CHAPTER 2 RESEARCH METHODOLOGY

2.1 Thin Film Processing by Pulsed Laser Deposition (Basic principles and advantages)

The current interest in the use of lasers, either for scientific investigations or for industrial applications, is directly linked to the unique properties of laser light. The high spatial coherence achieved with lasers permits extreme focusing and directional irradiation at high energy densities. The monochromaticity of laser light, together with its tenability, opens up the possibility of highly selective narrow-band excitation. Controlled pulsed excitation offers high temporal resolution and often makes it possible to overcome competing dissipative mechanisms with the particular system under investigation. The combination of all of these properties offers a wide and versatile range of quite different applications.

Material processing with laser takes advantages of virtually all of the characteristics of laser light. The light energy density and directionality achieved with lasers permits strongly localized heat- and photo-treatment of materials with a spatial resolution of better than its wavelength. The monochromaticity of laser light allows for control of depth of heat treatment or selective, nonthermal citation either within the surface of the material or within the molecules of the surrounding medium-simply by changing the laser wavelength.

The advantages of laser processing also include reproduction of the target stoichiometry, low contamination levels and in-situ control of the film properties. The controlled
melting of the thin metallic overlayers deposited on various structures has been used in the formation of metal silicides and ohmic contacts for large band gap semiconductors and in modifying the surface properties of ceramics.

Conceptually and experimentally, Pulsed Laser Deposition (PLD) is simple. Figure 1 shows a schematic diagram of a typical experimental setup. It consists of a multiple target holder and a substrate holder in a high vacuum chamber maintained by a turbomolecular pump. The target consists of bulk material oriented at an angle of 45° with respect to the incident laser beam. A high-power laser is used as an external energy source to vaporize materials and to deposit thin films. A set of optical components is used to focus and raster the laser beam over the target surface. The evaporated material is deposited onto a substrate placed parallel to the target at distance of 3-5cm. The substrate temperature can be varied from room temperature to 800°C. The film quality depends various parameters such as substrate temperature, laser energy density, pulse repetition rate, pressure in the chamber, and substrate-target geometry. The decoupling of the vacuum hardware and the evaporation power source makes this technique so flexible that it is easily adaptable to different operational modes without the constrains imposed by the use of internally powered evaporation sources. Film growth can be carried out in a reactive environment containing any kind of gas with or without plasma excitation. It can also be operated in conjunction with other types of evaporation sources in a hybrid approach.
In contrast to the simplicity of the hardware, the laser-target interaction is a very complex physical phenomenon. Theoretical descriptions are multidisciplinary and combine both equilibrium and nonequilibrium processes. The mechanism that leads to material ablation depends on laser characteristics, as well as the optical, topological, and thermodynamic property of target. When the laser radiation is absorbed by a solid surface, electromagnetic energy is converted first into electronic excitation and then into thermal, chemical, and even mechanical energy to cause evaporation, ablation, excitation, plasma formation, and exfoliation. Evaporations results in a ‘plume’ consisting of a mixture of energetic species including atoms, molecules, electrons, ions, clusters, micron-sized solid particulates, and molten globules. The collisional mean free path inside the
dense plume is very short. As a result, immediately after the laser irradiation, the plume rapidly expands into the vacuum from the target surface to form a nozzle jet with hydrodynamic flow characteristics. PLD is so versatile that with the choice of an appropriate laser, it can be used to grow thin films of any kind of material. The versatility is reflected in the rapidly growing list of materials deposited. A search by Beech in 1991 lists 128 different materials grown by PLD.

Figure 2. Schematic representation of the stages of laser target interactions during short pulse high power laser interaction with a solid. (Ref. 9)

In order to understand basic physical principle of PLD further, during each of the nanosecond laser pulse, laser-target interaction can be divided into three stages shown schematically in figure 2. Depending on the type of interaction of the laser beam with
the target there are three separate regimes: (i) interaction of the laser beam with the target materials resulting in evaporation of the surface layers, (ii) interaction of the evaporated material with the incident laser beam resulting in isothermal plasma formation and expansion, and (iii) anisotropic adiabatic expansion of the plasma and subsequent deposition. The first two regimes start with the laser pulse and continue through laser pulse duration. The third regime starts after the termination of the laser pulse.  

(i) Interaction of the laser beam with the target

Intense heating of the surface layers by high-power nanosecond laser pulses results in melting and evaporation of the surface layers. The heating rate, melting and evaporation during pulsed laser irradiation depend on: (i) laser parameters—pulse energy density $E$, pulse duration $\tau$, wavelength $\lambda$ and shape of the laser pulse and (ii) materials properties—reflectivity, absorption coefficient, heat capacity, density, thermal conductivity, etc.. The free carrier (hole) collisions provide the mechanism for the absorption of the phonon energy in the bulk surface.

The heating and melting effects of pulsed laser irradiation on materials constitute a three-dimensional heat flow problem. In nanosecond laser processing, the thermal diffusion distances are short, and the dimensions of the laser beam—large compared to the melt depth. Hence, the thermal gradients parallel to the interface are many orders of magnitude less than the thermal gradients perpendicular to the interface. This makes the problem for heat flow during PLD one dimensional governed by:

$$\rho_{i}(T)C_{p}(T)\frac{\partial T_{i}(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[K_{i}(T)\frac{\partial T_{i}(x,t)}{\partial x}\right] + I_{o}(t)[1-R(T)]e^{-\alpha(x/l)} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots
Where $x$ refers to the direction perpendicular to the plane of the sample and $t$ refers to the time. The subscripts $i=1, 2$ refer to the solid and liquid phase respectively. The terms $\rho_i(T)$ and $C_p(T)$ are respectively the temperature dependent density and thermal heat capacity per unit mass of the target material. $R(T)$ and $a(T)$ are the temperature dependent reflectivity and absorption coefficient of the material corresponding to laser wavelength. The term $I_0(t)$ is the time dependent incident laser intensity striking the surface which depends on the intensity and shape of the laser pulse. The term $K_i$ refers to thermal conductivities of the solid and liquid phases at the interface. The last term on the right hand side of the equation (1) is the heat generation term. Accurate numerical solution to this equation by finite difference method gives the evaporation characteristics of the pulsed laser irradiated materials. Using this method, the thermal histories of the laser-irradiated materials can be predicted. Thus the effects of the variations in the pulse energy density $E$, pulse duration $t$, and substrate temperature $T$ on the maximum melt depths, solidification velocities and surface temperatures can be computed.

Although the presence of a moving surface formed as a result of melting or evaporation, and time-dependent optical and material properties make it difficult the analytical solution, simple energy balance considerations can be taken into account to assess the effects of interaction of the laser irradiation with the materials. By using energy balance method the amount of material evaporated per pulse can be calculated. The energy deposited by the laser beam on the target is equal to the energy needed to vaporize the surface layers plus losses due to the thermal conduction by the substrate and the absorption by the plasma. The energy threshold $E_{th}$ represents the minimum energy
above which appreciable evaporation is observed. Since the losses in plasma and substrate change with pulse energy density, Eth varies with energy density too. Thus the heat balance equation is given by:

\[
\Delta x_i = \frac{(1 - R)(E - E_{th})}{\Delta H + C_v \Delta T} \]

where \(\Delta x_i\), \(R\), \(\Delta H\), \(C_v\) and \(\Delta T\) are the evaporated thickness, reflectivity, latent heat, volume heat capacity, and the maximum temperature rise, respectively. This equation is valid for conditions where the thermal diffusion distance \(\sqrt{2Dt}\) is larger than the absorption length, or attenuation distance of the laser beam in the target material \((1/a_t)\). In the above expression, \(D\) is the thermal diffusivity of the target, and \(t\) is the larger pulse duration. In equation 2 the energy threshold depends on laser wavelength, pulse duration, plasma losses, and the thermal and optical properties of the material.

(ii) Interaction of the laser beam with evaporated materials

The interaction of the high-power laser beam with the bulk target materials leads to very high temperature (>2000K), resulting in emission of positive ions and electrons from the free surface. The emission of electrons and positive ions from a solid surface exhibits an exponential increase with temperature. The thermionic emission of positive ions can be calculated by Langmuir-Saha equation:

\[
i_+ / i_0 = (g_+ / g_0) \exp[(\phi - I)kT] \]

where \(i_+\) and \(i_0\) represent positive and neutral ion fluxes leaving the surface at temperature \(T\). \(g_+\) and \(g_0\) are the statistical weights of the ionic and neutral states, \(\phi\) is the electron work function, and \(I\) is the ionization potential of the materials. The fraction
of ionized species increases with the temperature since \( I > \phi \). Although the surface temperature of the target is close to boiling point, higher temperatures can be induced in the evaporated plasma by the interaction of the laser beam with it. The penetration and absorption of the laser beam by the plasma depend on the electron-ion density, temperature, and the laser wavelength. The penetration or reflection of the incident laser beam depends on the plasma frequency: \( \nu_p = 8.9 \times 10^3 n_e^{0.5} \), where \( n_e \) is the electron concentration in the plasma. The plasma frequency should be lower than the laser frequency for the laser energy to be transmitted or absorbed. For example, for XeCl2 excimer-laser wavelength \( \lambda = 308 \text{ nm} \) the laser frequency is \( 9.74 \times 10^{14} \text{ sec} \) with critical electron density for reflection given by \( n_e = 1.2 \times 10^{22}/\text{cm}^3 \).

The material evaporated from the hot target is further heated by absorption of laser radiation. Although the laser evaporation for deposition of thin films occurs at much lower temperatures, the plasma temperatures are of the order of 10^4 K. Different mechanisms become important in the ionization of the laser generated species: impact ionization, photo ionization, thermal ionization and electronic excitation.

The primary absorption mechanism for plasma is the electron-ion collisions. The absorption occurs primarily by a process, which involves absorption of a photon by free electron. The absorption coefficient \( \alpha_p \) of the plasma is given by:

\[
\alpha_p = 3.69 \times 10^8 \left( Z^3 n_i^2 / T^{0.5} \nu^3 \right) \left[ 1 - \exp(-h\nu/kT) \right] \frac{1}{\left( \exp(1069.3 \nu^{-35.0238}) \right)} \]

\( \text{………………….}(4) \)

where \( Z, n_i, \) and \( T \) are the average charge, ion density, and temperature of the plasma, respectively, and \( h, k, \) and \( \nu \) are the Plank constant, Boltzman constant, and frequency of
the laser light respectively. The term \( I - \exp(-hv/kT) \) in equation (4) represents the losses due to stimulated emission. For KrF excimer laser (\( \lambda = 248 \text{nm} \)), the exponential term becomes unity for \( T \ll 40,000 \text{K} \) and can be approximately by \( hv/kT \) for \( T \gg 40,000 \text{K} \). The absorption term shows a \( T^{0.5} \) dependence for low temperature (\( T \ll 40,000 \text{K} \) for \( \lambda = 248 \text{nm} \), \( T \ll 40,000 \text{K} \) for \( \lambda = 1.06 \text{nm} \)) and \( T^{1.5} \) for high temperatures. As it is seen, the heating of the evaporated materials depends on the concentration of the ionized species, plasma temperature, wavelength, plasma temperature, wavelength, pulse duration, etc. Also the particle density in the plasma depends on the degree of ionization, evaporation rate, and the plasma expansion velocities.

Figure 3. Schematic diagram representing the different phases present during irradiation of a laser on a bulk target: (A) unaffected bulk target, (B) evaporated target materials, (C) dense plasma absorbing the laser radiation, and (D) expanding plasma transparent to the laser beam. (From ref. 9)
Because of the high expansion velocities of the leading plasma edge, the electron and ion densities decrease very rapidly with time. This makes the plasma transparent to the laser beam for larger distances away from the target surface. The inner edge of the plasma in a thin region close to the surface of the target it constantly absorbing laser radiation due to the constant augmentation of the plasma with evaporated particles. A schematic diagram of the laser interaction with the plasma target is shown in figure 3. The diagram shows that four separate regions can be distinguished during the laser pulse. These are: (1) unaffected bulk target, (2) evaporating target surface, (3) area near the surface of the target absorbing the laser beam, (4) rapidly expanding outer edge which is transparent to the laser beam. A dynamic equilibrium exists between (i) the plasma absorption and (ii) the rapid transfer of thermal energy into kinetic energy. These are two mechanisms controlling the isothermal temperature of the plasma. The initial dimensions of the plasma are of the order of a millimeter in the transverse direction, while they are less than 1µm in the perpendicular direction. During the isothermal regime and assuming an initial expansion velocity of $10^5-10^6$ cm/sec, the perpendicular dimension of the plasma is in the order of 10-100µm at the end of a 30nsec laser pulse. The rapid plasma expansion in vacuum results from the large density gradients. The plasma absorbing the laser energy can be simulated as a HT-HP gas which is initially confined in small dimensions and is suddenly allowed to expand in a vacuum. The equations of gas dynamics governing the expansion of the plasma consist of the equation of continuity and the equation of motion. The velocity, density, and the pressure profiles in the plasma are shown schematically in figure 4. It shows that the density is maximum while the minimum at the inner edge of the plasma. The plasma density and the pressure gradients are monotonically decreasing
from the surface of the target while the velocity increases linearly. In the initial stages of expansion the acceleration is very high when the expansion velocities are low. When the expansion velocities increase, the acceleration starts to diminish and ultimately becomes zero, resulting in the elongated plasma shape.

![Figure 4](image)

**Figure 4.** Schematic profile showing the density (n), pressure (P), and velocity (v) gradients in the plasma in x direction, perpendicular to the target surface. The density and plasma pressure are monotonically decreasing from the target surface, while the velocity increases linearly. (Ref. 9)

### (iii) Adiabatic plasma expansion and film deposition

After the termination of the laser pulse in vacuum there is no additional input of particles from the target into the plasma because there is no absorption of laser energy. Thus an adiabatic expansion occurs with a thermodynamic relation given by:

\[
T [X(t)Y(t)Z(t)]^{-1} = \text{const} \quad \text{..............................(5)}
\]

where the \( \gamma \) corresponds to the ratio of the specific heat capacities at constant pressure \( C_p \) and volume \( C_v \). During the adiabatic regime, the thermal energy is converted to kinetic
energy with the plasma achieving extremely high expansion velocities. The temperature drop is slow because (1) the cooling due to expansion is balanced by energy regained from recombination processes by ions, and (2) the plasma expands in one direction. The initial dimensions of the plasma are much larger in the transverse direction. The initial dimensions of the plasma are much larger in the transverse direction. The initial dimensions of the plasma are much larger in the transverse directions (y and z) which are in the order of millimeter, while in perpendicular direction (x) is in the order of 20-100µm. In the adiabatic expansion regime the velocity of the plasma increases in the direction of the smallest dimension.

References


2.2 Characterization Methods of Thin Films - Basic Principles and applications

The properties of thin films are determined by their chemical composition, the content and type of impurities in the thin film or on the surface, crystal structure of the thin film and on the surface, and the types and density of structural defects. In addition, as the applications of thin films extend to microelectronics, optoelectronics, magnets and other areas, electrical, optical and magnetic properties also have to be monitored and optimized. In particular to TiN, TaN thin films as diffusion barriers in Cu metalization and interconnects, electrical, chemical, and structural analysis should be monitored. For TiN nanocrystalline hard coating, TiN/AlN alloys and superlattices, hardness and structural information are the main properties need to be studied in detail. While for GaN, AlN and their superlattice growth, optical and structural characteristics are the major requirement.

Most experimental procedures including techniques are introduced in the experimental part in each chapter. In the following, several important techniques which have been extensively used during this research are discussed in detail. This study is focused on structural analysis, X-ray, TEM, and STEM techniques will be discussed in detail including basic principles and applications in materials science of thin film. Other analysis including mechanical and electrical property measurements will be described based on principles and definitions.

The listed methods will be discussed in the following sections:

1. X-ray diffraction (Structural: XRD)
2. Transmission Electron Microscopy (Structural: TEM)
3. Scanning Transmission Electron Microscopy (Structural: STEM)
4. Electron Energy Loss Spectroscopy (Elemental: EELS)

5. Nanoindentation (Mechanical: hardness)

6. Electrical resistivity (Electrical)

2.2.1 X-ray diffraction (Structural: XRD)

X-ray diffraction is one of the most important nondestructive experimental techniques used to address issues related to the crystal structure of solids, including lattice constant, identification of unknown materials, orientation of single crystals, preferred orientations of thin films, defects, stress, etc. Basic mechanism of X-ray analysis is based on that, when a parallel and monochromatic X-ray beam with a wavelength $\lambda$ and angle of incidence $\theta$ is diffracted by a set of planes, oriented in specific directions, there are sharp peaks corresponding to the spacing between the planes $d$, when the conditions of the Bragg’s law are satisfied:

$$2d \sin \theta = n\lambda$$ \hspace{1cm} (1)

These peaks are characteristic to the material and the crystal structure. The crystal structure of a specific material determines the diffraction pattern, and in particular the shape and size of the unit cell determine the relative intensities of these lines.

In the structural analysis by using X-ray of known wavelength $\lambda$, and measuring $\theta$, we can determine the spacing $d$ of various planes in the crystal. The essential features of an X-ray spectrometer are shown in figure 1. It should be noted that (1) the incident beam, normal to the reflecting plane, and the diffracted beam are always coplanar; and (2) the angle between the diffracted beam and the transmitted beam is always $2\theta$. X-rays from the tube T are incident on a crystal C which may be set at any desired angle to the
incident beam by rotation about an axis through O, which is the center of the spectrometer circle. D is a counter which measures the intensity of the diffracted x-rays, it can also be rotated about O and set at any desired angular position. Thus by measuring the peak positions, one can determine the shape and size of the unit cell, and by measuring the intensities of the diffracted beams one can determine the positions of atoms within the unit cell. Conversely, if the shape and size of the unit cell of the crystal are known, we can predict the positions of all the possible lines of the film.¹

![Figure 1. Schematic of X-ray spectrometer. (Ref. 1)](image)

In the deviation of the Bragg Law, certain ideal conditions are assumed, for example, the crystal is perfect and the incident beam is composed of strictly parallel and monochromatic radiation. It should be noted that only infinite crystal can be considered as a perfect crystal, and that a small size of an otherwise perfect crystal, can be considered as a crystal imperfection. This comes from the condition that the waves involved in a diffraction reinforce each other and there is a contribution for the destructive interference from the planes deeper into crystal. Destructive interference is therefore just as much a consequence of the periodicity of atom arrangement as it is the
constructive interference. As a result the width of the diffraction curve increase as the thickness of the crystal decreases. Schematic representation of the effect of the fine particle size on diffraction curves is shown in figure 2. The following expression gives the estimate of the particle size of very small crystals from the measured width of their diffraction curves: 

\[ t = \frac{0.9\lambda}{B \cos \theta_B}, \]

where \( B = \theta_1 - \theta_2 , \) ( from figure 2) is the width i.e. the difference between the two extreme angles at which the intensity is zero.

Another cause of line broadening of the x-ray line is due to the natural “spectral width” of the x-ray source which is proportional to \( \tan \theta \) and becomes quite noticeable as \( \theta \) approaches 90°. The effect of the mosaic structure of the crystal or film can also influence the broadening of the X-ray line. Thus if the angle of misorientation between the blocks of the mosaic structure is \( \varepsilon \), the diffraction will occur not only at an angle of incidence \( \theta_B \) but all angles between \( \theta_B \) and \( \theta_B + \varepsilon \). Another effect of the mosaic structure is to increase the intensity of the reflected beam with respect to that theoretically calculated for an ideally perfect crystal.
The diffracted beam is rather strong compared to the sum of all the rays scattered in the
same direction, because of the reinforcement (strengthening) which occurs, but extremely
weak compared to the incident beam. If the scattering atoms are not arranged in a regular,
periodic way then the x-rays will have a random phase relationship to one another and
neither constructive nor destructive interference takes place under such conditions. Then
the intensity of a beam scattered in a particular direction is simply the sum of intensities
of all X-rays scattered in that direction. If there are N scattered rays each with amplitude
A, and therefore with intensity $A^2$ in arbitrary units, then the intensity of the scattered
beam is NA$^2$. However, if the rays are scattered by atoms of a crystal in a direction
satisfying the Bragg Law, then they are all in phase and the amplitude of the scattered
beam is N times the amplitude A of each scattered X-ray or NA. Therefore the intensity
of the scattered beam is therefore $N^2A^2$, or N times as large as if the reinforcement had
not occurred. This explained why the X-ray intensity of a crystal is much higher than that
of an amorphous solid.

As stated earlier the intensities of the diffracted beams are determined by the positions of
the atoms in the unit cell. To establish an exact relationship between intensity and atom
positions is a complex problem because of many variables involved since the X-rays are
scattered by electrons, by atoms, and by all the atoms in the unit cell. When a
monochromatic beam of X-rays strikes an atom, two scattering processes occur. Tightly
bound electrons are set into oscillation and radiate X-rays of same wavelength as that of
the incident beam (coherent scattering). More loosely bound electrons scatter part of the
incident beam and slightly increase their wavelength with an amount depending on the
scattering angle (incoherent angle). Since the intensity of the coherent scattering is
inversely proportional to the square of the mass of the scattering particle, the net effect is that coherent scattering by an atom is due only to the electrons contained in the atom. The atomic scattering factor $f$, describes the efficiency of scattering of a given atom in a given direction, where $f \sim \sin \theta / \lambda$, and the values for $f$ for various atoms and various values of $\sin \theta / \lambda$ are tabulated. A typical variation for $f$ in the case of Cu is shown in Figure 3. The coherently scattered radiation from all the atoms undergoes reinforcement (constructive interference) in certain directions, and thus producing diffracted beams.

![Figure 3. The atomic scattering factor of copper. (Ref. 1)](image)

There are six factors affecting the relative intensities of the diffraction lines: (1) polarization factor, (2) structure factor, (3) multiplicity factor, (4) Lorenz factor, (5) absorption factor, and (6) temperature factor. Thus, the equation for relative intensity of a diffraction line is given by:

$$I = |F|^2 \rho \left( \frac{1 + \cos^2 \theta}{\sin^2 \theta \cos \theta} \right)$$

In equation 2, $F$ is the structure factor accounting for the resulting contribution of a unit cell for a specific hkl reflection, and it is a dimensionless which is the ratio of the
amplitude scattered by the unit cell to the amplitude scattered by one electron in the same
direction. The multiplicity factor \( p \) accounts for the relative proportion of the planes
contributing for same reflection, and can be defined as the number of different planes in a
form, having same spacing. (Example: \( p=6 \) for \{100\}planes in a cubic crystal, and \( p=8 \)
for the \{111\}planes; for a tetragonal crystal \( p=4 \) for \{100\} planes and \( p=2 \) for \{001\}
planes). The expression in the numerator in the brackets of Equation 2 is so called
polarization factor, and it arises from the fact that the incident X-ray beam is not
polarized. The term in denominator is the so called Lorenz factor and it is a sum of three
factors: (1) the value of maximum intensity \( I_{\text{max}} \) depends on the angular range of crystal
rotation over which the energy diffracted in the direction \( 2\theta \) is appreciable, and depends
as \( \sim 1/\sin \theta \), and therefore \( I_{\text{max}} \) is large at low scattering angles, and small at large
scattering angles; (2) the number of microcrystallites favorably oriented for reflection is
proportional to \( \cos \theta \) and is quite small for high angles of reflections; and (3) geometrical
factor giving the length of any diffraction line as proportional to \( R \sin 2\theta \), where \( R \) is the
radius of the camera, and hence the relative intensity per unit length of the line is
proportional to \( 1/\sin 2\theta \). The whole term in brackets in Equation 2 is called Lorentz-
polarization factor and it is plotted in Figure 4. The overall effect of these geometrical
factors is the reduction of reflection intensities at intermediate angles compared to those
in forward or backward directions. The absorption factor resulting in a decreased
intensity of a diffraction beam due to absorption of the incident beam cancel with the
temperature factor due to the thermal vibration of atoms, since the two factors depend on
the scattering angle in opposite ways.
The properties (mechanical, electrical, chemical, etc.) of a single phase aggregate are determined by two factors: (1) the properties of the single crystal of the material, and (2) the way in which the single crystals are put together to form composite mass. Thus the relative size, perfection, and orientation of the grains making up the aggregate or the film determine the properties of the materials.

The size of grains in a polycrystalline material has a pronounced effect on many of its properties, mainly increase in strength and hardness with the reduction of the grain size. X-ray diffraction can give semi-quantitative information about the grain size, along with the information about the crystal perfection and orientation. The size effect of the grains on the diffraction line is revealed by the line broadening. The diameter of the crystal particle $t$ is then measured as $0.9 \lambda / B \cos \theta$, where $B$ is the line broadening.

The crystal perfection or the effect of the strain, both uniform and nonuniform, also determines the diffraction line position and shape as shown in figure 5. If the grain or
film is given uniform tensile strain at right angles to the reflecting planes, their spacings become larger than $d_0$, and the corresponding diffraction line shifts to lower angles, but does not change its shape. However, nonuniform strain (on the top tension, one the bottom compression), cause line broadening.

Figure 5. Effect of lattice strain on the line width and position. (Ref. 2)

And finally, the presence or absence of a preferred orientation in the film can be revealed from the intensity distribution of lines parallel to the substrate surface. In such case only grains which can contribute to the hkl reflection are those whose (hkl) planes are parallel to the substrate surface. If the texture is such that there are very few such grains, the intensity of the hkl reflection will be very low. Extremely high intensity of the hkl planes
then would indicate that the corresponding film planes are preferentially oriented parallel or nearly parallel to the film surface.

References


2.2.2 Transmission Electron Microscopy (Structural: TEM)

Transmission electron microscopy (TEM) is a method used to obtain structural and morphological information from specimens that are thin enough to transmit electrons. This technique can help revolutionizing our understanding of materials by completing the processing-structure-properties down to the atomic levels. TEM has increasing applications, not only in materials science research, but also in the semiconductor device technology, biotechnology, and other material or microstructure related field. For example, In device fabrication, TEM has been extensively used to provide information about the geometry of patterned films, the uniformity of thickness and coverage, in addition to surface morphology and topography, including size and shape, and presence of compounds. Especially recently, the submicron technology has been introduced into device fabrication, the resolution of SEM and other normal surface techniques can not fulfill the requirements of detailed atomic structure study. TEM has become one technique which can probe detail structural and defect information. Additionally, TEM can also give cross-sectional view of interface regions, such as the interfacial reactions, perfection of devices, and diffusion study. The combination of TEM with other analytical techniques, such as STEM, EELS, and EDX, TEM has become a powerful technique which can combine imaging and chemical compositional study down to a single atom(or a column of atoms, strictly speaking). For example, JEOL 2010FEG (NCSU) has point to point resolution of 0.18 nm(TEM), combined with STEM with resolution of 0.12nm and EELS analysis.
In this section, major parameters of TEM are listed. Several important imaging and diffraction techniques are discussed and related examples for different techniques are presented.

**Resolution and Aberration**

The main parameter in a transmission electron microscope is its resolution. Dr. Duscher had a question in midterm of 2002 spring TEM course: “Xerox Microscopy: the patent author claimed to be able to image atoms after copying something with a copy machine 20 times with a magnification of 2. \(2^{20}=1048576\) Is it possible?” The answer is obviously “no”. Usually, the resolution of a Xerox copy machine is about 0.1µm. Although the magnification is increasing after several copies, the resolution has been decided by the first copy of the machine. This question clarified the difference between magnification and resolution.

According to classical Raleigh criterion without any aberration of lenses, the smallest distance that can be resolved is given approximately by:

\[
\delta = \frac{0.61\lambda}{\mu \sin \beta} \tag{1}
\]

where \(\lambda\) is the wavelength of the radiation, \(\mu\) the refractive index of the viewing medium, and \(\beta\) is the semi-angle of collection of the magnifying lens. Due to the coherency of electron beam in TEM and the short wavelength of the accelerated electrons (\(\lambda\) is in the order of hundredths of an A), the resolution limit is down to 1A (for 1MeV electrons \(\lambda=0.0087\)A, and \(a=5\times10^{-3}\) rad).

Spherical aberration, along with the chromatic aberration, and the stigmatism, are the main electromagnetic lens defects that limit the resolution of the electron microscope, shown in figure 1a. The spherical aberration is a lens defect arising from the non-
paraxiality of the electron beam, causing electrons leaving the point P at higher angles with respect to the optic axis of the microscope to cross (to focus) before the image plane, while electrons left the objective lens closer to the optic axis are focused on the image plane. Thus instead of a point, a disk with a radius \( r_s \) is formed, where \( r_s = C_s \beta^2 \), \( \beta \) is the angular aperture of the lens.

Chromatic aberration arises from the non-chromaticity of the electron beam, i.e. the electrons leaving the electron gun are with slight difference of the energy \( \Delta E \) (~3eV). This causes the faster electrons to be less strongly refracted from the objective lens than the lower energy electrons, as shown in figure 1b. The higher energy electrons thus are brought in focus beyond the image plane, which they pass at distance \( r_c = C_c \beta \Delta E / E \), where \( C_c \) is the chromatic aberration coefficient.

Astigmatism arises from the asymmetric magnetic field and it occurs when the lens exhibits different focal lengths, depending on the plane of the ray paths. Thus in figure, the rays traveling plane A are focused at \( P_A \) while those in plane B focus at point \( P_B \). This leads to the fact that a point on the object is imaged as a disk with radius \( r_A = \beta \Delta f_A \), where \( \Delta f_A \) is the maximum difference in focal length arising from astigmatism.

If all the astigmatisms are corrected and the sample is thin enough that chromatic aberration is negligible, then the spherical aberration error limits the resolution. The resolution is given by the combination of Rayleigh criterion and the aberration error.

\[
 r_{\text{min}} = 0.91 (C_s \lambda^3)^{1/4} \quad \text{(2)}
\]

This equation gives the practical resolution of the microscope. Here \( r \) is the spherical aberration error, and \( C_s \) is the spherical aberration, \( \lambda \) is the wavelength of electron.
Figure 1. Objective aberration (a) Spherical, (b) chromatic, (c) astigmatism. (Ref.1)

**Depth of Field and Depth of Focus**

Depth of field D, schematically shown in figure, is the value of extreme specimen positions on both sides of the theoretical object plane P of the objective lens, without destroying the resolution. A specimen shift D/2 with respect to the object plane P, results
in a disc of radius \( r = aD/2 \), where \( a \) is the objective angular aperture. In order to keep the resolution from diminishing, the diameter of this disk should be smaller than or equal to the resolution distance \( d \), so that \( aD = d \). The larger the depth (\( D \sim 500\text{A} \)), the better chance that the specimen is focused on its whole thickness.

Depth of focus \( D' \) is defined similarly in the final image plane as depth of field in the object plane. Now \( d' = dM \) and \( a' = a/M \), where \( M \) is the final magnification. Thus depth of focus \( D' = DM^2 \). Magnification of the order of \( 10^5 \) would give depth of focus \( \sim 500\text{m} \), which means that the fluorescent screen position is not critical.

**Image and Diffraction Modes**

The objective lens takes the electrons emerging from the exit surface of the specimen, disperses them to create a diffraction pattern (DP) in the back focal plane, and recombines them to form an image in the image plane. To see the diffraction pattern you have to adjust the imaging system lenses so that the back focal plane for the intermediate lens. Then the diffraction pattern is projected onto the viewing screen, see figure 2A. For imaging mode, you readjust the intermediate lens so that its object plane is the image plane of the objective lens. Then an image is projected onto the viewing screen, as shown in 2B.
Figure 2. The two basic operations of the TEM imaging system involve (A) Projecting the diffraction pattern on the viewing screen and (B) projecting the image onto the screen. In each case the intermediate lens selects either the back focal plane or the image plane of the objective lens as its objects. (Ref. 4)
Image mode and image contrast

The image contrast in TEM arises because of the scattering of the incident beam by the specimen. As the electron beam transverse the specimen, it changes both its amplitude and phase. These changes give rise to image contrast. There is a fundamental distinction between amplitude contrast and phase contrast which in many cases can both contribute to the image. The amplitude contrast can be described in terms of mass-thickness contrast and diffraction contrast (Williams and Carter 1996). Diffraction contrast is most widely used to identify defects and distinguish between different types of crystal defects. This type of contrast arises due to coherent elastic scattering at special (Bragg) angles. This intensity in a diffracted beam depends strongly upon the deviation parameter, \( s \). The crystal defects distort the diffracting planes and therefore, the diffraction contrast from regions close to the defect would depend upon the properties of the defects (such as strain field). To get good interpretable diffraction contrast, the specimen has to be tilted into two-beam conditions. Mass-thickness contrast arises from incoherent (Rutherford) elastic scattering of electrons, any scattered beam can contribute to the formation of the image.

Two-beam conditions, bright field and dark field

Two-beam conditions, bright field and dark field are specific imaging conditions when the specimen is tilted so that only one diffracted beam is strong. The electrons in the strongly excited hkl beam have been diffracted by a specific set of hkl planes and so the area that appears bright in the dark field (DF) mode is the area where the hkl planes are at Bragg condition. Therefore, the DF image contains specific orientation information. Bright field image is obtained when only the directly, transmitted beam is used for the formation of the image. However, when the image is created using only diffracted beam,
it is called dark field image. The specimen can be tilted to set up several different two-beam conditions. The DF images can be formed from each strongly diffracted beam after tilting the specimen, and each will give a different image. Bright field (BF) and DF images show almost complementary contrast under two-beam conditions. To further enhance the contrast from defects, the specimen has to be slightly tilted away from exact Bragg condition (where \( s=0 \)) towards positive value of \( s \). This way the interpretable images under kinematical diffraction conditions are obtained. Parameter \( s \) is called “deviation from Bragg Condition”.

Figure 3. Ray diagrams showing how the objective lens/ aperture are used in combination to produce (A) a BF image formed from the direct beam, (B) a displaced-aperture DF
image formed with a specific off-axis scattered beam, and (C) a CDF image where the incident beam is tilted so that the scattered beam remains on axis. (Ref. 4)

**Phase contrast and HRTEM**

Phase contrast is formed when the transmitted and diffracted beams recombine, as shown in figure, thus preserving their amplitudes and phases, and this way lattice images or even structure images can be formed. (see Figure 4.)

If details in the structure are to be seen which can give atomic structure, atomic positions, and defects in that structure, to obtain higher and higher resolution, information has to be included from higher and higher angles in reciprocal space, i.e. images should be taken with as many beams as possible-HRTEM. One of the approaches to model the image formation in atomic resolution mode, or high resolution mode is to consider the transmission electron microscope as a linear system, which is the information theory approach. For a linear system \( \alpha S_o + \beta S_o \Rightarrow \alpha S_i + \beta S_i \)

Where the expression on the left arrow is the input signals, and that on the right side out signal. Or in other words linear combination of input signals is transmitted by the system as a linear combination of output signals. Then analogy from the information theory as shown in figure 5: first, input signal is the object phase shift i.e. phase shift in the electron wave function cause by the specimen in TEM; Second, the action of the transmission system (TEM) is to take this input signal in the real space and consider it in Fourier space i.e. consider the input spectrum as object phase shift spectrum in TEM. The way input spectrum is achieved from input signal is by Fourier Transform. Third, then the output spectrum is achieved from image spectrum by multiplying it by transfer function or the
so-called phase contrast transfer function in TEM. Fourth, finally the output signal is taken by inverse Fourier Transform, achieving thus the image contrast. This scheme from the information theory can be used to explain the contrast in TEM.

Figure 4. Phase contrast imaging from a periodic object. The diffracted and transmitted beams recombine at the image plane. (Ref. 2)
Diffraction Mode and Selected Area Diffraction

The most common diffraction mode is the so-called parallel beam mode, with angular dispersion ~10^{-4}-10^{-5} rad, while for specific applications in convergent mode the angular aperture is of the order of 10^{-2} rad. The main features of the electron diffraction are: 1) very small wavelength of electrons compared to lattice parameters resulting in small diffraction angles. Thus the Bragg equation becomes: $2\theta = n\lambda/d_{hkl}$, and the diffraction angle $2\theta \sim 1^\circ$; and 2) There is a very strong interaction with the matter so the kinematic approximation does not apply. In transmission electron diffraction the specimen has to be very thin. With a thin single crystal, the resulting diffraction domains are in the form of fine rods, normal to the specimen. For a hkl reflection to be active, the reflection sphere has to intersect the corresponding diffraction domain. The observed reflections are those relative to the lattice planes (hkl) which have the incident direction [uvw] as a zone axis.
and therefore the reflection indices are those obeying the following expression (for the zero Laue zone):

\[ hu + kv + lw = 0 \]

This is an equation of the reciprocal lattice plane \((uvw)\) passing through the origin and containing lattice point \(hkl\).

**Selected Area Electron Diffraction**

Depending on the adjustment of the post objective lenses (intermediate lens, diffracted lens) on one of the planes, the final viewing screen or film displays either the electron diffraction pattern or the electron image of the object. The selected aperture inserted into the image plane limits an image selection area of diameter \(d_S' = d_S m\). Choosing a given aperture results in selecting a specific area of the specimen. The active area of SAD is of the order of \(d_S = 1 \mu m\), so with magnification of the objective lens \(m = 100\), the image selection area \(d_{S'} = 100 \mu m\). The diffraction length \(L\) is not directly expressed. The diffraction constant (or camera constant) \(K = ?L\), which describes the magnification of the diffraction pattern, can be determined from standard specimen knowing that \(?L = dR\), as shown in Figure. Here \(R\) is the distance between the transmitted beam and the diffracted spot corresponding to interplanar distance \(d\). The diffraction mode can be utilized in sub-modes, like selected-area electron diffraction, microdiffraction (or nanodiffraction), convergent beam electron diffraction etc.
References


2.2.3 Scanning Transmission Electron Microscopy and Electron Energy Loss Spectroscopy (Structural and elemental: STEM & EELS)

STEM with Z-contrast

Z-contrast techniques in scanning transmission electron microscopy (STEM) can provide strong compositional sensitivity at atomic level. Transmitted beam is used to get bright field STEM image. High-angle Rutherford-scattered electrons are collected by high angle annular dark field detector to obtain Z-contrast dark field images. Probe size is critical in obtaining atomic resolution Z-contrast image.

STEM mimics the parallel beam in a TEM by scanning strictly parallel to the optic axis at all times. It is a key feature of STEM that scanning beam must not change direction as the beam is scanned. Fig. 1 is an illustration of how the STEM achieves the parallel beam. Two pairs of scan coils are used to pivot the beam about the front focal plane of the upper objective (C3) pole piece. The C3 lens then ensures that all electrons emerging from the pivot point are brought parallel to the optic axis and an image of the C1 lens crossover is formed in the specimen plane. Now, if the objective lens is symmetrical, then a stationary diffraction pattern is formed on the back focal plane.

One big advantage of forming images this way is that no lenses is used in an SEM. So defects in the imaging lenses do not affect your image resolution, which is controlled by beam only. Hence chromatic aberration, which can limit TEM image, is absent in STEM images, which is advantageous if you are dealing with a thick specimen. Similar to TEM techniques, STEM can form its own bright field (BF) and dark field (DF) images.
BF STEM images

The basic principle of image formation in the scanning mode is fundamentally different from that for a static beam TEM image. In the TEM, a portion of the electrons emerging from an area of the specimen is selected and the distribution is projected onto a screen. While in STEM, the beam is scanned on the specimen by adjusting the scan coils; these same coils are used to scan the CRT synchronously. The electron detector acts as the interface between the electrons coming from the specimen and the image viewed on the CRT. Since it takes up to 2048 scan lines to build up an image on the CRT, the whole process of the creating a STEM image is much slower than TEM imaging.

In TEM, in order to form a BF image, an aperture is inserted into the plane of the TEM diffraction pattern and only allowed the direct electrons through it into the imaging
system. In STEM mode an electron detector, is used in exactly the same way as the aperture that it only allows the electrons that we want to contribute to the image to hit the detector. So a BF detector is inserted into the direct beam in the diffraction pattern.

**Annular DF images**

Annular detector, which surrounds the BF detector, is used to collect the scattered electrons ADF (annular dark field) detector is centered on the optics axis and has a hole in the middle, within which the BF detector sits, as can be seen in Fig. 2a. Fig. 2b shows the diffraction pattern collected by ADF. Fig. 2c and d gives complementary ADF (C) and BF (D) images.

Fig. 2. STEM image formation: A BF detector is placed in a conjugate plane to the back focal plane to intercept the direct beam (A) and a concentric annular DF detector intercepts the diffracted electrons (B). The signals from either detector are amplified and modulate the STEM CRT. The specimen (Au islands on the C film) gives complementary ADF (C) and BF (D) images. [5]
Magnification in STEM

STEM magnification is controlled by the scan dimensions on the specimen, not the lenses of the TEM. This is a fundamental difference between scanning and static image formation. Scanning images are not magnified by lenses. If the scanned area on the specimen is 1cm × 1cm, and the resultant image is displayed on a CRT with an area 10cm ×10 cm, then the magnification is 10×. If the scan dimension is reduced to 10nm, the magnification is 10^7 times.

Atomic structure determination

Atomic structure determinations can be made using the HAADF or Z-contrast imaging technique. Detecting the scattering at high angles and over a large angular range, allows each atom to be considered to scatter independently with a cross section approaching a Z^2 dependence on atomic number. This cross section effectively forms an object function that is strongly peaked at the atom sites. The detected intensity thus consists of a convolution of this object function with the probe intensity profile, by passing the phase problem that makes image interpretation difficult in conventional TEM.

The small width of this object function (~ 0.1Å) means that the spatial resolution is limited only by the probe size of the microscope. For a crystalline material in a zone-axis orientation, where the atomic spacing is greater than the probe size, the atomic columns can be illuminated individually. Therefore, as the probe is scanned over the specimen, an atomic resolution compositional map is generated in which the intensity depends on the mean square atomic number of the atoms in the columns. This result holds even for
thicker specimens where dynamical diffraction results only in columnar channeling and simply scales the scattering cross sections of the object function according to thickness. With this methodology, changes in focus and thickness do not cause contrast reversals in the atomic resolution image, so that atomic column sites can be identified unambiguously during the experiment. This enables atomic columns at grain boundaries to be located without the need for simulated images, even for column separations below the resolution limit which simple results in a single elongated image feature.

**EELS & Z-contrast**

EELS combined with the Z-contrast imaging technique in the scanning transmission electron microscope (STEM) can obtain detailed information on the composition, chemistry and structure of materials with atomic resolution and sensitivity. First, an atomic resolution Z-contrast image is used to first identify structural features of interest and then the electron probe is probed over the feature for spectral acquisition. This method greatly limits the number of spectra that need to be acquired from a given specimen, thus reducing total acquisition time and specimen stability problems. In addition, a key advantage of this methodology is that the collection conditions for the spectrum can be tailored to produce an incoherent, atomic resolution spectrum that can be correlated directly with the image. This means the image can be used as a reference atomic structure for theoretical modeling of the spectral fine-structure. Using multiple scattering analysis, the reference structure can be modified to reproduce the experimental spectrum, thus giving a 3-dimensional structural determination that is sensitive to single
atom vacancies and impurities. Basic configuration of STEM and EELS is shown in figure 3.

![Figure 3. Schematic of STEM and EELS (Ref. 13)](image)

**References**


2.2.4 Nanoindentation

Nanoindentation testing is used to measure the hardness of a material in small dimensions--its resistance to localized deformation. A tip with known (pyramidal) geometry is brought into contact with a material surface under an externally applied load and the projected area of the resulting impression is measured. The hardness number is then the applied load divided by the projected area of contact. In principle the test today stands the same, but the load and depth of penetration are continuously reordered and are orders of magnitude smaller. This allows for testing very small volumes, as is the case for a thin film on a substrate. Also not just hardness is measured with the indentation test anymore but a variety of other material properties are as well.

A prescribed load is applied to an indenter in contact with a specimen. As the load is applied, the depth of penetration is measured. The area of contact at full load is determined by the depth of the impression and the known angle or radius of the indenter. The hardness is found by dividing the load by the area of contact. Shape of the unloading curve provides a measure of elastic modulus.

Figure 1. The typical loading unloading curve of nanoindentation measurement. (Ref.5)
Figure 1 shows the typical loading unloading curve of nanoindentation measurement. According to the following calculations, the H and E can be obtained. All the related parameters are listed in figure 2.

\[
P = \frac{3}{4} E \frac{R^{1/2} h_e^{3/2}}{h} \Rightarrow \frac{dP}{dh} = 2E \frac{R^{1/2} h_e^{1/2} h}{h} \Rightarrow P = \frac{2}{3} \frac{dP}{dh} h_e \Rightarrow h_e = P \frac{3}{2} \frac{dP}{dh}
\]

\[
\Rightarrow h_p = h_e - h_a = h_t - \frac{3}{4} P \frac{1}{dP/dh} \Rightarrow A = 2\pi Rh_p \Rightarrow H = \frac{P_t}{A}
\]

Figure 3 shows multiple point measurement and single point measurement results. The Single-point method uses the Hertz equation directly with two data points. The multiple-point method fits a line to the unloading data and uses the derivative of the line. The multiple-point method takes a longer time to collect the data, but smoothes out any departures from the ideal elastic response. The Single-point method can accumulate data faster, thus reducing the effect of thermal drift, but the data must be good data.
Figure 3 Multiple point measurement and single point measurement results. (Ref.5)

References


5. A.C. Fischer-Cripps, Nanoindentation, Presentation in CSIRO Division of Telecommunications and Industrial Physics, Lindfield, NSW Australia.
2.2.4 Electrical Measurement (Resistivity)

1. Four-Point Probe measurement

It is the most common method for measuring semiconductor resistivity. The purpose of the 4-point probe is to measure the resistivity of any semiconductor material. It can measure either bulk or thin film specimen. Experimental setups for both of the cases are same, but the expressions are different. The 4-point probe setup usually consists of four equally spaced tungsten metal tips with finite radius. Each tip is supported by springs on the other end to minimize sample damage during probing. The four metal tips are part of an auto-mechanical stage which travels up and down during measurements. A high impedance current source is used to supply current through the outer two probes; a voltmeter measures the voltage across the inner two probes (See Figure 1) to determine the sample resistivity. Typical probe spacing \( s \) is about 1 mm.

![Figure 1. Schematic of 4-point probe configuration](image)

**Bulk sample**

It is assumed that the metal tip is infinitesimal and samples are semi-infinite in lateral dimension. For bulk samples where the sample thickness \( t \gg s \), the probe spacing, we
assume a spherical protrusion of current emanating from the outer probe tips. The
differential resistance is:

\[ \Delta R = \rho \left( \frac{dx}{A} \right) \]

We carry out the integration between the inner probe tips (where the voltage is measured):

\[ R = \int_{x_1}^{x_2} \rho \frac{dx}{2\pi x^2} = \frac{\rho}{2\pi} \left[ \frac{-1}{x} \right]_{x_1}^{x_2} = \frac{1}{2s} \frac{\rho}{2\pi} \]

where probe spacing is uniformly s. Due to the superposition of current at the outer two
tips, \( R = V/2I \). Thus, we arrive at the expression for bulk resistivity:

\[ \rho = 2\pi s \left( \frac{V}{I} \right) \]

**Thin film**

For a very thin layer (thickness \( t << s \)), we get current rings instead of spheres. Therefore,
the expression for the area \( A = 2pxt \). The derivation is as follows:

\[ R = \int_{x_1}^{x_2} \rho \frac{dx}{2\pi xt} = \int_{s}^{2s} \rho \frac{dx}{2\pi t \cdot x} = \frac{\rho}{2\pi t} \ln(x) \left[ ^{2s}_{s} \right] = \frac{\rho}{2\pi t} \ln2 \]

Consequently, for \( R = V/2I \), the sheet resistivity for a thin sheet is:
\[ \rho = \frac{k (\frac{V}{I})}{\ln 2} \]

Note that this expression is independent of the probe spacing \( s \). Furthermore, this latter expression is frequently used for characterization semiconductor layers, such as a diffused N+ region in a p-type substrate. In general, the sheet resistivity can be expressed as:

\[ R_s = k \left( \frac{V}{I} \right) \]

where the factor \( k \) is a geometric factor. In the case of a semi-infinite thin sheet, \( k = 4.53 \), which is just \( p/\ln2 \) from the derivation. The factor \( k \) will be different for non-ideal samples. So the sample resistivity and sheet resistance can be simply expressed as

\[ \rho = 4.532 \frac{V}{I} \quad \text{and} \quad \rho_s = 4.532 \frac{V}{I}, \]

respectively.

**2. van der Pauw Method**

The van der Pauw method for measuring resistivity is used in flat, arbitrary shaped samples. The contacts should be small and placed on the circumference of the sample. The sample should also be constant in thickness and should not contain any isolated holes.

A total of eight voltage measurements are required, as shown in figure 2.

Two values of resistivity, \( \rho_A \) and \( \rho_B \) are then computed as follows:

\[ \rho_A = \frac{1.1331 f_A I}{I} (V_2 + V_4 - V_1 - V_3) \]

\[ \rho_B = \frac{1.1331 f_B I}{I} (V_6 + V_8 - V_5 - V_7) \]

where \( \rho_A \) and \( \rho_B \) are resistivities in ohm-cm; \( ts \) is the sample thickness in cm; \( V1-V8 \) represent the voltages measured by the voltmeter; \( I \) is the current through the sample in
amperes; $f_A$ and $f_B$ are geometrical factors based on samples symmetry, and are related to the two resistance ratio $Q_A$ and $Q_B$, as shown below. ($f_A=f_B=1$ for perfect symmetry)

Figure 2. van der Pauw resistivity measurement conventions. (Ref. 4)
Q_A and Q_B can be calculated using the measured voltages as follows:

\[ Q_A = \frac{V_2 - V_1}{V_4 - V_3} \quad \text{and} \quad Q_B = \frac{V_6 - V_5}{V_8 - V_7} \]

And Q and f are related as follows:

\[ \frac{Q - 1}{Q + 1} = \frac{f}{0.693} \arccos \left( \frac{e^{0.693f}}{2} \right). \]

A plot of function is shown in figure 3. Note that if \( \rho_A \) and \( \rho_B \) are not within 10% of one another, the sample is not sufficiently uniform to accurately determine resistivity. Once \( \rho_A \) and \( \rho_B \) are known, the average resistivity \( \rho_{avg} \) can be determined as follows:

\[ \rho_{avg} = \frac{\rho_A + \rho_B}{2} \]

In this way, the resistivity of arbitrary shaped samples can be measured. Van der Pauw technique can also be used for Hall measurements.\(^4,5\)

Figure 3. Plot of f vs. Q (Ref. 4)
References


