA) enhances the RTFM whereas oxygen annealing (OA) degrades it.

The primary focus of this study is to elucidate the origin of RTFM in expitaxial SSO single crystal thin films through measurements of the impact of different post-growth annealing treatments on magnetic properties. X-ray photoelectron spectroscopy (XPS) and superconducting quantum interference device (SQUID) magnetization data indicate that the intrinsic point defects associated with oxygen vacancies are the most promising candidates to manifest RTFM in this system. As a consequence, it is postulated that large concentrations of intrinsic defects form an impurity band that is the source of d\textsuperscript{0} magnetism. The observed RTFM in SSO thin films is interpreted in terms of a bound magnetic polaron (BMP) model, where an impurity band resulting from oxygen vacancies locally trap electrons that occupy an orbital overlapping the surrounding magnetic moments.

5.2 Experimental Details

The structure of the SSO films is characterized by XRD $\theta$-$2\theta$ scans using a Rigaku x-ray diffractometer with Cu Ka radiation ($\lambda = 0.15418$ nm). Microstructural analysis is performed
using a JEOL-2010 field-emission high resolution transmission electron microscope (HR-TEM). X-ray photoelectron spectroscopy (XPS) is employed on a SPECS FlexMod equipped with an Al Kα monochromatic x-ray source (1486.7 eV) to clarify contamination concerns, characterize the surface state and estimate the oxygen vacancy content within the SSO thin films. The magnetic properties of three SSO films, one as-grown (pristine), one oxygen annealed (OA) post-growth, and one vacuum annealed (VA) post-growth, are measured using a Quantum Design SQUID magnetometer. Oxygen annealing is performed at 750 °C under full oxygen ambient (~760 torr) for 3 hours whereas vacuum annealing is performed at 750 °C for 3 hours at 5x10⁻⁶ torr. For the zero field cooled (ZFC) magnetic data, the sample is cooled to 5 K in the absence of magnetic field and the magnetization is measured while warming to 400 K in the presence of a 100 Oe magnetic field. The field cooled (FC) data is taken while warming the sample after cooling to 5 K in the presence of a 100 Oe field. Magnetization hysteresis is measured by sweeping the magnetic field from -1 T to +1 T at 300 K.

5.3 Results and Discussion

The in-plane magnetization hysteresis curves at 300 K for the three different sample types are shown in Fig. 5.1 (a); the diamagnetic background contribution has been subtracted. Clear saturation and hysteretic behaviors are observed, providing evidence of FM behavior at 300 K. The VA and OA samples show the largest and smallest saturation moments ($M_s$), respectively. The top left inset compares the coercivities ($H_c$) and $M_s$ for each sample, indicating that there is a significant enhancement in FM after VA. The bottom right inset shows the low-field portion of the magnetization hysteresis loops to delineate the FM behavior up to 300 K. During VA, oxygen vacancies migrate and form clusters in order to reduce the system energy, favoring a decrease in the strain free energy.¹⁶ Banerjee et al. demonstrated that the large moments can
be generated owing to oxygen vacancy clusters in un-doped ZnO. Coey et al. further proposed that oxygen vacancies can cause an obvious change of band structure of the host oxides and contributes significantly to the FM. According to the results shown here, the oxygen vacancies play a crucial role in tailoring the RTFM within the SSO system as well.

To gain additional insight, the temperature dependence of the magnetization has been studied through FC and ZFC measurements from 5 to 400 K; results are plotted in Fig. 5.1 (b). By taking the difference between these two quantities, $\Delta M = M_{\text{FC}} - M_{\text{ZFC}}$, the para- and diamagnetic contributions to the magnetization are subtracted, leaving only a measure of the hysteretic FM regime. The Curie temperature ($T_C$) of all samples is above 300 K. The pristine and VA samples display non-zero magnetization up to 400 K, implying a robust FM signature. The OA sample shows nearly zero magnetization at ~ 320 K. Thus, the thermo-remanent magnetization ($\Delta M$) has been enhanced significantly by VA as compared to OA in the entire temperature range. For the VA sample, which has the largest $H_c$ and $M_s$, the separation between the FC and ZFC data exists at a higher temperature, as seen in the Fig. 5.1 (b) inset. This is consistent with the presence of FM ordering and suggests that the enhanced FM upon VA is directly related to the creation of additional oxygen vacancies. The quantification of oxygen vacancies as analyzed by XPS O1s spectra is discussed below.
Fig. 5.1(a) Room-temperature magnetization hysteresis of pure SSO films under different post-growth annealing treatments. Inset (top left) compares of $H_c$ and $M_s$ under different treatments. Inset (right bottom) is the enlarged $M$–$H$ loops for $-0.04$ to $+0.04$ T, showing the hysteresis and coercivity more clearly. (b) Temperature dependence of the difference in magnetization between FC and ZFC for oxygen-annealed, pristine, and vacuum-annealed samples. The inset is the temperature dependence of the magnetization under a 100-Oe applied field.
Several mechanisms have been proposed to explain the origin of FM in DMSs. In addition to the magnetic doping effect, oxygen vacancies have been suggested as the origin of the magnetic behavior. An oxygen vacancy can catch an itinerant electron to form a “hydrogen-like” orbit with a finite radius and become a distorted oxygen vacancy O$^+$ site in the absence of applied electric field or doping. A polaron is a quasiparticle formed by a charged particle, such as an oxygen vacancy defect, and the resulting lattice polarization phonon field. The results here indicate that the oxygen vacancy constituted BMP model is a promising candidate for explaining the origin of RTFM in SSO. A clear magnetization hysteresis loop, with enhanced $M_s$ and $H_c$, is observed in the VA sample due to the increased concentration of oxygen vacancies. In the BMP model, oxygen vacancies are responsible for the shallow donors and strongly stabilize the ferromagnetic ground state. An electron associated with a donor defect, such as an oxygen vacancy, is confined in a hydrogenic orbit. As more oxygen vacancies are produced during VA, more electrons become bound to the oxygen vacancies. To maintain the local charge balance and stabilize the structure, other point defects such as cation interstitials or vacancies, are generated. As a result, the greater density of oxygen vacancies leads to more interactions with the host lattice environment for charge redistribution and produces more overlapping BMPs and more percolation, thereby enhancing the FM strength.

To better determine the suitability of the BMP model to the observed data, the M versus H data was fit to the BMP model following Chiorescu et al. According to the BMP model, the measured magnetization

$$M = M_0 L(\chi) + \chi_m H,$$

(4)

where the first term on the right hand side is the BMP contribution and the second term is the paramagnetic matrix contribution. Here, $M_0 = Nm_s$, where N is the number of BMPs involved.
and $m_s$ is the effective spontaneous moment per BMP. $L(\chi) = \coth (\chi) - 1/\chi$ is the Langevin function with $\chi = m_{\text{eff}} H / (k_B T)$, where $m_{\text{eff}}$ is the true spontaneous moment per BMP which, at higher temperature, can be approximated as $m_s = m_{\text{eff}}$. Thus, for a good approximation, the M-H data can be analyzed in terms of Eq. (4), with $M_0$, $m_{\text{eff}}$, and $\chi_{m}$ used as fitting parameters. The experimental data along with fitted data are shown in Fig. 5.2 for the OA, pristine and VA samples at 300 K. The resulting fitted curves closely follow the experimental data and the extracted parameters are tabulated in Table 5.2. The total BMP magnetization $M_0$ values are found to be of the order of 3-8 emu/cm$^3$. For the VA sample, $M_0$ is found to be the highest; this is due to higher oxygen vacancy concentration. The spontaneous moment per BMP, $m_{\text{eff}}$, is found to be of the order of $10^{-19}$ emu. Assuming $m_s = m_{\text{eff}}$, the BMP concentration is estimated to be of the order of $10^{19}$ cm$^{-3}$. The BMP concentration follows the trend of VA > pristine > OA, in accordance with $M_0$ values. The values are reasonable as compared to the required concentration of BMPs in order to percolate through a ZnO lattice ($\sim 10^{20}$ cm$^{-3}$).
Fig. 5.2 Initial portion of the M–H curve fitted with the BMP model [Eq. (4)] for (a) oxygen-annealed, (b) pristine, and (c) vacuum-annealed samples. The symbols are the experimental...
data and the solid lines are the fit using the BMP model. Extracted parameters are shown in Table 5.2.

Table 5.2: Fitting parameters extracted from the bound magnetic polarons model at 300 K

|                  | $M_0$ (emu/cm$^3$) | $m_{\text{eff}}$ (emu) | $\chi_m$     | $N$ (cm$^{-3}$) |
|------------------|---------------------|------------------------|--------------|----------------|--------------|
| Oxygen annealed  | 3.79                | $2.07 \times 10^{-19}$ | $7.73 \times 10^{-6}$ | $1.83 \times 10^{19}$ |
| Pristine         | 6.54                | $2.98 \times 10^{-19}$ | $6.88 \times 10^{-6}$  | $2.19 \times 10^{19}$ |
| Vacuum annealed  | 8.86                | $3.36 \times 10^{-19}$ | $4.27 \times 10^{-6}$  | $2.64 \times 10^{19}$ |

The oxygen vacancy concentrations are quantified using XPS spectra. The XPS survey spectra of the pristine sample is shown in Fig. 5.3 (a), indicating that Sr, Sn and O are the only elements observed, except for a small amount of environmental C; no additional peaks are detected. All peaks reported are charge corrected using the C 1s peak position at 284.5 eV as a reference point. Fig. 5.3 (b) shows the high-resolution O 1s XPS spectra of VA and OA samples. In both cases, the O 1s peak shows broad, asymmetric peaks that are fitted with two Gaussian peaks, indicative of two different oxygen contributions. The main emission peak (O$_\text{II}$) is detected at $\sim$ 529.4 eV and the accompanied smaller shoulder peak (O$_\text{I}$) is at $\sim$ 531.4 eV. The first peak is commonly ascribed to lattice oxygen$^{24}$, whereas Chung et al.$^{25}$ found that the peak around 530.7-531.6 eV is caused by oxygen inside a nonstoichiometric oxide within the surface region of the material; these are oxygen vacancies. Although it is not possible to convert the XPS data to precise values for the oxygen vacancy concentrations, the relative areas beneath the peaks are meaningful. The ratio between the areas under the two peaks,
$A(O_{I})/A(O_{II})$, are 0.18 and 0.14 for the VA and OA samples, respectively, and the ratio of the lattice oxygen peaks for each sample, $A(O_{II})_{VA}/A(O_{II})_{OA}$, is 0.96. Thus, oxygen vacancy concentration increases as the lattice oxygen peak decreases, providing evidence of a non-stoichiometric trend due to oxygen vacancy creation from vacuum annealing.

Quantitative values of the oxygen vacancy concentration, estimated from the O 1s peak, show a proportional correlation with the extracted BMP density. As the oxygen vacancy concentration increases, the number of trapped electrons and polarons also increases. The relative oxygen vacancy concentration is in accord with the changes in $M_s$, giving direct correlational evidence that the origin of RTFM may be oxygen vacancies.
Fig. 5.3 (a) XPS survey spectra of a pristine SSO thin film and (b) XPS high-resolution scan of the oxygen 1s peak for vacuum-annealed and oxygen-annealed SSO films. The O 1s spectra are decomposed into a main peak ($O_{II}$) and a shoulder peak ($O_{I}$).
5.4 Summary

In summary, the magnetic properties of single crystal TI candidate SSO thin films have been found to strongly depend on post-growth annealing treatments. Vacuum annealing enhances Ms and Hc while oxygen annealing degrades both properties. The difference between the effects of vacuum and oxygen annealing, supported by the XPS measurements of the oxygen vacancy concentration, indicate that the RTFM is not due to a magnetic impurity but rather due to the oxygen vacancy concentration. Furthermore, the results are explained quantitatively through the bound magnetic polarons model. A linearly proportional correlation is found between the extracted densities of BMP to the XPS O 1s values. These findings provide insight into defect-engineered RTFM of pure SSO and constitute an important step for development of practical spintronic devices.
5.5 References


Chapter 6 Tunable electronic structure in Sr$_3$SnO/c-YSZ/Si (001) heterostructures

In this chapter, we report a systematic study of the structural, physical and chemical behaviors of epitaxial thin films of emerging dilute magnetic semiconductor (DMS) Sr$_3$SnO (SSO) integrated with Si (100) prepared by various post-growth annealing treatments. The transport properties of these films are primarily governed by oxygen vacancies and the results are explained with the variable-range hopping model. The increased oxygen vacancy concentration generated by post-growth vacuum annealing results in a shorter hopping distance and reduced hopping energy and Coulomb gap, leading to lower resistivity; oxygen annealing shows the opposite effects. The work function ranges from 4.54 to 4.02 eV and shows a negative linear relationship with oxygen vacancy concentration, accompanied by a 0.42 eV shift in the surface Fermi level. The transport and ultraviolet photoelectron spectroscopy probes agree quantitatively on measurement of the resistivity and surface electronic structure. The results provide a direct and consistent explanation that the property changes in the bulk and at the surface are primarily attributed to oxygen vacancies, which are believed to be the carriers in the SSO thin films. The ability to manipulate the work function and oxygen vacancy concentration in epitaxial DMS SSO thin films offers great potential for the development of spintronic devices.
6.1 Introduction

The anti-perovskite structure is based on the reverse occupancy of metal and nonmetal elements in cubic corner and body center positions. Materials with the anti-perovskite structure exhibit a wide range of interesting physical properties, including superconductivity\(^1\), giant magnetoresistivity\(^2\), negative thermal expansion\(^3\), and the magnetocaloric effect\(^4\) effect due to the cooperative interactions among lattice, spin, and charge degrees of freedom. Early research indicates that the physical properties of these materials arises primarily from the complex magnetostructure and the induced variable band structure\(^5\). Klintenberg, using massive computing and data-mining of electronic structures, has identified oxides with the anti-perovskite structure having the band-inversion at the \(\Gamma\)-point in the presence of strong spin-orbit coupling (SOC)\(^6\); one such oxide is \(\text{Sr}_3\text{SnO}\) (SSO). The strong SOC interaction could induce band inversion which is a key ingredient of a topologically nontrivial material, characterizing as band insulators with gapless linear energy dispersion surface states\(^7\). More recently, Hsieh \textit{et al.}\(^8\) reported first-principles calculations of the SSO band structure and find that it lies very close to the topological phase transition point and not belonging to the inverted regime with opposite orderings of the d and p orbitals.

Recently, SSO has also been identified as a dilute magnetic semiconductor (DMS) material exhibiting a Curie temperature above 300 K\(^9\). SSO crystallizes in the cubic system with a band gap of \(~0.1\) eV and with room-temperature ferromagnetism (RTFM) that can be manipulated by engineering and controlling intrinsic defects\(^6,9\). For example, it has been shown that the RTFM in SSO can be tuned by manipulating oxygen vacancies and related defects. As the oxygen vacancy concentration increases, the magnetization increases monotonically, consistent with the oxygen vacancy bound magnetic polaron model\(^10\).
The integration of epitaxial SSO with mature Si technology is of key importance to realize its full potential in multifunctional device applications such as spintronics devices. Moreover, band alignment engineering of materials, which can be achieved by tuning the work function (Φ), is a main factor governing the electrical properties. For example, various surface treatments have been attempted to change the Φ for indium tin oxide (ITO) to reduce the hole injection barrier height for organic electroluminescence devices\textsuperscript{11}. Also, Φ tuning for metal gates on Hf-based gate dielectrics is paramount because it strongly affects the flat band voltage and threshold voltage shifts\textsuperscript{12}. Besides, the Φ difference at an electrode–insulator contact\textsuperscript{9} can give rise to the formation of electrical double layers, directly affecting the performance of field effect devices and the oxidation of the metallic contacts\textsuperscript{13}.

Here, significant changes in Φ in SSO thin films is achieved by varying the post-growth annealing treatment. The electrical and structural properties of SSO are studied systematically to understand the underlying physics of its properties. It is shown that the oxygen vacancy concentration plays a crucial role in controlling the electrical behavior. As the oxygen vacancy concentration increases, resistivity decreases. Analysis of the electrical transport properties shows that an increase in oxygen vacancy concentration decreases the Coulomb gap, the required hopping energy and hopping distance, facilitating electron hopping from one donor level to the other impurity level. Apart from the electronic structure, the shift in Φ also shows a strong dependence on the surface oxygen concentration. These results indicate that both the surface oxygen concentration and Φ increase with oxidation because the surface is rich in negatively charged oxygen and thus contributes to dipole formation.

The results clearly establish strong correlations between bulk and surface properties, as well as the variation of crystallinity, which can be attributed to the oxygen vacancy concentration.
Control and tuning of electronic transport, magnetic properties, work function and/or Fermi level is achieved by tailoring the intrinsic defects in SSO, enhancing its utility for practical applications.

6.2 Experimental Details

The SSO/c-YSZ/Si (001) thin-film heterostructures were grown in a multitarget PLD chamber (base pressure = 10^{-6} Torr). Ultraviolet pulses (25 ns) from a KrF excimer laser (λ=248 nm, 5 Hz repetition) were focused to sequentially ablate c-YSZ, SrO, and SnO_{2} targets. The SSO films require alternating laser pulses; here a 5:1 ratio of SrO:SnO_{2} pulses was used at 750 °C under 5 × 10^{-3} torr oxygen pressure. The films were then annealed within the PLD chamber at 750 °C under 1 × 10^{-1} torr oxygen pressure for 3 hours, facilitating diffusion and thus the formation of high quality SSO films. More details regarding sample preparation have been published previously^{9}.

The structure of the films is characterized by XRD θ-2θ scans using a Rigaku x-ray diffractometer with Cu Ka radiation (λ= 1.5418Å°). Microstructural analysis is performed using a JEOL-2010 field-emission high resolution transmission electron microscope (HRTEM), operated at 200 KV, equipped with a Gatan image filter tuning attachment which has a point-to-point resolution of 1.8 Å. Selected area electron diffraction (SAED) from cross-section samples is used to confirm the single crystalline growth and the epitaxial relationships.

The temperature dependence of the electrical resistivity is measured using a standard van der Pauw configuration with indium contacts on four square corners in a Quantum Design Physical Property Measurement System (PPMS) system. Oxygen annealing (OA) is performed at 750 °C under full oxygen ambient (~760 torr) for 3 hours whereas vacuum annealing (VA) is performed at 750 °C for 3 hours at 5×10^{-6} torr. The Ultraviolet Photoelectron Spectroscopy
(UPS) measurements were conducted in a SPECS FlexMod (UVS 300) ultraviolet photoelectron spectrometer equipped with a monochromatic He ultraviolet source He I (21.2 eV). A 5 V bias was applied to enhance the extraction of high binding energy (BE) electrons, and to successfully determine the energy of the high BE edge. The samples were mounted with Cu clips which electrically ground the film to reduce the possibility of any charging effects. All samples were referenced with a clean gold sample and a proper connection of the samples on the same stub ensured that the samples are in electronic equilibrium with the spectrometer.

**6.3 Results and Discussion**

Fig. 6.1 (a) displays the \( \theta-2\theta \) XRD pattern of the SSO/c-YSZ/Si (001) heterostructure from OA, pristine and VA samples. Both c-YSZ and SSO exhibit [001] preferred orientation single crystallographic peaks, suggesting highly textured films. Note that no additional peaks are observed for OA, pristine or VA samples, excluding the possibility of formation of any other phase. Fig. 6.1 (b) shows high-resolution XRD of the VA sample; both c-YSZ (002) and SSO (002) peaks shift to lower 2\( \theta \) compared to the bulk value. The nonstoichiometric SSO results from the interaction and exchange of oxygen with the surrounding gas atmosphere; i.e., oxygen vacancies form to satisfy thermodynamic equilibrium. Depending on the position of Fermi energy relative to the defect states associated with oxygen vacancies, these defects could be \( V_0^0 \), \( V_0^+ \) and \( V_0^{++} \), which are neutral, singly charged and doubly charged, based on the following equations:

\[
V_0^0 \rightleftharpoons V_0^+ + e^- \quad (5)
\]
\[
V_0^+ \rightleftharpoons V_0^{++} + e^- \quad (6)
\]
Though oxygen vacancies can produce either one or two electrons according to the oxygen partial pressure and temperature, here, we simply refer to oxygen vacancies. Fig. 6.1 (c) shows that the largest full width at half maximum (FWHM) and peak shift results from VA, suggesting that the lattice expansion is produced owing to the increase in concentration of intrinsic defects (presumably oxygen vacancies), and thus affects the elastic energy associated with lattice disorder. Alternatively, oxygen can diffuse into the film through OA and release the compressive stress originating from the intrinsic defects, contributing to the close 2θ value compared to bulk materials. Generally speaking, oxygen vacancies cause changes to the crystal structure to some extent, and, therefore one expects that the electrical properties will also be strongly affected since electrical behavior is usually influenced by the local lattice relaxation.
Fig. 6.1 (a) θ-2θ XRD pattern of the SSO/c-YSZ/Si (001) heterostructure for oxygen annealed (OA), pristine and vacuum annealed (VA) samples, (b) high-resolution XRD pattern for SSO (002) and c-YSZ (002) peak positions for three samples, with respect to their bulk values and (c) is the full width at half maximum and 2θ shift for each sample.

The temperature dependent resistivities for OA, pristine and VA samples in the temperature range 5 K – 285 K are shown in Fig. 6.2 (a). The resistivity of all samples decreases with
increasing temperature \((T)\), indicating semiconducting behavior. Note that c-YSZ is an electrical insulator and the resistivity of Si substrate is several orders-of-magnitude higher than that of SSO, so the resistivities measured by transport are dominated by the SSO; minimal current is transported in the other layers. The conduction mechanism of SSO thin films is best described using the variable range hopping (VRH) model, assuming a constant density of states (DOS) in a region extending to several \(k_B T\) around the Fermi energy \((E_F)\). The temperature dependence of the hopping resistivity \(\rho\) is given by the hopping relation, \(\rho(T) = \rho_\infty \exp \left( \frac{T_0}{T} \right)^s\), where \(\rho_\infty\) is associated with the phonon frequency and density and \(T_0\) is the characteristic temperature\(^{14}\). The value of the exponents, which indicates the nature of the hopping process, is critically dependent on the temperature range, the magnitude of the overlap of the wave function and the impurity bandwidth\(^{15}\). The data suggests that two transport mechanisms exist for all samples, one with \(s = 1/2\) and the other with \(s=1/4\). These are readily fit in the lower (up to 10 K) and higher (170 K – 285 K) temperature regimes, respectively.

Fig. 6.2 (b) plots the electrical resistivity data as \(\ln \rho\) versus \(T^{-1/2}\), resulting in a straight line up to 10 K for all samples, satisfying the \(s = 1/2\) behavior expected from the Coulomb gap model with the parabolic relationship \(\varepsilon^2 = |E - E_F|^2\). This characteristic behavior is consistent with the Efros and Shklovskii (ES) VRH mechanism, which is valid based on the consideration of single-electron transition and non-interacting hopping excitations between single-particle states\(^{14}\). The detailed of ES-VRH resistivity model, \(\rho(T) = \exp[2(C/k_BT)^{1/2}]\), where \(C\) \(\equiv\) Coulomb gap, have been reported previously\(^{14,16}\). All samples give a satisfactory fit with a \(T^{-1/2}\) slope and the estimated Coulomb gap displayed in Table 6.2, showing that the annealing influences the transport properties of SSO. Since long-range Coulomb interactions lead to depletion and dissociation of electrons from holes, it requires energy in the presence of a gap.
Therefore, the larger Coulomb gap near $E_F$ is expected to impede conductivity. The estimated Coulomb gap for OA, pristine and VA are 2.087, 1.308 and 0.726 meV, respectively, consistent with the resistivity results ($\rho_{OA} > \rho_{pristine} > \rho_{VA}$). Thus, it is conceivable that the additional oxygen vacancies created by VA enable electrons with less excitation energy to surmount the Coulomb potential (which exists between the occupied and unoccupied sites) and act to reduce Coulomb gap.

The straight line plot in the higher temperature region (170 K – 285 K) is shown in Fig. 6.2 (c) for OA, pristine and VA samples, showing that the temperature exponent is $1/4$ rather than $1/2$, obeying the $\ln \rho \propto (1/T)^{1/4}$ relationship, a signature of the Mott VRH law\textsuperscript{16}. In Mott VRH conduction theory, the electrons hop between the localized states existing inside the energy distribution region of the impurity band that are close to $E_F$, even though the distance is greater than between nearest-neighbor sites. The VRH Mott model has been applied to SSO previously,\textsuperscript{9} yielding several Mott parameters: characteristic temperature ($T_0$), the DOS at the Fermi level in the absence of electron-electron interactions ($N(E_F)$), the most probable hopping distance ($R_{\text{hop,Mott}}$) and the average hopping energy ($W_{\text{hop,Mott}}$)\textsuperscript{17,18}. These parameters are summarized in Table II along with the resistivity for OA, pristine and VA samples at 285 K. The data in Table 6.3 satisfy the Mott requirements over the temperature range under consideration.

The $N(E_F)$ appears to be highest in the VA sample, leading to the decrease in resistivity and giving rise to the shortest hopping distance and reduced required hopping energy. These results imply that as the oxygen vacancy concentration increases with VA, the number of trapped electrons increases to form a cavity, changing the SSO electronic structure. Therefore, the electron wave functions in separate defects begin to overlap, widening the impurity levels to a
quasi-continuous narrow band of energy levels within the energy gap and facilitating the conduction process between localized states within the band with less energy. It is clear from these results that not only the phonon-assisted quantum-mechanical tunneling process, as ES and Mott VRH, govern the charge transport properties in SSO thin films, that there also exists a strong correlation between post-growth annealing ambient and the corresponding hopping parameters which is controlled primarily by the oxygen vacancy concentration. Fig. 6.2 (d) shows the relationship between resistivity and carrier concentration at room temperature for OA, pristine and VA samples. These results indicate that the VA sample has the highest carrier concentration and the lowest resistivity. The relative oxygen vacancy concentration estimated from XPS\textsuperscript{10} for each sample is plotted in Fig. 6.2 (e), following the same trend as carrier concentration. This suggests that the electron population can be altered over several orders-of-magnitude by simply controlling the oxygen vacancy concentration through different post-growth annealing ambient in SSO system, with higher oxygen contents yielding smaller carrier concentration and, therefore, it is believed that the carriers in SSO are due to oxygen vacancies.
Fig. 6.2 Resistivity as a function of temperature (5 K - 285 K) for oxygen annealed (OA), pristine and vacuum annealed (VA) samples; (b) lnρ vs. T-1/2 at low temperature (5 K - 10 K) for all samples; (c) lnρ vs. T-1/4 at high temperature (170 K - 285 K) for all samples along with best fit results obtained by least-square fitting, (d) carrier concentrations and resistivity for each condition, and (e) relative area of oxygen vacancy peak extracted from XPS.
Table 6.2: Fitting values of the ES-VRH conduction mechanism

<table>
<thead>
<tr>
<th></th>
<th>Slope ($T^{-1/2}$)</th>
<th>Coulomb gap (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OA</td>
<td>9.842</td>
<td>2.087</td>
</tr>
<tr>
<td>Pristine</td>
<td>7.793</td>
<td>1.308</td>
</tr>
<tr>
<td>VA</td>
<td>4.287</td>
<td>0.726</td>
</tr>
</tbody>
</table>

Table 6.3. Value of resistivity and the Mott VRH conduction parameters at 285 K

<table>
<thead>
<tr>
<th></th>
<th>$\rho_{RT}$ ($\Omega$-cm)</th>
<th>$T_o$ (K)</th>
<th>$N(E_F)$ ($m^{-3}eV^{-1}$)</th>
<th>$R_{hop,Mott}$ (nm)</th>
<th>$W_{hop,Mott}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OA</td>
<td>6.7x10^{-2}</td>
<td>12.098x10^4</td>
<td>1.72x10^{21}</td>
<td>1.652</td>
<td>27.86</td>
</tr>
<tr>
<td>Pristine</td>
<td>1.3x10^{-2}</td>
<td>9.310 x 10^4</td>
<td>2.24x10^{21}</td>
<td>1.594</td>
<td>26.10</td>
</tr>
<tr>
<td>VA</td>
<td>3.1x10^{-3}</td>
<td>8.407 x 10^4</td>
<td>2.48x10^{21}</td>
<td>1.537</td>
<td>25.16</td>
</tr>
</tbody>
</table>

In many oxide systems, oxygen vacancies act as intrinsic donors and have profound influence on physical and chemical properties of these materials\textsuperscript{15,19}. In our previous work, ferromagnetism was studied by systematically changing the oxygen vacancy concentration in SSO samples,\textsuperscript{10} and the saturation moments ($M_s$) and coercivities ($H_c$) were found to be proportional to the oxygen vacancy concentration, confirming that VA enhances $M_s$ and $H_c$ while OA degrades both properties. To shed some light on the role of vacancies, UPS is carried out to investigate the variation of $\Phi$ and the occupied electronic valence states among OA, pristine and VA samples. It should be mentioned that $\Phi$ is not a material constant, but can be
modified through mainly carrier doping or modification of surface dipole\textsuperscript{20}. Many reports have shown that one can change \( \Phi \) substantially by manipulating the oxygen content during growth conditions\textsuperscript{15,20}.

In this study, the \( \Phi \) of all samples is determined by the difference between the highest binding energy (BE) cutoff and the energy source (He I excitation source 21.2 eV). Electrons close to the highest BE cutoff edge are the slowest of the spectrum, meaning they have a kinetic energy of nearly zero after leaving the sample surface, i.e. they had barely enough energy to overcome the BE of the material. The comparison of the highest BE cutoff edge for OA, pristine and VA is shown in Fig. 6.3(a). The enlarged UPS spectra are displayed in the inset of Fig. 6.3(a) for clarity, revealing that the cutoff edge follows VA>pristine>OA order in a discernible way. Subtracting the BE values seen in the inset from 21.2 eV, the \( \Phi \) are estimated to be 4.54, 4.38 and 4.02 eV for OA, pristine and VA samples, respectively. By definition, \( \Phi \) is the difference between the bulk chemical potential of the electrons and the electrostatic potential energy of the electrons in the vacuum just outside the surface\textsuperscript{21}. It is surmised that the dipole layer is easier to form under OA compared to VA, and these dipoles increase the electrostatic potential energy outside the surface, resulting in higher \( \Phi \). Similar results have been reported in SnO\textsubscript{2} and In\textsubscript{2}O\textsubscript{3}\textsuperscript{20,22}.

It is known that the higher Fermi level implies in general carrier doping, hence the higher conductivity is expected. The Fermi level is defined as the \( E_{\text{F}} \)-Evalance band maximum (\( E_{\text{VBM}} \)) in the low BE region where \( E_{\text{F}} \) is at BE=0 and \( E_{\text{VBM}} \) is determined by the intersection between linear fitting to the leading edge of the spectra and the background\textsuperscript{20}. Fig. 6.3(b) shows that the Fermi level for OA, pristine and VA are 2.97, 3.14 and 3.39 eV, respectively. It is evident from
the results that the Fermi level follows the trend of VA > pristine > OA, in accordance with conductivity and the respective oxygen vacancy concentrations.

Another striking feature is observed in Fig. 6.3 (c) near the low BE valence band region from +2 to -0.5 eV, which is related to the resulting DOS produced under various post-growth annealing conditions. Physically, the integrated area beneath difference spectra corresponds to the number of carriers per unit volume in the film. The gap states near $E_F$ are attributed to the oxygen vacancies generated by VA and decreased by OA. It is speculated that when an $O^{2-}$ ion is removed, the cation oxidation states must be reduced in order to maintain charge neutrality. As a result, a previously empty band becomes partially occupied with electrons, giving rise to an increase in occupied states close to the $E_F$ in the valence band spectra. The gap states gradually increase upon the formation of oxygen vacancies.
Fig. 6.3 UPS spectra for oxygen annealed (OA), pristine and vacuum annealed (VA) samples (a) the highest binding energy cutoff edge (the inset shows the expanded view); (b) the difference between valence band maximum and Fermi energy (EVBM-EF) and (c) gap states in the valence band region
6.4 Summary

Both physical and chemical properties of SSO are dependent on the oxygen vacancy concentration. The correlations between work function (Φ) and the transport properties extracted from ES and Mott-VRH fitting of the results suggest that the higher DOS near the E_F is associated with the lower Φ and smaller Coulomb gap. Increasing the oxygen vacancy concentration results in a shorter hopping distance and smaller required hopping energy, which assists electron transport and provides lower resistivity. It is therefore believed that the carriers in SSO are due to oxygen vacancies. The evidence indicates that the DOS near the E_F, for VA, is 50% higher than OA, whereas Coulomb gap is 35% less as compared to OA. Meanwhile, Φ decreases around 0.5 eV by VA compared to OA. The Fermi level shifts 0.42 eV and follows the trend of VA>pristine>OA which is consistent with conductivity value and oxygen vacancy concentration. Apart from the changed electronic structure, however, crystal modifications also arise from the post-growth annealing treatment by considering the prevailing oxygen vacancy defect models. No additional peaks are observed for OA, pristine or VA samples, excluding the possibility of formation of any other phase. The only difference among each sample is the FWHM and the peak shift related to the bulk value, showing the analogous trend with the oxygen vacancy concentration; as the oxygen vacancy concentration increases, both values increase accordingly. It is conceivable that lattice expansion after VA, due to the increase in concentration of intrinsic defects (presumably oxygen vacancies), affects the elastic energy associated with lattice disorder and therefore the larger FWHM is expected. This research provides a comprehensive and detailed analysis of an emerging DMS, SSO, with respect to structural, physical and chemical properties after different post-growth annealing treatments, needed for future spintronics devices.
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Chapter 7 Strong evidence for topological surface states in epitaxial Bi$_2$Se$_3$ thin film
grown by pulsed laser deposition through magneto-transport measurements and angle-
resolved photoemission spectroscopy

We report epitaxial growth of Bi$_2$Se$_3$ thin films on Al$_2$O$_3$ (0001) substrates with over 13% lattice misfit via domain matching epitaxy, where critical thickness is less than a monolayer. X-ray and electron diffraction patterns confirm that the layers are epitaxial with (0001) Bi$_2$Se$_3$\parallel(0001)Al$_2$O$_3$ and [2\overline{1}10] Bi$_2$Se$_3$\parallel[2\overline{1}10] Al$_2$O$_3$ (or) [2\overline{1}10] Bi$_2$Se$_3$\parallel[1\overline{1}20] Al$_2$O$_3$ without the presence of interfacial pseudophormic layer. X-ray photoemission spectroscopy reveals that the films are Se-deficient, in agreement with electrical transport data showing n-type carriers and metallic behavior. Magneto-resistance (MR) measurements show a cusp feature corresponding to weak antilocalization and linear-MR shows a non-saturating trend up to 9 T. These results demonstrate the potential of PLD for fabricating high quality Bi$_2$Se$_3$ films.
7.1 Introduction

Topological insulators (TI), a new quantum state of matter, have been identified as promising materials to be a new platform for coherent spin-polarized electronics. Three dimensional (3D) TI are characterized by insulating bulk states and protected metallic surface states (SS), where the spins of electrons in SS are tightly locked to their momentum due to the strong spin-orbit coupling, and thus backscattering in the Dirac fermions by nonmagnetic impurities is prohibited due to the protection by time-reversal symmetry\(^1\). They possess unique gapless SS with linear energy-momentum dispersion characteristics that coexist with gapped bulk states. Recently, angle-resolved photoelectron spectroscopy (ARPES)\(^2\) has confirmed that Bi\(_2\)Se\(_3\) is a 3D TI with a single massless Dirac cone for the SS. Apart from ARPES, considerable efforts have focused on magneto-transport studies of various quantum transport phenomenon, including weak anti-localization (WAL)\(^3\)\(^\text{-}\)\(^5\), two-dimensional (2D) Shubnikov-de Haas oscillations\(^6\) as well as non-saturating linear magneto-resistance (LMR)\(^7\)\(^,\)\(^8\) associated with these SS. Yet, direct evidence of SS from transport data is elusive owing to high levels of unintentional doping. Therefore, MR data of 3D TI have been analyzed in terms of a multichannel-conduction model which considers the potential contributions from both surface and the bulk states; sophisticated analytical approaches are required to pinpoint the difference\(^6\),\(^9\),\(^10\).

Several techniques have effectively prepared Bi\(_2\)Se\(_3\) thin films, including electrodeposition\(^11\), solvo-thermalization\(^12\) and thermal evaporation\(^13\), but these approaches produce polycrystalline films suitable for thermoelectric studies but not desirable for TI based integrated solid state devices. Most high quality epitaxial Bi\(_2\)Se\(_3\) thin films have been grown by molecular beam epitaxy (MBE)\(^14\)\(^\text{-}\)\(^16\), but there has been little progress on the growth of
Bi$_2$Se$_3$ thin films using pulsed laser deposition (PLD) because the resulting films are often polycrystalline$^{17-19}$. Though MBE is able to produce high quality epitaxial Bi$_2$Se$_3$ thin film, it is difficult to deposit multi-layered heterostructures in a single run; hence, this may hinder the practical applications of TI. Recently, the growth of TI-based multi-layered heterostructures have attracted much interest, for example, low-power spintronic applications could be facilitated by developing TI tunnel junctions with dielectric or ferromagnetic insulators$^{20}$ or multichannel Dirac fermions could be utilized in sprotronics by inserting normal insulators between multiple TI layers$^{21,22}$. Also, normal band insulator- 3D TI or semimetal-3D TI heterostructures, such as Sb$_2$Se$_3$-Bi$_2$Se$_3$$^{23}$ and Bi-Bi$_2$Se$_3$ (Bi$_2$Te$_3$)$^{24,25}$ heterostructures offers a new platform to study topological phase. PLD is an excellent technique which is capable of multi-target assembly and then rotating and positioning any target of interest in line with the laser beam without breaking the vacuum. PLD has been used to grow a variety of high quality functional epitaxy oxide thin films, including multiferroics$^{26}$, magnetic semiconductors$^{27}$ and high temperature superconductors$^{28}$. Therefore, if one can grow high quality epitaxial TI by PLD and fabricate multi-layered heterostructures of these materials in-situ, opportunities to study the novel physics arising from the resulting interfacial couplings may lead to multifunctional spintronic device applications.

In this study, we report the growth of high quality epitaxial Bi$_2$Se$_3$ thin films on Al$_2$O$_3$ (0001) substrates using PLD. The (0001) epitaxy of Bi$_2$Se$_3$ on (0001) Al$_2$O$_3$ occurs via domain matching epitaxy (DME), which is based on matching of integral number of lattice planes across the film-substrate interface and the size of the domain equals integral multiples of planar spacing$^{29-31}$. This idea is fundamentally different from the conventional lattice matching epitaxy where lattice constants are matched one-to-one across the film-substrate interface to
grow epitaxial films with less the 7-8 % misfit. By invoking the concept of DME, epitaxy can be explained in our system where the lattice misfit of 13% between the film \(a_{\text{Bi}_2\text{Se}_3} = 4.143\) Á and the substrate \(a_{\text{Al}_2\text{O}_3} = 4.758\) Á is accommodated by integral matching of 7/6 and 8/7 planes with a domain variation frequency parameter of 0.736\(^{29-31}\). Under these misfit conditions, critical thickness for pseudomorphic growth is less than a monolayer, therefore, equilibrium structure of \(\text{Bi}_2\text{Se}_3\) is formed from the beginning. Relatively low repetition rate (0.2 Hz) and low deposition temperature (~250 °C) are key elements to achieving high quality \(\text{Bi}_2\text{Se}_3\) epitaxial films. Such low deposition temperature minimizes the loss of volatile compounds via re-evaporation from the surface of the growing film. Detailed structural characterization has demonstrated that PLD grown \(\text{Bi}_2\text{Se}_3\) films exhibit a high density of twin boundaries and stacking faults. High carrier concentration is believed due to the presence of Se vacancies and is considered to be electrically active, behaving as n-type carriers. Furthermore, magneto-transport measurements of PLD-grown \(\text{Bi}_2\text{Se}_3\) thin films are presented and discussed. At low magnetic field (B), the MR exhibits a weak antilocalization (WAL)\(^3-5\) cusp which reflects the nontrivial topology of the SS and is suppressed when the temperature increases. In addition, at high fields, LMR appears, reflecting a positive, weak temperature-dependence and a non-saturating trend up to \(B = 9\) T. The linearity of the MR is interpreted through the quantum MR model proposed for a zero gap band structure with Dirac linear dispersion\(^{32}\).

### 7.2 Experimental Details

\(\text{Bi}_2\text{Se}_3/\text{Al}_2\text{O}_3\) (0001) heterostructures were grown in a multitarget PLD chamber (base pressure = \(1 \times 10^{-6}\) Torr). Ultra-violet pulses (25 ns) from a KrF excimer laser (\(\lambda = 248\) nm, 0.2 Hz repetition) were focused on a stoichiometric polycrystalline \(\text{Bi}_2\text{Se}_{3.5}\) target with a 0.9
J/cm$^2$ pulse fluence. Deposition takes place with a substrate temperature of 250 °C and a pressure of $3 \times 10^{-6}$ Torr. Before deposition, the Al$_2$O$_3$ (0001) substrate was ultrasonically cleaned for 30 minutes using acetone, methanol and de-ionized water to remove organic contaminants. The structure of the films is characterized by x-ray diffraction (XRD) 0-2θ scans using a Rigaku x-ray diffractometer with Cu Ka radiation ($\lambda = 1.5418\text{Å}$) to examine the out-of-plane orientation. The in-plane orientation is evaluated by φ-scan XRD in a Panalytical Empyrean x-ray diffractometer with a Xe-proportional counter detector. Microstructural analysis is performed using a JEOL-2010 field-emission high resolution transmission electron microscope (HR-TEM). Selected area electron diffraction (SAED) from cross-section samples is used to confirm single crystalline growth and the epitaxial relationships. The TEM sample was prepared using a focus ion beam (FIB) technique. X-ray photoelectron spectroscopy (XPS) on a SPECS FlexMod equipped with an Mg Kα monochromatic x-ray source ($1254.6$ eV) clarifies contamination concerns, characterizes the surface states and estimates the Bi:Se ratio within Bi$_2$Se$_3$ thin films. Transport measurements use a standard van der pauw configuration with indium contacts on four square corners in a Quantum Design Physical Property Measurement System (PPMS) system with a magnetic field up to 9 T under different temperature regimes. Angular-dependence measurements were performed with a horizontal rotator in the PPMS. ARPES was performed using a He I light source (Specs UVS 100, $h\nu = 21.2$ eV). The sample was rotated with respect to the electron analyzer to measure the dispersion of the occupied electronic states.

7.3 Results and Discussion

Fig. 7.1 (a) shows a typical XRD 0-2θ scan of a Bi$_2$Se$_3$ film grown on an Al$_2$O$_3$(0001) substrate. The highly c-axis oriented growth is evident from the peaks corresponding to the
{003} family whose positions agree well with those of c-axis oriented epitaxial Bi$_2$Se$_3$ films reported in the literature$^{33}$. No other diffraction peaks exists, excluding the formation of other phases. To establish the epitaxial relationships between the substrate and the film, Φ-scan XRD on the \{01\overline{1}5\} planes of the film and \{01\overline{1}2\} planes of the substrate are obtained in a skew-symmetric geometry by tilting the sample from 0° to 360°. These are seen in Fig. 7.1 (b); epitaxy is evident from the peaks present. The presence of six peaks corresponding to Bi$_2$Se$_3$ \{01\overline{1}5\} planes indicates twin growth which is confirmed by TEM. A schematic depicting twin/domain growth and direction in this study is illustrated in Fig. 7.1(c). In one case, the Bi$_2$Se$_3$ basal plane is aligned with that of Al$_2$O$_3$ and in the other there is a rotation of 60°/180°. The epitaxial relationships are written as \(0001)\text{Bi}_2\text{Se}_3 \parallel (0001)\text{Al}_2\text{O}_3\) (out-of-plane) and \([2\overline{1}10]\text{Bi}_2\text{Se}_3 \parallel [2\overline{1}10]\text{Al}_2\text{O}_3\) (or) \([2\overline{1}10]\text{Bi}_2\text{Se}_3 \parallel [11\overline{2}0]\text{Al}_2\text{O}_3\) (in-plane).
Fig. 7.1 (a) XRD (θ-2θ) pattern of a Bi$_2$Se$_3$ film, (b) in-plane φ-scan {015} planes of the film and {012} planes of the substrate, respectively, and (c) the schematic depicting twin/domain growth. In one case, the basal plane of Bi$_2$Se$_3$ is aligned with that of Al$_2$O$_3$, and in the other there is a rotation of 60°/180°.
Fig. 7.2 (a) shows the bright field XTEM image of the Bi$_2$Se$_3$/Al$_2$O$_3$ interface. The interface is sharp and no evidence of any interfacial reaction is observed. It should be noted, however, that the contrast along the interface is attributed to sample preparation and not due to the film itself. To further confirm the epitaxial relations, an SAED pattern for the Bi$_2$Se$_3$/Al$_2$O$_3$ interface is seen in the Fig. 2(a) inset. The zone axis patterns corresponding to [2$\bar{1}$10]Bi$_2$Se$_3$ and [1$\bar{1}$20]Al$_2$O$_3$ are in agreement with the Φ-scan data. The HRTEM image in Fig. 7.2 (b) shows a clean Bi$_2$Se$_3$/Al$_2$O$_3$ interface; the fast fourier transform (FFT) diffraction patterns are also shown. The misfit strain is accommodated by the coherently strained layer below a critical thickness whose self-energy of dislocation equals to the strain energy. In a large misfit condition, 13 % in our system, the critical thickness is less than one monolayer. Beyond the critical thickness, it becomes energetically favorable to form dislocations which relieve the remaining strain in the system. Since the Bi$_2$Se$_3$ rhombohedral crystal lattice exhibits three-fold symmetry around the [0001] axis, twins are expected in the epitaxial film. Twin growth is found in the HRTEM image in Fig. 7.2 (c). The SAED pattern for the region covering only Bi$_2$Se$_3$ (Fig. 7.2 (c) inset) displays extra spots in addition to those belonging to the [2$\bar{1}$10] zone. These are attributed to the formation of twins, one of which can be seen in the marked region in Fig. 7.2 (c). Similar spots were reported for Bi$_2$Se$_3$ thin film grown on Si(111) and InP(111) by another group$^{34}$. 


Fig. 7.2 (a) Bright fields XTEM image of Bi$_2$Se$_3$/Al$_2$O$_3$ interface. Inset: SAED pattern of the heterostructure, (b) HRTEM along [11-20] zone axis patterns, cross-sectional images of epitaxial Bi$_2$Se$_3$/Al$_2$O$_3$ interface. The insets show the FFT patterns, and (c) HRTEM along [2-1-10] Bi$_2$Se$_3$ zone axis patterns where the arrows indicate two twin boundaries lying on the Bi$_2$Se$_3$ film. Inset: SAED pattern of the Bi$_2$Se$_3$ film.
XPS was used to characterize the film stoichiometry. Fig. 7.3(a) shows the XPS spectra recorded from an as-grown film. Binding energies of each peak were calibrated using C 1s at 285 eV. It shows that only Bi and Se are present; no additional peaks are detected, except for a small amount of environmental C and O 1s peak due to the oxidation of the film that occurs after exposure to the atmosphere. A high-resolution scan of the Se 3d region is given in Fig. 7.3(b), indicating asymmetric peaks at about 54.8 eV and 54.0 eV, corresponding to the reported values for the binding energies of Se 3d{3/2} and Se 3d{5/2}, respectively. The peak separation energy of 0.8 eV and the spin-orbit split peak doublet of area of 2:3 between 3d spectra is consistent with a previous report. Other double peaks at 158.7 eV and 164.0 eV are from Bi 4f{7/2} and 4f{5/2}, respectively, as shown in Fig. 7.3(c). The splitting energy of 5.3 eV and the 3:4 area ratio are also in accordance with reported values. In an attempt to precisely determine the peak positions, Lorentz-Gauss profiles and the Shirley background have been taken into account for the deconvolution of Bi 4f and Se 3d spectra. The binding energies of the Se 3d peaks show a redshift of about 1.7 eV with respect to those of pure bulk Se, while the binding energies of Bi 4f show a blueshift of about 1.7 eV. The opposite chemical shifts are caused by the net charge flow with hybridized bonds between Bi and Se. In addition, from the XPS spectra one can also estimate the surface composition by \[ \frac{\rho_{\text{Se}}}{\rho_{\text{Bi}}} = \frac{I_{\text{Se}}}{I_{\text{Bi}}} \frac{S_{\text{Se}}}{S_{\text{Bi}}} \] where \( \rho \) is the atomic density, \( I \) is the integrated intensity of the characteristic peak and \( S \) is the atomic sensitivity factor. Considering the atomic sensitivity factors (\( S = 2.9 \) for Bi and \( S = 0.44 \) for Se) for x-ray scattering, the stoichiometry calculated from the peak area of Bi 4f and Se 3d is \( \approx \frac{\rho_{\text{Se}}}{\rho_{\text{Bi}}} = 1.45 \), which is close to stoichiometric Bi\(_2\)Se\(_3\), with slight Se deficiency.
Fig. 7.3 (a) XPS spectra of a Bi$_2$Se$_3$ film, (b) XPS high-resolution scan of Se-3d peak, and (c) the Bi-4f peak.
Fig. 7.4(a) shows the resistivity versus temperature for a 50 nm thick film for temperatures ranging from 5 K - 300 K, revealing metallic behavior and a residual resistivity value of $7.25 \times 10^{-4} \, \Omega \cdot \text{cm}$ at 5 K. Similar metallic features have also been reported in MBE grown Bi$_2$Se$_3$ thin films and are attributed to the presence of intrinsic defects, e.g. Se vacancies, which are typically present and readily generated during film deposition.$^{39,40}$ The Hall resistance at 300 K, 100 K and 5 K show a linear dependence on magnetic field (-5 T to +5 T) in the inset of Fig. 7.4(a), and the negative R$_{xy}$ for all temperatures indicates that the Fermi energy remains above the Dirac point, suggesting the majority charge carriers are electrons. In addition, the XPS measurements indicate a Se deficiency (~3 %) in the films, confirming the existence of Se vacancies. These vacancies are donors which donate electrons to the conduction band and behave as n-type carriers. As the Se vacancy concentration ($V_{\text{Se}}$) increases, the electron concentration also increases, leading to a Fermi level shift into the bulk conduction band. The Hall carrier concentration and mobility were calculated as shown in Fig. 7.4(b). The Hall carrier concentration remains nearly constant with temperature, $\sim 2.5 \times 10^{19} \, \text{cm}^{-3}$, higher than in MBE grown films$^{39,40}$ but consistent with previous studies$^{41}$. The Hall mobility is in the range of 340-310 cm$^2$/Vs, showing a slight increase with decreasing temperature. It is believed that the low mobility of bulk carriers may enhance the surface state contribution due to the suppression of bulk carrier interference with quantum oscillations$^{42,43}$.
Fig. 7.4 (a) Resistivity as a function of temperature (5-300 K); inset: Hall measurements at 300 K, 100 K and 5 K and (b) Temperature-dependent carrier concentration and mobility for the same sample.
In MR measurements, B is fixed in the z-direction and the Hall voltage probes in the y direction; i.e. $\theta = 90^\circ$ where $\theta$ is the angle between B and the current I, as illustrated in the inset of Fig. 5(a). MR(B,T) for 50 nm thick Bi2Se3 films, measured with B ( -9 to +9 T) perpendicular to the film plane, is shown in Fig. 7. 5(a). At temperature (T = 2 K), the normalized MR % shows a distinctive dip in resistance in the low field region, a signature of WAL in TI films3-5. This WAL effect results from strong spin-orbit coupling, which shows the absence of backscattering giving rise to the destructive interference between the two time reversal symmetry loops when there is no magnetic field5. As B increases, this quantum interference is destroyed and backscattering increases, leading to the sharp increase in resistance seen in Fig. 7. 5(a). The enlarged MR at low B (-2 T to +2 T) is shown in Fig. 7. 5(b), revealing the existence of WAL as a function of T in a discernible way. WAL gradually weakens as temperature increases, eventually disappearing entirely at T = 48 K; thus, the dependence on B is quadratic-like at low field. The MR cusp feature at low B is broadened and finally disappears with increasing temperature owing to the decrease in the phase coherence length44.

In addition to the WAL effect in the MR of Bi2Se3 at low temperature and low B, a 2D, non-saturating linear MR (LMR) alludes to the topologically protected SS in TI. According to the quantum Abrikosov’s model45, the linear, positive MR is expected in a gapless semiconductor with a linear E-\kappa dispersion, such as the SS of the TI studied. Since TI possess the Dirac SS, the origin of linear MR in TI has been suggested to be associated with the Landau level splitting of the Dirac cone in the presence of a strong magnetic field32. Hu et al.8 claimed, however, that the quantum LMR could also be present under relatively smaller B, i.e., when electrons occupy several Landau levels. Recently, Tang et al.7 reported that the LMR observed
in Bi$_2$Se$_3$ nanoribbons is of quantum origin and attributed to the topological surface states (TSS). He et al. 32 further confirmed that the LMR is associated with the gapless TSS in a MBE-grown Bi$_2$Se$_3$ thin film on Si (111). As seen in Fig. 7.5 (c), the MR measured for B ranging from -1 T to 9 T and as a function of temperature follows a linear-like dependence above a certain threshold without saturation. In the nearly linear region (5 T - 9 T), the slope, dMR/dB, changes slightly with temperature (~15% over the range T = 2 K to 150 K). This is consistent with quantum LMR theory that the MR should be linear and virtually temperature-independent.33 Considering the comparable phenomenon of our films with previous reports6,7,32,46, it is thus reasonable to ascribe the LMR observed in our Bi2Se3 films to the quantum origin proposed by Abriskov45. It is evident from the results that the classical LMR model of Parish-Littlewood47,48 is not applicable in the present case. According to the P-L classical model, the mobility is expected to be linearly proportional to the slope of the LMR as the temperature changes. Here, the Hall mobility decreases by only 2% over the range of temperature studied, while the slope dMR/dB decreases by 15%. Although both quantities exhibit similar tendencies qualitatively with temperature, they lack a quantitative correlation.
Fig. 7. (a) Magneto-resistance of a Bi$_2$Se$_3$ film measured at $\theta = 90^\circ$ as a function of temperature. Inset: geometry of the measurement setup, (b) enlarged view of MR near zero fields showing the robustness of the WAL effect as a function of temperature and (c) for increasing field, the MR quickly becomes linear and is non-saturating up to 9 T.
It should be mentioned that the WAL and LMR reflect the Dirac nature of the 2D SS and the 3D contribution of bulk spin-orbit coupling. It is known that the direct probing of the topological nature by magneto-transport remains a major challenge\textsuperscript{9-11} since it is a bulk sensitive experiment. Even small imperfections in the near-stoichiometric crystals will lead to metallic behavior in the bulk and thus overwhelm or mask the surface contribution\textsuperscript{49}. Especially in TI thin films, carriers may scatter into additional conducting channels (from top to bottom surface, or into the conduction bulk). As a result, one cannot rule out a possible role of the bulk channel based on these results to describe the quasi-2D character of the LMR and WAL effects. It is reported that MR is only sensitive to the perpendicular component of B, which could demonstrate directly the 2D SS of TI\textsuperscript{50}. The angular dependent MR of Bi\textsubscript{2}Se\textsubscript{3} thin films at 2 K and 7.5 T are shown in Fig. 7.6. It is known that the 2D surface states of the TIs are only sensitive to the perpendicular component of the magnetic field $B \cos \theta$, where $\theta$ is the angle between magnetic field and the normal direction of the thin films (Fig. 7.6 inset). The observed angular dependence of MR can be well fitted by a $|\cos \theta|$ function. This suggests that the MR curve shows an obvious 2D response. Thus, the observed LMR behavior from Bi\textsubscript{2}Se\textsubscript{3} might be from the energy-momentum (E-k) linear relationship of 2D topological surface state.
Fig. 7.6 The angular dependent MR of Bi$_2$Se$_3$ thin films at 2 K and 7.5 T (0-360°)

According to the Hikami–Larkin–Nagaoka (HLN) theory, the equation for 2D magnetoconductance (MC) is:

$$
\Delta G_{\text{WAL}}(B) = G(B) - G(0) \equiv \alpha \frac{e^2}{2\pi^2\hbar} \left[ \Psi\left( \frac{1}{2} + \frac{\hbar}{4eBL_\phi^2} \right) - \ln\left( \frac{\hbar}{4eBL_\phi^2} \right) \right]
$$

Here $\psi(x)$ is the digamma function and $l_\phi$ is the phase coherence length. $\alpha$ is a coefficient reflecting the strength of the spin-orbital coupling and magnetic scattering. The value of $\alpha$ is 1, 0, -0.5 for the orthogonal, unitary and symplectic case, respectively. For perfect WAL, the coefficient $\alpha$ has a value of -0.5 (symplectic case), which indicates a single coherent 2D channel. In our case, $\Delta G$ at $T=2$ K in the perpendicular field fits the HLN equation quite well.
and yields $\alpha = -0.426$ (Fig. 7.7 (a), suggesting one single surface channel dominates the WAL transport behavior.

To explore further the dimensionality and robustness of the system in terms of conduction, we plotted the $l_\phi$ as a function of temperature (2-50 K). Fig. 7.7 (b) shows plot of extracted $l_\phi$ with temperature. Like other TI systems, our result are seen to exhibit power law dependence of $l_\phi$ on temperature ($l_\phi \sim T^{-0.43}$) which is close to the 2D transport which ought to show a dependence, $l_\phi = T^{-0.5}$. Hence, power law dependence of coherence length on temperature again supports the fact that WAL indeed originates from topologically protected surface states.

Fig. 7.7 (a) HLN fitting at $T= 2$ K and $H= 7.5$ T and (b) the phase coherence length as a function of temperature.

Fig. 7.7 (a) Fitted curves with HLN equation and (b) phase coherent length as a function of temperature
The TI surface states in our sample was directly revealed by angle-resolved photoemission spectroscopy (ARPES). Fig. 7.8(a) shows the clear surface electronic band dispersion structure of bulk conduction band (BCB) and bulk valence band (BVB) where the possible weak surface states were also observed in between. We plotted the figure into E-K spacing (Fig. 7.8 (b)) and estimated that the Fermi level is located at 150 meV above the BCB minimum in the Bi$_2$Se$_3$ sample. This result is consistent with the transport data where showing the n-type carrier dominates in this sample. The surface states are also able to be observed, showing a linear dispersion of energy vs momentum in the bulk band gap which connect between BCB and BVB.
Fig 7.8 ARPES result of (a) valence band structure with clear band dispersion between BCB and BVB and (b) surface states connected between BCB and BVB.
7.4 Summary

In conclusion, we have grown successfully epitaxial Bi$_2$Se$_3$ thin films on Al$_2$O$_3$ (0001) substrates by PLD using DME, where the lattice misfit of 13% between the film and the substrate is accommodated by integrated matching of 7/6 and 8/7 planes with a domain variation frequency parameter of 0.736$^{29,30}$. The critical thickness for pseudomorphic growth is less than one monolayer and the atomic steps formed within the second monolayer which provides the nucleation sites for the dislocation. Low repetition rate and low deposition temperature are crucial parameters for obtaining single crystalline films. The film crystallinity and chemical composition have been confirmed via XRD ($\theta$-2$\theta$ and $\varphi$-scans) and XPS, respectively. The microstructure observed by HRTEM reveals the existence of twin boundaries and stacking faults within the Bi$_2$Se$_3$ films. Temperature-dependent resistivity and Hall measurements show n-type metallic behavior. In particular, a WAL effect originating from the suppression of the time-reversal coherent backscattering was observed at low T and low B; the WAL effect vanishes at T = 48 K. At field up to B = 9 T, the slope of the LMR shows nearly temperature-independent and non-saturating trends. The observed angular dependence of MR can be well fitted by a $|\cos\theta|$ function. This suggests that the MR curve shows an obvious 2D response. The coefficient $\alpha$ has a value of -0.5 which indicates a single coherent 2D channel. The phase coherence length ($l_\varphi$) has power law dependence on temperature ($l_\varphi \sim T^{-0.43}$), and this is close to the 2D transport. The observation of LMR phenomenon can be considered as signatures of the existence of TSS. Further improvements in crystalline quality and a reduction of defects are expected from an optimization of the laser and substrate variables and control of the ambient pressure. The results demonstrate that PLD is not only a potential technique for fabricating TI thin film heterostructures, but also paves the way for in-situ synthesis of multi-
layered heterostructures on silicon substrate for further investigation of the physics arising from interfacial coupling, such as magnetic monopoles\textsuperscript{51} and Majorana Fermions\textsuperscript{52}.
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Chapter 8 Control of intrinsic defects and magnetotransport properties of Bi$_2$Se$_3$/c-sapphire epitaxial heterostructures

We have synthesized Bi$_2$Se$_3$ epitaxial thin films on c-sapphire substrates, where Se-related defects and strains are controlled precisely during pulsed laser deposition. This allows us to tune electrical and magnetotransport properties and probe the role of defects and strains as a function of processing conditions systematically. The defect microstructure has been studied in detail using high resolution X-ray diffraction and high-angle annular dark field scanning transmission electron microscopy. Magnetotransport measurements show a strong dependence on microstructure which is associated with the Se-content. With higher Se content, the film experiences large compressive strain along the [001] direction which is accompanied by the partial suppression of one family of twin domain formation. As a result, the insulating behavior becomes more pronounced at low temperature which is understood in terms of the quantum correlation induced by electron–electron interactions. The compressive strain enhances spin-orbit coupling and topological characteristics. These results shed light on the importance of controlling the intrinsic defects during the growth of Bi$_2$Se$_3$ thin films, providing an effective way to suppress the bulk conductivity and establish the correlation between microstructure and strain.
8.1 Introduction

It is known that one difficulty with the synthesis of Topological insulators (TI) Bi$_2$Se$_3$ is that there is degenerative n-doping due to the tendency of Se vacancy formation. The formation of point defects, Se vacancies, changes the electrostatic interaction in the vicinity of crystal atoms and results in a strain field around the defects. It is believed that strain engineering is a powerful method to affect the properties of materials, especially for two-dimensional materials, such as graphene and MoS$_2$. Tao et al. reported that tensile strain is efficient in reducing the band gap of pristine single-layer MoS$_2$ (P-MoS$_2$), improving carrier mobility and introducing vacancy-related magnetism. Blanc et al. claimed that a zero-energy Landau level, predicted in nanorippled graphene, could indeed develop in the regions where strains vary. It is, however, the experimental studies of the interplay between defect-induced strain and magnetotransport properties in epitaxial 2D materials in general, and Bi$_2$Se$_3$ thin films in particular, that are lacking. In this work, we not only introduce a novel growth approach by pulsed laser deposition to control effectively the formation of undesirable defects, such as Se vacancies, but also demonstrate the ability to manipulate them and engineer the strain induced by defects, opening up a wide range of possibilities from fundamental studies of microscale effects to future “straintronics” applications.

Bi$_2$Se$_3$-type materials share a rhombohedral layered structure with five covalently bonded atomic layers grouped into a quintuple layer (QL) with an atomic order of Se(1)-Bi-Se(2)-Bi-Se(1). Each QL layer is weakly bound by van der Waals forces along the c-axis to form a 3-D crystal structure. This structure is marked by highly anisotropic bonding in the lateral and longitudinal directions. The bulk band topology of these 3D TIs is predicted to be sensitive to uniform uniaxial strain. Young et al. demonstrated by density-functional theory (DFT) that
interlayer (inter-QL) interactions play a crucial role in determining the topological behavior, whereas the intralayer interactions within a QL have little effect. They claimed that longitudinal compressive strain along the Bi$_2$Se$_3$ [001] direction not only strengthens the Coulombic interaction between sites and reduces the conventional gap, but also magnifies the spin-orbit coupling and increases the topological gap. On the one hand, Liu et al. carried out first-principles calculations on strained Sb$_2$Se$_3$ and Bi$_2$Se$_3$ and found that the Sb$_2$Se$_3$ can be changed into a TI by applying compressive strain longitudinally along the c-axis. On the other hand, tensile strain can lead to lattice expansion and transform Bi$_2$Se$_3$ into a normal insulator. Furthermore, Hirahara et al. reported that the three-dimensional trivial insulator could become a topological insulator in two dimensions by making 1–8 bilayer Bi(111) thin films grown on Bi$_2$Te$_3$(111) substrates due to the lattice distortion in Bi, inducing a change in the surface-state band dispersion. Numerous reports have shown that the strain should be treated as an important parameter which can significantly influence the topological insulating phase. Understanding and optimizating strain-engineered materials will become a fertile area for exploring new functionalities and related applications.

There are three primary sources of strain that are cumulative during the growth of thin film heterostructures: lattice misfit; thermal misfit, and microstructure/defect related strains. The lattice misfit strain can be relaxed completely by nucleation of dislocations at the free surface in large misfit (ε ≥ 10%) systems. In the Bi$_2$Se$_3$/c-sapphire system, a misfit strain around 13% should lead to full relaxation as the critical thickness is less than a monolayer. The thermal expansion coefficient of Bi$_2$Se$_3$ is of the order of 20 × 10$^{-6}$/K while that of Al$_2$O$_3$ is about 1 × 10$^{-6}$/K$^9$.$^{10}$ This large difference in the thermal expansion coefficients of the film and substrate is responsible for the in-plane tensile strain (~1%) and the strain perpendicular to the film being
compressive. The elimination of Se vacancies provides additional compressive stress along the film normal. It is found that Se-vacancy-induced strain plays a critical role in controlling electrical and magnetotransport properties.

The fingerprint of TI materials is the massless Dirac fermion surface states and it has been confirmed by surface-sensitive spectroscopic techniques\textsuperscript{11,12,13}; however, transport measurements of the surface states in thin films have not yet been clearly demonstrated because it is usually dominated by the bulk conductivity due to the overwhelmingly high density of bulk states that coexist with the surface states. Recently, the topological surface states have been experimentally probed via molecular doping, such as calcium or antimony\textsuperscript{14,15,16}, or with the aid of top- and back-gating\textsuperscript{17} that lowers the Fermi level into the band gap.

In the present report, we perform an effective way to suppress the bulk conductivity via manipulating the defect induced strain during thin film growth, with no reliance on external doping. The microstructural strains that are associated with point defects (presumably Se vacancies) and planar defects (twin boundaries/stacking faults) are found to bring about a remarkable change in the physical properties. By tailoring the Se content in \( \text{Bi}_2\text{Se}_3 \) thin films, we control the compressive (tensile) strain along the c-axis which is correlated with the suppression (enhancement) of twinning, leading to the substantial difference in electrical and magnetotransport properties. This hallmark for the unraveling of the relationships between microstructure and the related TI properties is crucial for the performance of future microelectronic devices and opens the way to new strain-related functionalities.

\subsection*{8.2 Experimental}

The \( \text{Bi}_2\text{Se}_3/\text{Al}_2\text{O}_3 \) (001) thin-film heterostructures were grown in a multitarget PLD chamber (base pressure = \( 10^{-6} \) Torr). Ultraviolet pulses (25 ns) from a KrF excimer laser
(λ=248 nm, 0.1 Hz repetition) were focused on a stoichiometric polycrystalline Bi$_2$Se$_8$ target and a pure Se target, both with a 0.9 J/cm$^2$ pulse fluence. The Al$_2$O$_3$ (001) substrates were cleaned ultrasonically in acetone, methanol and de-ionized water to remove organic contaminants before deposition. Two groups of thin film samples were prepared; one group is from an ablated Bi$_2$Se$_8$ target at 150 °C under $3 \times 10^{-1}$ torr Ar pressure (denoted as “pristine” hereafter) and the other group is grown using alternating laser pulses; here a 1:1 ratio of Bi$_2$Se$_8$:Se pulses was used at 150 °C under $3 \times 10^{-1}$ torr Ar pressure (denoted as “extra-Se” hereafter).

The structure of the films is characterized by X-ray diffraction (XRD) θ–2θ scans using a Rigaku X-ray diffractometer with Cu Ka radiation ($\lambda = 1.5418$ Å) to examine the out-of-plane orientation. The in-plane orientation is evaluated by Φ-scan using a Philips X-Pert Pro X-ray diffractometer equipped with a high resolution goniometer. A hybrid monochromator, consisting of a parabolic-shaped multilayer mirror and a special channel-cut Ge crystal, was used to condition the beam.

High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) microstructural analysis was performed using a FEI probe-corrected Titan G2 60-300 operated at 200 kV. In the HAADF imaging mode, the large-angle elastically scattered electrons are collected by a high-angle annular detector with an acceptance angle in the range of 75–170 mrads, where scattered electrons produce contrast proportional to $Z^2$.

Magnetotransport characterization was performed on 10 mm x 10 mm thin films using standard four-probe methods in the van der Pauw geometry in magnetic fields up to 2 T in an Ever Cool Quantum Design PPMS system with a base temperature as low as 2 K. A custom built gold coated pogopin setup was used to make contacts and keep the same distance between
the contacts on the films. Angular-dependence measurements were performed with a horizontal rotator in the PPMS.

8.3 Results and Discussions

It is commonly accepted that n-type carriers in Bi$_2$Se$_3$ TI are generated from Se-vacancy formation, i.e., each Se vacancy donates at most two itinerant electrons as $Se_{se} \leftrightarrow V_{se}^+ + Se_{(g)} + 2e^-$ in the Kroger-Vink notation$^{18}$, and the strain field established by those defects (or lattice distortions) results in the formation of dislocations and twin boundaries in order to maintain the minimum free energy of the system. The presence of defect-induced strain is analogous to a small electric field which can influence the physical properties. Liu et al.$^6$ reported that the in-plane tensile (or compressive) strains in Bi$_2$Se$_3$ could lead to periodic depressions (or expansions) in the [0001] direction along the low-angle tilt grain boundary which significantly modify the band topology. They showed via tunneling spectroscopy and DFT calculations that the 2D Dirac surface states are enhanced under compressive strain along the c-axis and destroyed under tensile strain.

Fig. 8.1 (a) shows typical XRD θ-2θ patterns of pristine and extra-Se Bi$_2$Se$_3$ thin films grown on sapphire (001) substrates. The presence of only (003n) reflections corresponding to Bi$_2$Se$_3$ in both films reveals the formation of highly textured films along the substrate c-axis (or epitaxial layer) without secondary phases. The high resolution XRD on the Bi$_2$Se$_3$ (0015) plane was carried out to investigate the strain present in the film; results are displayed in Figure 8.1 (b). C-sapphire substrate (006) peaks are precisely aligned from which we can calibrate the (0015) and other Bi$_2$Se$_3$ peaks. The peak positions of the (0015) diffraction planes appear at 2θ = 47.60° and 47.64° for pristine and extra-Se films, respectively, which can be more readily identified in the Fig. 8.1 (b) inset. This suggests that the extra-Se film, with d$_{(0015)} = 1.9088$ Å,
is under larger longitudinal compressive strain compared to the pristine film whose $d_{(0015)} = 1.9103 \text{ Å}$.

XRD $\Phi$-scan measurements were made using Bi$_2$Se$_3\{015\}$ planes at $2\theta=29.48^\circ$ and $\Psi=57.9^\circ$, while $\{012\}$ planes were used for the substrates at $2\theta=25.58^\circ$ and $\Psi=57.6^\circ$; the results are shown in Fig. 8.1 (c). The presence of six peaks indicates not only both films (pristine and extra-Se) are epitaxial, but also shows the existence of two domains in the film which are rotated by $60^\circ$ with respect to each other. It is noted that on the pristine film the Bi$_2$Se$_3$ layers display two types of pyramidal domains with nearly equal intensity, whereas on the extra-Se film, the intensity of one triplet decreases. This occurs at the other in-plane rotation angles in the XRD patterns as the substrate $\{012\}$, indicating the partial suppression of one family of twin domains. A similar tendency is found in Bi$_2$Se$_3$ using Fe-doped InP(111)A substrates on account of the surface roughness$^{19}$ or by employing vicinal substrates such that the in-plane twinning is suppressed due to directional flow of surface steps$^{20}$. 

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Fig. 8.1 Typical XRD patterns of Bi$_2$Se$_3$/c-sapphire pristine and extra-Se films: (a) out-of-plane θ-2θ patterns and (b) high resolution XRD. The inset shows an enlargement of the Bi$_2$Se$_3$ (0015) diffraction planes for both samples and (c) shows in-plane Φ-scan patterns obtained from Bi$_2$Se$_3$ {01-15} and c-sapphire {01-12} reflections.
The definition of a twin boundary is a mirror image misorientation of the lattice structure along a twin boundary, which can be treated as an example of coherent interface. A disruption of the long-range stacking sequence over many atomic spacings produces a twin region (twin domain). The six-fold symmetry in the Φ-scan originates from the coexisting domains described by the stacking sequences of “...ABC...” and “...CBA...”. Normally, on c-sapphire substrates, the two stacking sequences take place with the same probability so the existence of twin domains cannot be avoided. Apparently, the first Se atom between each other QL is capable of orienting the hexagonal lattice structure, but the choice for the second atomic layer (Bi), whether “B” or “C”, is not controllable, allowing the formation of both ABC and ACB stacking sequences and the formation of twin domains. The formation of a twin can be triggered by the clustering of Se vacancies on the basal plane, equivalent of a missing Se plane. Here, we show that as the Se vacancies are decreased during Bi2Se3 film growth, the formation of twins is reduced, and the higher compressive strain is employed along the longitudinal direction. Twin suppression has brought about improved electronic properties of the material, which are exhibited/manifested by reduced bulk carrier contribution and enhanced topological surface states.

HAADF-STEM was used to further explore the correlation between microstructure and properties; atomically resolved images of the pristine film are shown in Fig. 8.2 with different magnifications and sample locations. The atomically ordered structure can be seen in Fig. 8.2(a) where the horizontal arrows and the kinks in the zig-zag lines identify twin boundaries. These are the lamellar twins which are formed at the boundary of the different stacking sequences parallel to the growth plane. These misorientations are usually directly associated with the crystal’s electronic structure. Tarakina et al. 21 reported that the possibility of forming a
lamellar twin is attributed to three different nonequivalent atomic positions in the Bi$_2$Se$_3$ crystal structure: at the edge Se(1), middle Se(2) and Bi positions within a quintuple layer. The formation of such a twin is probably most plausible from an energetics point-of-view$^{22}$. It can be seen more clearly in Fig. 8.2(b) that the lamellar twin only occurs at the edge of the Se layer in the quintuple layer, which connects to the following layer by weak van der Waals interactions and is in good agreement with the Tarakina et al. results$^{21}$. A similar microstructure has been reported experimentally and predicted by *ab initio* calculations for bulk Bi$_2$Te$_3^{23}$. Additionally, we observed stacking faults in the pristine film, indicated by vertical arrows in Fig. 8.2(c). The stacking fault is produced by the extension of perfect dislocations in close packed structures. Fig. 8.2(d) shows an enlargement of the stacking fault as displayed in Fig. 8.2(c). Such planar defects are undesirable and expected to influence the electrical properties of the film negatively. DFT calculations by Seixas et al.$^{24}$ have demonstrated that the presence of stacking faults in Bi$_2$Se$_3$ can lead to the appearance of different polymorphs, influencing the surface states of the TI. Fig. 8.2(e) is a high resolution image of a pristine film along the [001] projection, with a well-defined sequence of Se1-Bi-Se2-Bi-Se1 within each QL; the two bright spots correspond to the heavier Bi atoms and the three weaker ones correspond to the Se atoms as expected, as well as the van der Waals gaps. The red circle represents Bi while blue and green circles are Se(1) and Se(2), respectively. The first unit cell (the 3 first QL) has a c lattice parameter of 30.71 Å while the second and third unit cells have c lattice parameters of 30.19 Å and 29.67 Å, respectively. The average of c lattice parameter of three unit cell is 30.19 ± 0.05 Å.
Fig. 8.2 Cross-sectional HAADF-STEM images of a pristine sample: (a) overview image of the film, (b) enlargement of image (a) showing a lamellar twin boundary, (c) a stacking fault within the film, (d) enlargement of the stacking fault seen in (c), and (e) high resolution image of each Bi$_2$Se$_3$ quintuple layer, consisting of two bright spots (Bi) and three fainter spots (Se).
Fig. 8.3(a) shows the HAADF-STEM images of an extra-Se film revealing a continuous stacking sequence without any twin boundary interruptions, i.e., two adjacent grains coalesce without rotational mismatch. No stacking faults are observed in the extra-Se film. Fig. 8.3(b) and Fig. 8.3(c) show the atomic layer-by-layer images; the stacking sequence can be clearly visualized along the c-direction revealing that the extra-Se film shows no planar defects and has better crystallinity in the region studied. The average c lattice parameter from three unit cells is $29.37 \pm 0.05 \text{ Å}$ which is smaller than that of the pristine film, $30.19 \pm 0.05 \text{ Å}$, indicating that the extra-Se film is under larger compressive strain along the c-axis. In addition, the HAADF-STEM images are consistent with XRD Φ-scan results which show that additional Se suppresses twin formation. It is worth mentioning that although there are no twin boundaries or stacking faults observed in the HAADF-STEM images of the extra-Se films, twin formation cannot be eliminated completely on c-sapphire substrate as confirmed by XRD Φ-scan results.

The HAADF-STEM interface images of the extra-Se films show the presence of a “poor crystalline quality” layer in Fig. 8.3(d); a similar area is also observed in the pristine films. The thickness of this observed interfacial layer is not uniform across the film. Even though the contrast is much weaker, one can still see the existence of Bi planes within this layer, suggesting that the first layer does not cover the surface continuously but is composed of domains which have their own nucleation sites during the initial stages of growth. Therefore, this interfacial layer consists of some well-crystallized regions and an amorphous-like area which is due to small misalignment, causing a lower contrast in the HAADF-STEM images. The following QL are well-crystallized, clearly resolved periodically and not affected by the initial poor crystalline quality at the interface. Thus this interface is not considered an
appreciable factor in determining TI properties. Similar formation of an interface layer has been reported previously\textsuperscript{20}.

Fig. 8.3 Cross-sectional HAADF-STEM images of an extra-Se film: (a) overview image of the film, (b) enlargement of image (a) from the middle section, (c) high resolution image showing perfect ordering of the quintuple layers without any twin boundary interruptions, and (d) the interface region, showing the coexistence of highly crystalline and poorly-crystalline areas.
Fig. 8.4(a) shows the temperature dependence of the four-terminal longitudinal resistivity \( \rho_{xx} \) from 2 K to 300 K, revealing qualitative differences in the electrical properties between pristine and extra-Se films. Generally, \( \rho_{xx}(T) \) decreases almost linearly when \( T \) decreases from 300 K to around 30 K for both films, suggesting typical metallic behavior \( \left( \frac{d\rho_{xx}}{dT} > 0 \right) \) and consistent with the scattering of degenerate electrons with acoustical phonons that are populated based on the classical equipartition distribution\(^{25}\). For the extra-Se film, however, an upturn at \( \sim 30 \) K in the resistivity is seen that is absent in the pristine film whose resistivity displays a plateau below 25 K. The upturn behavior has been attributed to competition between acoustical phonon scattering (from degenerate semiconducting) and ionized impurity scattering (in the intermediate range between degeneracy and non-degeneracy of the free carriers) where the conduction is activated by a thermal process\(^{26}\). Below \( \sim 30 \) K, the resistivity exhibits an exponential increase with respect to \( 1/T \) \( \left( \frac{d\rho_{xx}}{dT} < 0 \right) \) for the extra-Se film, which is understood in terms of the quantum correction induced by electron–electron interactions\(^{27}\).

This behavior is not apparent in the high carrier concentration materials whose temperature dependence of resistivity mainly comes from the electron-phonon interactions, indicating static disorder as the dominant scattering mechanism\(^{25}\).

It is clear that the extra-Se film shows essentially metallic behavior with a significant upturn at \( \sim 30 \) K, followed by an insulating ground state as the film is cooled further. This typical low carrier concentration signature is likely due to the suppression of phonon effects or the freezing out of bulk carriers at low temperature\(^{27,28}\). The basic carrier types of the two films are n-type, as their Hall resistances are negative. The Hall coefficient in the extra-Se film at 2 K corresponds to an electron carrier concentration \( n_e \sim 2 \times 10^{19}/\text{cm}^3 \). This is a significant decrease in the bulk electron contribution compared to the pristine film whose carrier concentration is
an order of magnitude higher, \( n_c \sim 2 \times 10^{20} / \text{cm}^3 \). In addition, the resistivity upturn is not observed for the pristine film, showing that phonon scattering plays a dominant role as a consequence of high carrier concentration. To elucidate the origin of the resistivity upturn at low temperature, the Figure 4(a) inset displays the normalized resistivity \( (\rho / \rho_{\text{min}}) - \ln T \). The dashed lines are guides for the eye to show that the slope of the extra-Se film is much larger than that of the pristine film, revealing the electrical conductivity in the weakly disordered two-dimensional (2D) regime is suppressed and the contribution of bulk carriers is reduced by increased Se content\(^\text{29}\). A similar logarithmic temperature dependence of the resistivity has been observed in several TI samples\(^\text{27,29,30}\). Furthermore, the upturn temperature, varying from ~30 K to 5 K, has also been reported in bulk, thin film and nano-ribbons of Bi\(_2\)Se\(_3\), though they may be derived from different effects\(^\text{29,31}\).

Fig. 8.4 Resistivity as a function of temperature for pristine and extra-Se films. The inset shows the normalized resistivity vs. \( \ln T \); the broken lines are guides to the eye.
Fig. 8.5(a) and (b) show the normalized magnetoresistance (R(H)/R(0)) of pristine and extra-Se films as a function of temperature and magnetic field perpendicular to the films. The magnetoresistance behavior is similar to the results reported for TI bulk, films, and nanoribbons\textsuperscript{32}; namely, positive magnetoresistance over the entire measured magnetic field regime and a sharp cusp-like minimum at B=0 up to T= 25 K for both films. Such a positive magnetoresistance in TIs is usually attributed to the weak antilocalization (WAL), the quantum correction in the spin-orbit-coupled surface state due to the wave nature of the electrons in a disordered metallic system\textsuperscript{33}. According to the theory\textsuperscript{28,29}, the helical surface states are associated with \(\pi\)-Berry’s phase which is related to the accumulation of Dirac fermions traveling along two time-reversed self-intersecting loops. This results in destructive quantum interference, prohibiting backscattering\textsuperscript{29,34}. The features decrease as B increases, leading to a sharp increase in R(H)/R(0) as the time reversal symmetry is broken along with increased backscattering and thus suppression of the WAL. With increasing temperature, the WAL effect also becomes weaker and is invisible at 50 K for both films.

Fig. 8.5(c) compares R(H)/R(0) for pristine and extra-Se films under perpendicular magnetic field (from -2 T to +2 T) at 2 K, 3 K and 10 K; the inset magnifies the low field magnetoresistance at 2 K. The magnetoresistance of the extra-Se film shows a steeper increase at low field (-0.5 T ~ +0.5 T) than the pristine film, where the zero field cusp remains but is confined to a progressively narrower field scale. In the low magnetic field regime, R(H)/R(0) shows the strong temperature dependence for the weak-field component in both films, suggesting the typical quantum origin. The temperature dependence for the high-field component, however, is negligibly small which means the slope, \(d[R(H)/R(0)]/dB\), is weakly dependent on temperature in both films, implying a classical origin. Pristine films begin to
saturate at an earlier stage compared to the extra-Se film whose behavior shows a weak linear dependence along with the increasing measured magnetic field. None of the curves evolve into a parabolic-like $B^2$ dependence, originating from the Lorentzian deflection of carriers under perpendicular magnetic field, which is more pronounced in thicker samples, suggesting the increased contribution of bulk effects$^{35}$.

It is known that the WAL effect induced by 2D surface states is characterized by the sole dependence on the perpendicular component of the applied field. Therefore, we conducted an angle-dependent study to verify the dominance of the 2D component in WAL; both films were measured at different field orientations from $0^\circ$ and $90^\circ$ at 2 K. Here $\theta = 0^\circ$ corresponds to magnetic field parallel to the (001) film surface and $\theta = 90^\circ$ is perpendicular to the (001) film surface; the top right insets of Fig. 8.5(d) and 5(e) illustrate the measurement geometry. Fig. 8.5(d) and 5(d) show that both cusp features are the sharpest with the magnetic field perpendicular to the basal plane and flatten as the magnetic field is rotated from $\theta = 0^\circ$ to $\theta = 90^\circ$. $R(H)/R(0)$ decreases with increasing $\theta$, indicating 2D transport behavior under perpendicular magnetic field, with the extra-Se film showing stronger angular dependence than the pristine film. One possible reason may be the higher carrier concentration and higher density of twin boundaries in the pristine film, suppressing the contribution from the surface states to the conductivity and thereby mastering the surface properties. It is believed that the coexistence of two domains could give rise to undesirable consequences, and if two adjacent domain boundaries are highly dissimilar, then the helical surface states may even be induced at the twin boundaries as the translational symmetry of the crystal is broken$^{24}$. 

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Fig. 8.5 Normalized magnetoresistance, \( R(H)/R(0) \), versus temperature and perpendicular magnetic field. (a) A pristine film, (b) an extra-Se film, and (c) a comparison of the pristine and extra-Se films at 2 K, 3 K and 10 K. The inset enlarges the 2 K data for \(-0.5 \, \text{T} \) to \(+0.5 \, \text{T} \). (d) and (e) show the angular-dependence of \( R(H)/R(0) \) at 2 K for the pristine and extra-Se films.
8.4 Summary

The XRD $\theta$-2$\theta$ measurements show that the extra-Se film contains higher longitudinal compressive strain along the [001] direction with smaller $d_{(0015)} = 1.9088$ Å compared to the pristine film whose $d_{(0015)} = 1.9103$ Å. This compressive strain magnifies the spin-orbit effect and increases the topological gap. The average values of the c lattice parameter, estimated from STEM-HAADF images, is $29.37 \pm 0.05$ Å in the extra-Se films and $30.19 \pm 0.05$ Å in the pristine films, consistent with XRD results. The extra-Se films have less Se vacancies, reducing lamellar twin boundary formation compared to the pristine films, as confirmed by STEM-HAADF. Additionally, XRD $\Phi$-scans of the extra-Se films show a significantly decreased intensity of one triplet which occurs at the other in-plane rotation angle as the substrate {012}, indicating the partial suppression of one family of twin domains. The magnetotransport measurements clearly show that the extra-Se films possess superior properties, and it is reasonable to conjecture that the higher longitudinal compressive strain, reduced number of Se vacancies and lamellar twin boundaries are the dominant factors. It is unlikely, however, that the transport in the extra-Se films is only due to the helical surface state contribution, owing to the substantially reduced electron concentration in the bulk; the quantum effects associated with the surface states are considerably larger in magnitude compared to the pristine films. We have shown the potential of strain engineering as a new strategy to optimize the TI properties of Bi$_2$Se$_3$ thin films. Understanding the strain induced by defects and the ability to control properties will be crucial for the performance of the future microelectronic devices. A novel deposition approach successfully minimizes the Se deficiency, with no external doping. These studies exhibit correlations between point defects, strains and physical properties in epitaxial
Bi$_2$Se$_3$ thin films, suggesting new avenues for engineering its properties through the introduction of defects and manipulating them in a controllable manner.
8.5 Reference


Chapter 9 Microstructure and transport properties of epitaxial topological insulator

Bi$_2$Se$_3$ thin films grown on MgO (100), Cr$_2$O$_3$ (0001) and Al$_2$O$_3$ (0001) templates

We report the epitaxial integration of defect-induced room temperature ferromagnetic insulators, Cr$_2$O$_3$ and MgO, with topological insulators Bi$_2$Se$_3$ on c-sapphire substrate by pulsed laser deposition. The structural, magnetic and magnetotransport properties of ~15 nm Bi$_2$Se$_3$ thin films are investigated on each template. The lattice misfit of Cr$_2$O$_3$/Bi$_2$Se$_3$ and MgO/Bi$_2$Se$_3$ are ~16 % and ~39 %, respectively, where the critical thickness for pseudomorphic growth is less than one monolayer. The insulating behavior is more pronounced due to the additional scattering of the surface states of the Bi$_2$Se$_3$ layer by interfacing with MgO and Cr$_2$O$_3$. The weak antilocalization effect from the surface states is clearly suppressed, accounting for the presence of magnetic bottom layers. This work demonstrates an effective way to study the emergence of a ferromagnetic phase in topological insulators by the magnetic proximity effect in Bi$_2$Se$_3$, a step toward unveiling their exotic properties.
9.1 Introduction

Topological insulators (TIs) have received considerable attention due to their novel properties arising from strong spin-orbit coupling and massless Dirac-cone-like surface states protected by time reversal symmetry (TRS)\(^1,\)\(^2\). The special kind of surface states is expected to exhibit various unique quantum phenomena which may bring revolutionary developments in low power electronics and topological quantum computation. While such unique systems offer nontrivial surface states that can be utilized to perform dissipationless spin transport, it is equally important to break TRS of TIs to create a variety of exotic topological effects including the half-integer quantum Hall effect\(^3\), the topological magnetoelectric effect\(^4\), and the magnetic monopole\(^5\). One major drawback for the implementation of TIs into real electronics devices, such as field effect transistors, is their linear energy spectra, which normally allows incident electrons to pass through a potential barrier via Klein tunneling without reflection, leading to an appreciable off-current and thus a poor on/off current ratio\(^6,\)\(^7\). Therefore, opening a surface energy gap and generating of massive surface carriers by breaking TRS is the key for both fundamental physics research and new materials displaying exotic phenomena aimed at technological applications.

Two routes for breaking TRS have been developed by introducing ferromagnetic ordering within TIs. The first involves doping the TI host with specific elements; for example, by which ferromagnetism has been observed in Mn-doped \(\text{Bi}_2\text{Te}_3\) single crystals \(^8,\)\(^9\) and Mn- and Cr-doped \(\text{Bi}_2\text{Se}_3\) thin films \(^10,\)\(^11\). However, it is difficult to separate the surface and the bulk phases using this approach. Furthermore, doping of magnetic elements inevitably introduces crystal defects, magnetic scattering centers and impurity states in the insulating gap, which are detrimental to mobility and the transport of surface states in TIs \(^12-14\). In contrast, the second
route is based on introducing ferromagnetism to the TI surface by proximity to a ferromagnetic insulator (FMI). Suitable FMIs have the potential to achieve strong and uniform exchange coupling via contact with TIs without significant spin-dependent random scattering of helical carriers at magnetic atoms\textsuperscript{15-17}. To date, the prototype three dimensional (3D) TI material, Bi\textsubscript{2}Se\textsubscript{3}, has drawn much attention for the study of proximity effect with FMIs. Several FMI materials have been investigated to interface with Bi\textsubscript{2}Se\textsubscript{3}, such as EuS, GdN, and Y\textsubscript{3}Fe\textsubscript{5}O\textsubscript{12} (YIG). However, the relatively low ferromagnetic transition temperature (T\textsubscript{c}) of these materials, restricts device applications, for example the T\textsubscript{c} for Bi\textsubscript{2}Se\textsubscript{3}/EuS, Bi\textsubscript{2}Se\textsubscript{3}/GdN and Bi\textsubscript{2}Se\textsubscript{3}/YIG are ~ 15.7 K, ~ 13 K and 130 K, respectively\textsuperscript{18-21}.

Here we employ MgO and Cr\textsubscript{2}O\textsubscript{3} controllable defect-induced room temperature FMI materials, as substrates for Bi\textsubscript{2}Se\textsubscript{3} growth and demonstrate proximity-induced ferromagnetism in Bi\textsubscript{2}Se\textsubscript{3}. The MgO and Cr\textsubscript{2}O\textsubscript{3} are selected as the FMI templates not only based on processing perspectives related to epitaxial thin film growth, but, also for device applications. Using domain matching epitaxy\textsuperscript{22}, the misfit strain is relieved within a couple of monolayers as a result of the large lattice misfit; the lattice misfit for MgO/Bi\textsubscript{2}Se\textsubscript{3} is ~16 % and for Cr\textsubscript{2}O\textsubscript{3}/Bi\textsubscript{2}Se\textsubscript{3} is ~39 %. As a result, the critical thickness of pseudomorphic growth is less than one monolayer and the misfit strain can be engineered and confined near the interface, with the rest of the film grown free of lattice misfit strain. From the practical point of view, both MgO and Cr\textsubscript{2}O\textsubscript{3} are considered potential candidates for tunnel barriers in magnetic tunnel junctions (MTJs), where the contact resistance is spin dependent and becomes comparable to the spin independent resistance of the normal metal\textsuperscript{23-25}. In addition to being crucial components for nonvolatile magnetoresistive random-access memory and low-noise magnetic sensors based on the tunneling magnetoresistance effect\textsuperscript{26}, MgO and Cr\textsubscript{2}O\textsubscript{3} show room-
temperature ferromagnetism (RTFM), associated with a strain-dependent defect-mediated mechanism. Li et al.\textsuperscript{27} showed that undoped MgO thin films grown by pulsed laser deposition (PLD) have the RTFM signature and that the ferromagnetism exhibits strong correlation between magnesium vacancies (\(V_{Mg}\)) and the crystallinity. They found that reduced crystallinity increases the ferromagnetic spin-order of MgO thin films due to increased \(V_{Mg}\). As for Cr\textsubscript{2}O\textsubscript{3}, though bulk Cr\textsubscript{2}O\textsubscript{3} is an antiferromagnetic with \(T_N = 307\) K, He et al.\textsuperscript{28} showed the existence of a roughness-insensitive ferromagnetic state at the Cr\textsubscript{2}O\textsubscript{3} (0001) surface, and confirmed its spin-polarized property using experimental and theoretical approaches. Later, Punugupati et al.\textsuperscript{29} demonstrated that epitaxial Cr\textsubscript{2}O\textsubscript{3} thin films exhibit ferromagnetic-like hysteresis loops with high saturation and finite coercivity up to 400 K due to oxygen related defects whose concentration is controlled by the strain present in the films.

In this research, we present structural, magnetic, and magnetotransport characterization of TI/FMI heterostructures. Two hybrid structures are studied based on proximity-induced ferromagnetism in a TI: Bi\textsubscript{2}Se\textsubscript{3}/Cr\textsubscript{2}O\textsubscript{3}/c-sapphire and Bi\textsubscript{2}Se\textsubscript{3}/MgO/c-sapphire. The key advantage here is that the TRS breaking occurs mostly at the TI/FMI interface, rather than affecting the majority of bulk states. Furthermore, the approach avoids the creation of secondary phases, clusters or defect agglomerations which result from the doping 3d transition metal impurities into TIs.

\section*{9.2 Experimental}

All samples presented here were grown using PLD (\(\lambda = 248\) nm and \(\tau = 25\) ns). Three heterostructures were studied: Bi\textsubscript{2}Se\textsubscript{3}/Cr\textsubscript{2}O\textsubscript{3}/c-sapphire, Bi\textsubscript{2}Se\textsubscript{3}/MgO/c-sapphire and Bi\textsubscript{2}Se\textsubscript{3}/c-sapphire, which are referred hereafter to as Cr\textsubscript{2}O\textsubscript{3}-bilayer, MgO-bilayer, and control sample, respectively. This enables us to compare the structural, magnetic and transport properties of
Bi$_2$Se$_3$ thin films grown on a non-magnetic substrate to those grown on FMI substrates. The Cr$_2$O$_3$ film was deposited from a Cr target that was held at 650 °C under an oxygen partial pressure of 5 x 10$^{-2}$ Torr with laser energy density ~ 3.2 J/cm$^2$. The MgO thin film was deposited at the same temperature under an oxygen partial pressure of 5 x 10$^{-5}$ Torr along with ~ 2.8 J/cm$^2$ laser energy density. The detailed Bi$_2$Se$_3$ growth conditions have been reported previously $^{30}$. All Bi$_2$Se$_3$ films have the same thickness, ~15 nm, well above the 6 nm threshold; below which the wavefunctions of the top and bottom surfaces overlap substantially, resulting in a hybridization gap near the Dirac point where the transport characteristics are similar to those brought by strong magnetic interactions $^{31-33}$. The thicknesses of the Cr$_2$O$_3$ and MgO films were around 100 nm.

To characterize the crystal structure, x-ray diffraction (XRD) was performed using a Rigaku X-ray diffractometer with CuKα1 radiation ($\lambda = 1.54056$ Å$^{-1}$). Phi-scans were performed by Philips X-Pert Pro X-ray diffractometer equipped with a high resolution goniometer to investigate the crystallographic relationship between substrate and grown layer. Microstructural and growth characteristics of the heterostructures were investigated using a JEOL-2010 field emission transmission electron microscope (TEM), operating at 200 kV with a point-to-point resolution of 1.8 Å, and, with high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) using a FEI probe-corrected Titan G2 60–300 operated at 200 kV. Magnetotransport characterization was performed on 10 mm x 10 mm thin films using a standard four-probe method in the van der Pauw geometry in magnetic fields up to 5 T in an Ever Cool Quantum Design PPMS system with a base temperature as low as 2 K. A custom-built gold-coated pogo pin setup was used to make contacts and ensures the same distance between the contacts on the films. Angular-dependence measurements were
performed with a horizontal rotator in the PPMS. The magnetic properties were measured by applying magnetic field parallel and perpendicular to the Bi$_2$Se$_3$ (003n) surface using a Super Conducting Quantum Interference Device (SQUID).

9.3 Results and Discussions

Fig. 9.1(a) displays a XRD θ-2θ pattern of a Cr$_2$O$_3$-bilayer sample. Both the Cr$_2$O$_3$ and Bi$_2$Se$_3$ layers exhibit c-axis preferred orientation crystallographic peaks, suggesting films are highly textured. To confirm the epitaxial growth of the films and establish the epitaxial relationships, XRD in-plane Φ-scans were used. Fig. 9.1(b) shows the Φ-scans obtained by exciting (104) lattice planes of Cr$_2$O$_3$ and sapphire and (015) planes of Bi$_2$Se$_3$. The three fold symmetry illustrates that the Cr$_2$O$_3$ is rhombohedral and grows epitaxially on c-sapphire without any in-plane rotation. The presence of Bi$_2$Se$_3$ six peaks indicates that the film is epitaxial as a result of the existence of two domains. A schematic showing the alignment of two different domain variants of Bi$_2$Se$_3$ on a Cr$_2$O$_3$ template is seen in Fig. 9.1(c). In one case, the Bi$_2$Se$_3$ basal plane is aligned with that of Cr$_2$O$_3$ and in the other there is a 60°/180° rotation. The epitaxial relationships are written as (0001)Bi$_2$Se$_3$$||$(0001)Cr$_2$O$_3$$||$(0001)Al$_2$O$_3$ and [2-1-10]Bi$_2$Se$_3$$||$[2-1-10]Cr$_2$O$_3$$||$[2-1-20]Al$_2$O$_3$ (or) [2-1-10]Bi$_2$Se$_3$$||$[11-20]Cr$_2$O$_3$$||$[11-20]Al$_2$O$_3$. 
Fig. 9.1 Typical XRD patterns of Bi$_2$Se$_3$/Cr$_2$O$_3$/c-sapphire heterostructures: (a) out-of-plane 0-20 patterns, (b) in-plane Φ-scan patterns excited from the Bi$_2$Se$_3$ {015}, Cr$_2$O$_3$ and c-sapphire {104} planes and (c) schematic showing the alignment of two different domain variants of Bi$_2$Se$_3$ on the Cr$_2$O$_3$ template.
The out-of-plane XRD θ-2θ pattern of the MgO-bilayer sample is shown in Fig. 9.2(a). The MgO is completely orientated in the (111) plane and Bi$_2$Se$_3$ exists only the (003n) reflections, suggesting a highly textured single-phase heterostructure. The in-plane orientation relationship between Bi$_2$Se$_3$, MgO and c-sapphire substrate was established by Φ-scan; the scan results are shown in Fig. 9.2(b). It can be seen that the Φ-scan for (200) planes of MgO results in six sharp peaks, confirming the epitaxial growth. The presence of these reflections is attributed to the threefold symmetry of MgO film growth which is epitaxial with two domain types that have 60° in-plane rotation with respect to each other about the [111] growth direction. The occurrence of two in-plane orientations is explained by stacking sequences in the [111] direction which make up a face centered cubic (fcc) structure. Any fcc on a hexagonal (0001) or rhombohedral (001) systems, when grow in the [111] direction, has two possible orientations. An fcc structure is described as having an ABCABC… type stacking in the closed-packed direction. During the nucleation on the closed packed plane (cpp) of Al$_2$O$_3$, the first monolayer plane sets in one orientation which is the same everywhere if the substrate surface has no steps. Fixing this first monolayer cpp as a reference and denoting it as A, the next cpp monolayer grows as a B or a C layer. Upon further growth in the [111] direction the fcc can stack as either ABCABC… or ACBACB….. These two possibilities are random and manifest themselves in two different fcc with a 60° in-plane rotation with respect to each other. Here, all constituent layers within the heterostructure were found to be epitaxial with the relationships: (0001)Bi$_2$Se$_3$$\parallel$$$(111)\text{MgO}$$||$$$(0001)\text{Al}_2\text{O}_3$$ and $$(10-10)\text{Bi}_2\text{Se}_3$$||$$$(11-10)\text{MgO}$$||$$$(10-10)\text{Al}_2\text{O}_3$$; a schematic showing the relative orientations between each layer is presented in Fig. 9.2(c).
Fig. 9. 2 Typical XRD patterns of Bi$_2$Se$_3$/MgO/c-sapphire heterostructures: (a) out-of-plane $\theta$-20 patterns, (b) in-plane $\Phi$-scan patterns excited from the Bi$_2$Se$_3$ \{015\}, MgO \{200\} and c-sapphire \{104\} planes and (c) schematic showing the relative orientations between each layer.
Detailed microstructural analysis was performed by HRTEM and HAADF-STEM on both Cr$_2$O$_3$ and MgO–bilayer samples. All the images present here were taken in the c-sapphire [11-20] zone axis. Fig. 9.3(a) and Fig. 9.3(b) show the interfaces within Cr$_2$O$_3$/c-sapphire and Bi$_2$Se$_3$/Cr$_2$O$_3$, indicating that both are clean, sharp and reaction free. The fast Fourier transform (FFT) diffraction patterns in the insets confirm the highly epitaxial growth of the Cr$_2$O$_3$ layer. The atomically ordered structure of Bi$_2$Se$_3$ is observed in Fig. 9.3(b) where the horizontal arrows and the kinks in the zig-zag lines identify twin boundaries which are in agreement with the Φ-scan results. The Bi$_2$Se$_3$ layered structure, formed by Bi and Se, are stacked along the c-direction in five layer packets Se$_1$-Bi-Se$_2$-Bi-Se$_1$ that connect to each other by weak van der Waals bonds that are also shown in Fig. 9.3(b), indicating the high quality of Bi$_2$Se$_3$.

Fig. 9.3(c) shows the interface between MgO and c-sapphire in an MgO-bilayer. Fig. 9.3(d) shows more clearly the existence of a ~ 2 nm spinel structure that formed at the interface when MgO was grown at 650 °C. This interfacial layer, identified as MgAl$_2$O$_4$, was not observed when the deposition was carried out at 550 °C. It should be noted that the presence of this ~ 2 nm interfacial layer at the MgO/c-sapphire interface does not affect the subsequent MgO growth as a rocksalt phase with the [111] axis aligned parallel to the substrate normal. The inset FFT diffraction patterns confirms the epitaxial growth of MgO. Since electrical current will only flow through the Bi$_2$Se$_3$ surface, i.e., charge transport is restricted solely to the upperlaying Bi$_2$Se$_3$ due to the highly insulating nature of MgO, the existence of ~2 nm MgAl$_2$O$_4$ should not affect the transport properties. Fig. 9.3(e) shows an HRTEM image at the Bi$_2$Se$_3$ and MgO interface, showing a clean and sharp interface with no evidence of any interfacial reaction which is crucial for a strong proximity effect in hybrid structures. Lamellar twins are found at the boundaries of the different stacking sequences parallel to the growth
plane in Bi$_2$Se$_3$; these are seen in the marked region in Fig. 9.3(e). The microstructure results are consistent with the XRD Φ-scan with six peaks seen presented in Bi$_2$Se$_3$ bilayer.
Fig. 9.3(a) HRTEM image of Cr$_2$O$_3$/c-sapphire interface, (b) cross-sectional HAADF-STEM image of the Bi$_2$Se$_3$/Cr$_2$O$_3$. The horizontal arrows identify twin boundaries; (c) HRTEM images of the MgO/c-sapphire interface, (d) enlargement of the image in (c), showing the
spinel structure at the MgO/c-sapphire interface and (e) cross-sectional HAADF-STEM image of the Bi$_2$Se$_3$/MgO interface in the c-sapphire [11-20] zone axis.

Fig. 9.4 compares the resistivity versus temperature for all three sample types, directly revealing the influence of the magnetic layer on transport in Bi$_2$Se$_3$. At high temperatures, all films show metallic behavior. Although they have approximately the same temperature coefficients in resistivity, the bilayer samples have larger resistivity (or suppressed conductivity), compared to the control sample, with the highest resistivity found in the MgO-bilayer for all temperatures. As the temperature decreases, the resistivity shows a minimum and then increases as the temperature decreases further, suggesting stronger electron-electron interactions in two-dimensional (2D) systems. A comparison of the low-temperature insulating behaviors of all samples is shown in the inset of Fig. 9.4. The insulating behavior in the bilayer samples is more pronounced than in the control sample. The onset temperature of the insulating behavior is also higher in the bilayer samples. These results suggest that the magnetic layers may be responsible for the stronger insulating behavior in the bilayer samples. The onset temperature in the MgO-bilayer sample (~42 K) is higher than that in the Cr$_2$O$_3$-bilayer sample (~28 K) which is explained on the basis of their microstructural differences.
Fig. 9.4 Resistivity as a function of temperature for the Cr$_2$O$_3$-bilayer, the MgO-bilayer and the control sample. The inset shows the normalized resistivity versus T

Fig. 9.5 (a) shows the low magnification bright-field TEM image of a cross-section of the MgO-bilayer sample where Bi$_2$Se$_3$ contains a small misorientation between two grains, labelled A and B respectively. The selected area electron diffraction (SAED) pattern in Fig. 9.5 (b) further confirms that the Bi$_2$Se$_3$ spot is split into two components with coherence; the angle between these two spots is less than 2 degrees. The observation of extra diffraction patterns with the same radius in Bi$_2$Se$_3$ is believed due to the small angle grain boundaries, referred to as sub-grain boundaries, when the Bi$_2$Se$_3$ was grown on MgO. It should be noted that the sub-grain boundaries are not distinctly sharp owing to the fact that these boundaries can run in any direction leading to an overlap of neighboring domains in the projected TEM
zone direction. Nonetheless, such small-angle tilt grain boundaries are not observed in the Cr$_2$O$_3$-bilayer samples. The SAED pattern of Cr$_2$O$_3$-bilayer sample is shown in Fig. 9.5 (c), and no evidence of the sub-grain diffraction patterns is observed. Therefore, the higher resistivity and onset temperature in the MgO-bilayer sample could be associated with grain boundary scattering, which could increase the resistivity.
Fig. 9. (a) Low magnification TEM image of an MgO-bilayer sample, showing two small misorientated Bi$_2$Se$_3$ grains (labelled A and B), (b) selected area diffraction pattern of an MgO-bilayer sample, showing the small misorientation (depicted by the small arcs) in Bi$_2$Se$_3$, and (c) selected area diffraction pattern of the Cr$_2$O$_3$-bilayer.
The normalized magnetoresistances (MR) as a function of temperature (2 K–25 K) and magnetic field perpendicular to the films are compared in Fig. 9.6 (a) and 6(b) for Cr₂O₃-bilayer versus control sample and MgO-bilayer versus control sample, respectively. The shape of the MR in bilayer structures are drastically different from the control samples, though they have overall positive MR, and at low magnetic field the MR exhibits the weak antilocalization (WAL) cusp feature. This WAL could reflect the nontrivial topology of the surface states and is suppressed when the temperature increases as a result of the decreasing coherence length. At higher magnetic fields (> 4 T), the MR of the control sample does not saturate and follows a linear-like dependence, showing a positive, weak temperature-dependence up to B = 5 T. The linearity of the MR can be interpreted through the quantum MR model proposed for a zero gap band structure with Dirac linear dispersion. In contrast, the bilayer samples quickly saturate at low magnetic field (~2.5 T). Fig. 9.6 (c) compares the MR at T= 2 K for all samples as a function of perpendicular magnetic field. As a result of proximity with Cr₂O₃ and MgO, the localization behavior of the Bi₂Se₃ is significantly altered. The enlarged part in Fig. 9.6 (c) clearly shows that the introduction of magnetic components reduces the sharpness of bilayer samples, the cusp features at low magnetic field, indicating a weakened WAL effect which may be associated with an increase of backscattering of Dirac fermions.
Fig. 9. 6 Normalized magnetoresistance, $R(H)/R(0)$, versus temperature and perpendicular magnetic field for (a) Cr$_2$O$_3$-bilayer sample versus control sample and (b) MgO-bilayer sample versus control sample. (c) $R(H)/R(0)$ comparison of three samples at $T = 2$ K for -2.5 T to +2.5 T (enlarged part is for -0.3 T to + 0.3 T).
To understand the origin of the weakened WAL effect in the bilayer samples, the low-field magnetoconductance (MC) data is analyzed quantitatively using the Hikami-Larkin-Nagaoka (HLN) equation and the phase coherence length ($l_\phi$) as a function of temperatures is extracted for all samples:

$$\Delta G_{WAL}(B) = G(B) - G(0) \cong \alpha \cdot \frac{e^2}{2\pi^2 \cdot \hbar} \left[ \Psi \left(1 + \frac{\hbar}{4eBl_\phi} \right) - \ln \left(\frac{\hbar}{4eBl_\phi} \right) \right]$$

where $l_\phi$ is the phase coherence length, $\Psi$ is the digamma function, and $\alpha$ is a coefficient determined by the type of localization. Fig. 9.7 (a-c) show the temperature dependence of the phase coherence length ($l_\phi$) for the three sample types, extracted using HLN equation. Theoretically, the coherence length is proportional to $T^{-1/2}$ and $T^{-3/4}$ for 2D and 3D systems, respectively. The monotonic decrease of the coherence length with increasing temperature is observed in both bilayer and the control samples, similar to other TI systems. The fitting gives $l_\phi = T^{-0.4289}$ for the control sample, $l_\phi = T^{-0.4271}$ for the Cr$_2$O$_3$-bilayer sample and $l_\phi = T^{-0.4144}$ for the MgO-bilayer sample, suggesting the dominant dephasing mechanism is $e$-$e$ interactions in 2D surface states.

Yet, the Cr$_2$O$_3$-bilayer sample has the smallest $l_\phi$ among all samples whereas the MgO-bilayer and control samples have similar $l_\phi$. $l_\phi(T)$ is plotted in Fig. 9.7 (d). The noticeable difference in $l_\phi$ between Cr$_2$O$_3$-bilayer and MgO-bilayer samples is explained by the anisotropic magnetization in Cr$_2$O$_3$ and MgO layers.
Fig. 9.7 Temperature dependence of the phase coherence length for (a) a control sample, (b) a Cr$_2$O$_3$-bilayer sample, (c) an MgO-bilayer sample and (d) the comparison of all three.

It is important to note that in TI/FMI hybrid structures, even though strong exchange coupling exists across the interface, no gap in the topological surface states is expected with in-plane magnetization. When the magnetic easy axis of the ferromagnetic material (FM) is out-of-plane, a gap opens in the surface states of the vicinal TI$^{33,38}$. The magnetic properties were measured with the applied magnetic field parallel (Fig. 9.8) and perpendicular (Fig. 9.9)
to the Bi₂Se₃ (003n) surface for all bilayer sample types. The control samples are diamagnetic in both directions, consistent with previous reports³⁹. The in-plane magnetization at 300 K and 5 K for Cr₂O₃ and MgO-bilayer samples provide the evidence of ferromagnetic signatures with clear saturation and hysteresis. Interesting, the Cr₂O₃-bilayer sample is paramagnetic with observable coercivity in the out-of-plane direction, whereas the MgO-bilayer is diamagnetic in this orientation. The considerable reduction of ℓ in the Cr₂O₃-bilayer is likely caused by additional inelastic scattering, such as electron-magnon scattering, to the topological surface states proximate to the magnetic layer with a perpendicular anisotropy component³²,⁴⁰.
Fig. 9.8 Magnetic hysteresis loops for in-plane magnetic field for (a) a control sample, (b) a Cr$_2$O$_3$-bilayer sample and (c) an MgO-bilayer sample.
Fig. 9.9 Magnetic hysteresis loops for out-of-plane magnetic field for (a) a control sample, (b) a Cr$_2$O$_3$-bilayer sample and (c) an MgO-bilayer sample.

The angular dependence of the resistance was measured by rotating the samples 360 degrees in a 7.5 T magnetic field at $T = 2$ K; the result are presented in Fig. 9.10. It is known that the WAL induced by 2D surface states is characterized by a sole dependence on the perpendicular component of the applied magnetic field (0 and 180 degrees). A strong dependence of the resistance on angle is observed for the control sample; the data is accurately described by a
cosine function. For the bilayer samples, the WAL contribution from the bottom surface states expected to be limited or may coexist with a 3D bulk Fermi surface owing to the magnetic layers. Therefore, both bilayer samples seem to suppress the surface transport channel, as well as the WAL, in the topological surface states. We attribute these transport phenomena to the increased magnetic scattering at the TI/FMI interface.
Fig. 9.10 The angular dependence of resistance at 7.5 T, 2 K for (a) a control sample, (b) a Cr2O3-bilayer sample and (c) an MgO-bilayer sample.
9.4 Summary

We have demonstrated the growth of new platforms for topological insulator/ferromagnetic insulator heterostructures by interfacing Bi$_2$Se$_3$ with Cr$_2$O$_3$ and MgO thin films, showing proximity-induced interfacial magnetization. The lattice misfit of Cr$_2$O$_3$/Bi$_2$Se$_3$ and MgO/Bi$_2$Se$_3$ are ~16 \% and ~39 \%, respectively, where the critical thickness of pseudomorphic growth is less than one monolayer. The Bi$_2$Se$_3$ bilayers are characterized by atomically sharp and reaction-free interfaces. The insulating behavior in the bilayer samples are more pronounced and the onset temperatures are higher as compared to the control sample. The MgO-bilayer sample has the largest resistivity and the highest onset temperature (~42 K) due to the existence of small misorientations between grains in the Bi$_2$Se$_3$ thin films. This could give rise to an increase in resistivity owing to grain boundary scattering. The shortest phase coherent length ($l_\phi$) in the Cr$_2$O$_3$–bilayer samples is attributed to the additional inelastic scattering between the Cr$_2$O$_3$ and Bi$_2$Se$_3$ interface with a perpendicular anisotropy component. Our hybrid structures demonstrate the suppression of the 2D surface channel as well as a weakened WAL in the TSS. However, stronger perpendicular magnetocrystalline anisotropy is required to observe the time-reversal symmetry breaking and further investigation is needed to establish the exact mechanism for ferromagnetism in these heterostructures.
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Chapter 10 Summary

This dissertation presents a systematic investigation on the two potential material systems which can be used for spintronics devices. The first is diluted magnetic semiconductor (DMS) and the second is topological insulator (TI). Sr$_3$SnO is the emerging room temperature DMS material and Bi$_2$Se$_3$ is the typical TI material. We have systematically studied the structural, chemical, electrical, and magnetic properties of Sr$_3$SnO and Bi$_2$Se$_3$ grown by PLD under different growth conditions and annealed in different ambient. The outcome of the research is summarized in the following sections:

1. Epitaxial integration of dilute magnetic semiconductor Sr$_3$SnO with Si (001) substrate
   - The epitaxial Sr$_3$SnO (SSO) is successfully integrated with the technologically important substrate Si (001).
   - We find that the electrical transport is governed by variable-range-hopping conduction mechanism.
   - We show that SSO exhibits ferromagnetic semiconducting (also known as the dilute magnetic semiconductor, DMS) behavior at room temperature.
   - Such a novel DMS material integrated with Si (001) computer chip may open a new avenue for next generation spintronic devices.

2. Oxygen vacancy enhanced room-temperature ferromagnetism in Sr$_3$SnO/c-YSZ/Si (001) heterostructures
   - The magnetic properties of single crystal Sr$_3$SnO (SSO) thin films have been found to strongly depend on post-growth annealing treatments.
   - We find that post-growth vacuum annealing enhances saturation moments ($M_s$) and coercivities ($H_c$) while oxygen annealing degrades both properties, suggesting oxygen vacancies play a crucial role in tailoring the room temperature ferromagnetism (RTFM) within the SSO system.
   - We demonstrate that the observed RTFM in SSO thin films can be quantitatively interpreted through a bound magnetic polaron (BMP) model.
• We show that a linearly proportional correlation between the extracted densities of BMP to the X-ray photoelectron spectroscopy O 1s values.

3. Tunable electronic structure in Sr₃SnO/c-YSZ/Si (001) heterostructures

• The systematic study of the structural, physical and chemical behaviors of epitaxial thin films of an emerging diluted magnetic semiconductor (DMS), Sr₃SnO (SSO), integrated with Si (100) prepared by various post-growth annealing treatments are reported.

• On the basis of detailed XRD studies, no additional peaks are observed for oxygen annealed, pristine and vacuum annealed samples, excluding the possibility of formation of any other phase. The only difference is the full width at half maximum and the peak shift related to the bulk value, showing the analogous trend with the oxygen vacancy concentration which is revealed from x-ray photoelectron spectroscopy; as the oxygen vacancy concentration increases, both values increase correspondingly.

• The increased oxygen vacancy concentration generated by post-growth vacuum annealing results in a shorter hopping distance and reduced hopping energy and Coulomb gap, leading to lower resistivity; oxygen annealing shows the opposite effects. It is therefore believed that the carriers in SSO are due to oxygen vacancies.

• The evidence indicates that the density of states near the Fermi energy, for vacuum annealed, is 50% higher than oxygen annealed, whereas Coulomb gap is 35% less as compared to oxygen annealed. Meanwhile, the work function ranges from 4.54 to 4.02 eV and shows a negative linear relationship with oxygen vacancy concentration, accompanied by a 0.42 eV shift in the surface Fermi level.

• The transport and ultraviolet photoelectron spectroscopy probes agree quantitatively on measurement of the resistivity and surface electronic structure. The results provide a direct and consistent explanation that the property changes in the bulk and at the surface are primarily attributed to oxygen vacancies.
• The ability to manipulate the work function and oxygen vacancy concentration in epitaxial DMS SSO thin films offers great potential for the development of spintronic devices.

4. Evidence for topological surface states in epitaxial Bi$_2$Se$_3$ thin film grown by pulsed laser deposition through magnetotransport measurement and angle-resolved photoemission spectroscopy

• The epitaxial Bi$_2$Se$_3$ thin films grown successfully on Al$_2$O$_3$ (0001) substrates by pulsed laser deposition (PLD) using domain matching epitaxy (DME) paradigm, where the lattice misfit of 13% between the film (aBi$_2$Se$_3 = 4.143$ Å) and the substrate (aAl$_2$O$_3 = 4.758$ Å) is accommodated by integrated matching of 7/6 and 8/7 planes with a domain variation frequency parameter of 0.736.

• Under these misfit conditions, the critical thickness for pseudomorphic growth is less than one monolayer, and therefore an equilibrium structure of Bi$_2$Se$_3$ is formed from the beginning.

• X-ray and electron diffraction patterns confirm that the layers are epitaxial with (0001)Bi$_2$Se$_3$$\parallel$(0001)Al$_2$O$_3$ and [21̅1] Bi$_2$Se$_3$$\parallel$[21̅1] Al$_2$O$_3$ (or) [21̅1]Bi$_2$Se$_3$$\parallel$[11̅2]Al$_2$O$_3$ relationship.

• X-ray photoemission spectroscopy (XPS) reveals that the films are Se-deficient, in agreement with electrical transport data showing n-type carriers and metallic behavior.

• Magneto-resistance (MR) measurements show a cusp feature corresponding to weak antilocalization (WAL) and linear-MR (LMR) shows a non-saturating trend up to 9 T. The observation of WAL and LMR phenomenon can be considered as signatures of the existence of topological surface states (TSS).

• The observed angular dependence of MR can be well fitted by a $|cos\theta|$ function, suggesting an obvious 2D response. The coefficient $\alpha$ has value of -0.5 which indicates a single coherent 2D channel. The phase coherence length ($l_\phi$) has power law dependence on temperature ($l_\phi \sim T^{-0.43}$), and this is close to the 2D transport.
The results demonstrate that PLD is not only a potential technique for Topological insulators (TI) applications, but also paves the way to in-situ synthesis of multi-layered heterostructures based on TI materials.

5. Control of intrinsic defects and magnetotransport properties of Bi$_2$Se$_3$/c-sapphire epitaxial heterostructures

- A novel growth approach to minimize the selenium (Se) vacancies in Bi$_2$Se$_3$ epitaxial thin films grown on c-sapphire substrates by pulsed laser deposition which can suppress the bulk conduction and enhance the surface states transport properties.
- Magnetotransport measurements show a strong dependence on microstructure which is associated with Se content in Bi$_2$Se$_3$ thin films. It is found that Se-vacancy-induced strain plays a critical role in controlling electrical and topological insulator properties. The less-Se vacancies films contain the higher longitudinal compressive strain along the [001] direction and can successfully minimize the lamellar twin boundaries and stacking fault formation, magnifying the spin-orbit effect and increases the topological gap.
- The XRD θ-2θ measurements confirm that the extra-Se films contain higher longitudinal compressive strain along the [001] direction with smaller d(0015)=1.9088 Å compared to the pristine films (with more Se vacancies), whose d(0015) = 1.9103 Å. The average values of the c lattice parameter, estimated from STEM-HAADF images, is 29.37 ± 0.05 Å in the extra-Se films and 30.19 ±0.05 Å in the pristine films, consistent with XRD results.
- On the basis of detailed XRD studies, the Φ-scans of the extra-Se films further demonstrate that a significantly decreased intensity of one triplet which occurs at the other in-plane rotation angle as the c-sapphire substrate {012}, indicating the partial suppression of one family of twin domains due to the higher Se content.
- This work sheds light on the importance of controlling the intrinsic defects during the growth of Bi$_2$Se$_3$ thin films, providing an effective way to suppress
the bulk conductivity and establish the correlation between microstructure and the related topological insulator properties, suggesting new avenues for Bi$_2$Se$_3$ thin film growth and engineering its properties through the manipulation of intrinsic defects.

6. Microstructure and transport properties of epitaxial topological insulator Bi$_2$Se$_3$ thin films grown on MgO (100), Cr$_2$O$_3$ (0001) and Al$_2$O$_3$ (0001) templates

- The detailed structural, magnetic, and magnetotransport characterizations of new platforms for topological insulator (TI)/ferromagnetic insulator (FMI) heterostructures are present.
- Two hybrid heterostructures, Bi$_2$Se$_3$/Cr$_2$O$_3$/c-sapphire and Bi$_2$Se$_3$/MgO/c-sapphire, are studied based on proximity-induced ferromagnetism in a TI by interfacing the Bi$_2$Se$_3$ thin films with defect-induced FMI materials, Cr$_2$O$_3$ and MgO, respectively.
- The high resolution TEM images and XRD in-plane phi-scan results confirm that the Bi$_2$Se$_3$ thin films are grown in a highly epitaxial nature on MgO (100), Cr$_2$O$_3$ (0001) and Al$_2$O$_3$ (0001) templates.
- Under the large lattice misfit between Bi$_2$Se$_3$/MgO is ~16 % and for Bi$_2$Se$_3$/Cr$_2$O$_3$ is ~39 % , the misfit strain is relieved within a couple of monolayers and can be confined near the interface based on domain matching epitaxy paradigm.
- The insulating behavior of the low temperature region is more pronounced as Bi2Se3 layer interface with the MgO and Cr$_2$O$_3$ thin films due to the additional scattering of the surface states.
- The monotonic decrease of the coherence length ($l_\phi$) with increasing temperature is observed in all three sample types while the notice difference in $l_\phi$ between Cr$_2$O$_3$-bilayer and MgO-bilayer samples is explained by the anisotropic magnetization in Cr$_2$O$_3$ and MgO layers.
- The weak antilocalization effect from the surface states are clearly suppressed for both hybrid heterostructures, accounting for the presence of magnetic bottom layers.
This work demonstrates an effective way to study the emergence of a ferromagnetic phase in topological insulators by the magnetic proximity effect in Bi$_2$Se$_3$, a step toward unveiling their exotic properties.