This chapter presents the brief description of experimental techniques used in the synthesis and characterization for nanomaterials. Plused Laser Deposition (PLD), Chemical Method and Vapor Liquid Solid (VLS) Method have been discussed in detail. Excellence of any material emerges out by its proper characterization. The Characterization techniques namely X-ray diffraction (XRD), Spectroscopic Studies, Scanning Electron Microscopy (SEM) with EDAX and Atomic Force Microscopy (AFM) has been discussed in detail in this chapter."
2.1 Introduction

The performance of materials depends on their properties. The properties depend on the atomic structure, composition, microstructure, defects and interfaces which are controlled by thermodynamics and kinetics of the synthesis. A current concept of synthesizing and processing of advanced materials emphasizes the tailored assembly of atoms and particles from the atomic or molecular scale to the macroscopic scale. Intrinsic and extrinsic bulk (microcrystalline) semiconductors are generally synthesized using high temperature thermal diffusion, molecular deposition techniques like chemical vapour deposition, atomic layer epitaxy, gas phase deposition techniques, vacuum evaporation etc. During the last three decades, researches have reported number of synthesis techniques for the preparation of various nanocrystals [1-4].

2.2 Techniques for Synthesis of Nanomaterials

A number of synthesis techniques have been reported for the synthesis of various semiconductor nanocrystals in the literature of nanoscience and nanotechnology. As per the approaches adopted in the synthesis of nanomaterials all synthesis techniques are broadly classified into two general category as listed below and shown in figure 2.1.

1. Top- down approach

2. Bottom–up approach.

Before discussing the synthesis processes adopted in the present research work, a brief review of Top-down and Bottom-up approaches of synthesis of nanostructured materials are discussed in the following sections:

2.2.1 Top-Down Approach

Top down approach involves the breaking down of the bulk material into nano-sized structures or particles. Top-down synthesis techniques are extension of those that
have been used for producing micron sized particles in microelectronics. Top-down approaches are inherently simpler and depend either on removal or division of bulk material or on miniaturization of bulk fabrication processes to produce the desired structure with appropriate properties. The biggest problem with the top-down approach is the imperfection/impurities of surface structure. Examples of such techniques are high-energy wet ball milling, electron beam lithography, atomic force manipulation, gas-phase condensation, aerosol spray, etc.

Figure 2.1: Schematic representation of ‘bottom-up’ and ‘top-down’ synthesis processes [5].

2.2.2 Bottom-Up Approach

The alternative approach, which has the potential of creating less waste and hence the more economical, is the ‘bottom-up’. Bottom-up approach refers to the build up of a material from the bottom: atom-by-atom, molecule-by-molecule, or cluster-by-cluster.
Many of these techniques are still under development or are just beginning to be used for commercial production of nanopowders. Organometallic chemical route, reverse-micelle route, sol-gel synthesis, colloidal precipitation, hydrothermal synthesis, template assisted sol-gel, electrodeposition, Vapour Liquid Solid (VLS) method etc. are some of the well known bottom–up techniques reported for the preparation of semiconducting nanoparticles.

Nanoparticles have attracted great interest in recent years because of their unique chemical, physical, optical, electrical and transport properties which are different from those of either the bulk materials or single atoms [6, 7]. Due to the vast surface area, all nanostructured materials possess a huge surface energy and thus, are thermodynamically unstable or metastable. One of the great challenges in fabrication and processing of nanomaterials is to overcome the surface energy and to prevent the nanomaterials from growth in size driven by the reduction of overall surface energy. Due to high surface energy of the nanoparticles, they are extremely reactive and most systems without protection or passivation of their surfaces undergo aggregation [8]. Organic stabilizers are usually used to prevent nanoparticles from aggregation by capping their surfaces [9].

Chemical reactions for material synthesis can be carried out in the solid, liquid, or gaseous states. The steps of the processes involved in the production of nanoparticles are summarized in the figure 2.2. The more conventional solid-state synthesis approach is to bring the solid precursors (such as metal oxides or carbonates) into close contact by grinding and mixing, and subsequently to the heat treatment at high temperatures to facilitate diffusion of atoms or ions in the host material by chemical reaction. The diffusion of atoms depends on the temperature of the reaction and grain boundary contacts. The transport across grain boundary is also affected by impurities and defect located there. The mixing and grinding steps are usually repeated throughout the heat
cycle, and generally involve a great deal of effort to mix materials at the nanoscale and also to prepare fresh surfaces for further reactions. For systems that do not contain means to inhibit grain growth (such as grain growth inhibitors and immiscible composites), grain growth at elevated temperature reaction leads to solids with large grain size.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Reaction</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid</td>
<td>Creation</td>
<td>Liquid</td>
</tr>
<tr>
<td>Liquid</td>
<td>Vapour</td>
<td>Separation</td>
</tr>
<tr>
<td>Gas</td>
<td>Primary Generation</td>
<td>Solid</td>
</tr>
<tr>
<td></td>
<td>Secondary Generation</td>
<td>Drying</td>
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<td></td>
<td></td>
<td>Harvesting</td>
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<tr>
<td>Chemistry</td>
<td></td>
<td>Calcintion</td>
</tr>
</tbody>
</table>

**Figure 2.2: The processes involved in the production of nanoparticles.**

Compared to solid state synthesis, diffusion of matter in the liquid or gas phase is typically and advantageously many orders of magnitude larger than in the solid phase, thus the synthesis of nanostructured materials can be achieved at lower temperatures. Low temperatures reaction also discourages detrimental grain growth. Many materials can be synthesized in aqueous or non aqueous solutions. But the wet-chemical synthesis of extrinsic semiconductor nanomaterials faces new problems that are not encountered in bulk materials. The synthesis parameter such as temperature, pH of the solution, reactants concentration and reaction time should be ideally correlated with factors such as supersaturation, nucleation and growth rates, surface energy and diffusion coefficients, in order to ensure the reproducibility of reactions. The main uses of bottom-up and top-
down techniques in different device fabrication with their different synthesis processes are briefly summarized in figure 2.3 as below:

![Figure 2.3: The use of bottom-up and top-down approaches in manufacturing.](image)

In this present research work, ZnO Nanostructures are synthesized by both Top-down and Bottom-up approaches using Wet Chemical Method, Vapor Liquid Solid (VLS) Method and Pulsed Laser Deposition (PLD) technique.

### 2.3 Pulsed Laser Deposition

Pulsed laser deposition is a method of materials growth, in which, a short pulsed laser beam is focused onto a target beyond the material's ablation threshold creating plasma of the target material to expand towards and deposit onto a substrate under vacuum, as is shown in figure 2.4. This ejected material is comprised of ions, atoms and molecules as it propagates and on reaching the substrate, they diffuse on the surface and arrange themselves in one or more crystallographic orientations. As this method was initially used for maintaining the stoichiometry of complex materials, it was later realized
that it can also be used in the growth and control of micron- and nano-sized structures [10].

Figure 2.4: Overview of a pulsed laser deposition system as a laser ablates target material towards a substrate under vacuum.

With the pulsed laser deposition method of crystalline growth, the expanding plume is the beginning of the growth process. As the ablated plume expands under some finite vacuum pressure, it propagates towards a substrate for film deposition. The substrate is typically crystalline in order to facilitate the growth of a crystalline film, but is not necessary.

2.3.1 Crystal Seeding

As each plume of laser ablated material adiabatically expands towards the surface of a substrate, we will consider the initial interaction with the surface just prior to the first particle touching the surface. We can also begin by treating each of the species of the
plume individually as they strike the substrate surface. In this section, the interaction between the plume and the substrate surface is developed first assuming a perfect crystal.

- **Surface Interaction**

  When a particle from the expanding plume first comes into contact with a substrate surface, it will have some potential energy ‘$\phi$’ of attractiveness or repulsion with the surface as a function of distance $r$ between the two objects. This potential energy function is commonly represented by the Lennard-Jones potential, which is

  \[
  \phi(r) = \varepsilon_B \left( \left( \frac{r_e}{r} \right)^{12} - 2 \left( \frac{r_e}{r} \right)^6 \right)
  \]

  (2.1)

  Where $\varepsilon_B$ is the minimum potential energy located at a distance $r_e$ where the particles are at equilibrium. At any interatomic separation distance greater than $r_e$ the incoming particle will adsorb to the substrate surface, which arises from the $r^{-6}$ term. This term is commonly known as the weak vander Waals interaction. If the separation is less than $r_e$ than the particle will experience repulsion by the $r^{-12}$ term due to the Pauli Exclusion Principle.

- **Adatom Surface Movements and Nucleation**

  For those impinging particles that become adsorbed to the substrate or film surface, we begin to look at the basic motions of travel they undergo. Those particles that either ricocheted off the surface or desorbed due to an excess amount of latent energy no longer concern us anymore.

  Assume initially that these atomic sized particles are cubic and are being deposited onto an array of packed crystalline cubes, i.e. an atomically at substrate surface. This model is close enough to gain perspective to what occurs initially. One particle that first interacts with the surface will have some initial energy before reaching the surface itself. This free energy particle, say with energy $\varepsilon_0$, will adhere to the surface provided the
activation energy level is surpassed. Once this free particle adheres to the surface, it is known as an adatom. This lone adatom will have just the single contact, or nearest neighbour, with one face of the cube. This interaction between the surface and the nearest neighbor would thus reduce the overall potential energy of the initially free particle, $\varepsilon_0$, to $\varepsilon_A$ for the adatom. This single bond is weak enough to allow the adatom to travel the surface until it interacts with another adatom like itself, a dislocation on or in the surface, or simply becomes a location for which other species of the plume become attracted.

As the adatom travels along the surface, there are a number of locations which it may come across in its journey, including another adatom, a step location, a kink-location, a hole within a step, or even a hole in the surface itself, as shown in figure 2.5. First we take a look at a situation where an adatom encounters a step on the surface. It will then have 2 nearest neighbours and the potential energy of the adatom would reduce to that of a step particle $\varepsilon_S$. Theoretically, two free adatoms conjoining would be in itself the beginning of a step, or more commonly referred to as a nucleation site for nanostructured growth.

Next, if an adatom migrates into a corner formed by two perpendicular steps, also known as a kink, where half of its bonds would be incorporated into the depositing film and would have kink energy of $\varepsilon_K$. If the adatom joins to separate steps to form a ledge, it bonds with 4 nearest neighbours and would have energy of $\varepsilon_L$. As a film is deposited onto a substrate and particles begin to fill in all of the dislocations, vacancies are eventually left in the film. A particle that fills this vacancy would bond with 5 nearest neighbours and would have energy of $\varepsilon_V$. Lastly, an adatom can also be thought of as a particle buried within the bulk of the crystalline film. This bulk adatom with all bonds shared, would have the lowest potential energy of $\varepsilon_B$, same as found in prior equation (2.1).
Figure 2.5: Image of the terrace-kink-step model and the 5 main dislocation sites: (a) an adatom, (b) a step, (c) a kink, (d) a ledge or terrace and (e) a vacancy. (b) is also depicted as a stand-alone nucleation site which would have the same nearest neighbours as a step. A bulk adatom within the film is not depicted.

As the adatoms randomly diffuse across the surface and a monolayer after monolayer form, various dislocation sites will develop. As they do, the locations with a greater number of unsatisfied nearest neighbours will be attracted to those with lower potential energies. Before each monolayer begins to develop, it first initiates at nucleation sites across the substrate and subsequent film layers. Initially some free-traveling adatoms become seeds which develop into these nucleation sites.

The rate of 2D nucleation at each of these locations is given by a fairly complex rate equation which will not be listed here. It is, however, at these nucleation sites that will attract impinging particles as they near the surface or travel along the surface depending on the mode growth discussed later. If they are not affected by the nucleation sites, then they may either form their own site or randomly travel the surface until encountering some surface defect [10].
Depending on the conditions of growth, various ways in which the films will develop must be considered. The manner in which they crystallise and grow will be discussed in the following section.

2.3.2 Thin Film Crystallisation and Growth

As the atoms and molecules travel across the surface of the substrate and either seed a growth site or find a niche on a preexisting one, layers start to form. Throughout this upwards growth, numerous atomic and nanometric scaled occurrences start to emerge. As mentioned in the previous section, this is not a perfect crystal scenario and defects do commonly occur due to such issues as lattice matching, stress, strain, dislocations and other such defects found in most crystals.

- **Stress, Strain, Lattice Mismatch & Epitaxial Relationships**

  We assumed an influx of particles which were cubic to help develop a generic model for explaining adatom and surface attraction, however as mentioned the systems in common practice are usually much more complex. Therefore, not only is the perfect crystal scenario difficult to achieve in the laboratory, but resultant film outcomes due to certain growth conditions for some materials are still being investigated. This vast array of both deposited materials and choice of substrate material causes unique sets of stresses and associated strains between a substrate and the depositing material.

  Stress is given as the amount of work applied to a surface area and strain is the amount of (dimensionless) deformation that a material undergoes due to the stress. As the crystalline lattice structure of a substrate may and usually does, vary from that of a deposited material as a bulk, the result is a mismatch between the lattices of the substrate and the film. Between these two materials, there exists a quantifiable mismatch, \( \delta \) by the simple relationship:
\[ \delta = \frac{a_f - a_s}{a_s} \times 100\% \] (2.2)

Where \( a_f \) and \( a_s \) are the lengths of the crystal unit cell for the film and substrate, respectively.

Epitaxy, by definition, is used to describe the growth of one crystalline material on the surface of another with either a similar lattice structure a film on a substrate. As the substrate and film lattices can be described by some percentage of mismatch, they are also correlated by a comparison between a particular plane and directional orientation for each. This standard way of linking the crystalline orientations of both the substrate crystal and material crystal is called an epitaxial relationship. This is done by expressing a relationship between parallel crystalline planes in each and then defining parallel orientational directions within the planes. The epitaxial relationships are chosen for simpler planes and orientations, as they can be quite difficult to calculate for more complex crystals. Note that these epitaxial relationships, while particularly defining of the growth orientation, are not necessarily unique.

The stresses and strains on the material lattice during deposition due to attributing these lattice mismatches and epitaxial relationships, various modes in which the film develops can occur are given below.

- **Growth Modes**

  There are 5 different crystal growth modes that can possibly occur. A diagram of the progress of these 5 growth modes are depicted in figure 2.6 showing as the film is less than 1 monolayer (ML) through to more than 2 monolayers. The first is the layer-by-layer or Frank-van der Merwe growth mode (see figure 2.6(a)) [11-13]. This mode is the simplest growth where a stable monolayer will form on the surface of the substrate before another one begins and eventually ends with a smooth film. The second type of growth mode is the step-flow growth mode (see figure 2.6(b)). This is similar to the layer-by-
layer growth except the layers form as a series of planar steps. The eventual film may have an atomically terraced effect rather than a smooth surface. The third mode seen in figure 2.6(c) is the island or Volmer-Weber growth mode. This growth mode begins because adatoms nearing the surface are more attracted to nucleated growth sites rather than the interaction between the adatom and the surface. This causes an island-like structure to form directly on the substrate surface. As more and more adatoms join the nucleation sites, these islands dominate the overall film growth. As islands develop and meet other islands, they tend to merge and cover the whole substrate.

The fourth is a combination of the layer-by-layer growth with an additional island growth mode on top (see figure 2.6(d)). This is more commonly known as the Stranski-Krastanov or SK-mode. This growth mode is simply a combination of the last two modes where first a layer-by-layer film will develop. Eventually a stress may build up in the developing thin film where eventually it is more structurally and thermodynamically stable to begin a 3D island-type growth. From this point on, as with the Volmer-Weber mode, the islands will then dominate the remainder of the film growth. As more material is deposited and the islands meet, they tend to merge and form another layer underneath while continuing island growth.
Figure 2.6: Image depicting the progression of crystal growth over time of monolayer coverage [12]. The five modes of crystal growth shown are (a) layer-by-layer, (b) step-flow, (c) island growth, (d) layer-by-layer with island growth and (e) columnar growth.

The fifth and last type called columnar growth mode (see figure 2.6(e)) is somewhat similar to both the Volmer-Weber and SK growth modes where merging islands form a connected structure underneath. However in with columnar growth, as the columns widen and eventually meet, they retain their shape throughout the entire thickness of the deposited film. The transition stage from a 2D layer-by-layer growth mode to a 3D island growth mode is when the potential for a particle's attraction to another particle overcomes its potential attraction to the substrate or surface. This simply means that until there is enough stress built up in the film, it will fail to grow more stable vertically and will continue growing parallel to the substrate surface.

- **Cluster Formation**

In addition to the crystal growth modes just listed, there is also another form of
crystallisation that has been under investigation by some research groups [14, 15]. Evidence from this research points towards in-plume crystallisation and is sometimes referred to as nanoparticle-assisted PLD (NAPLD). The formation of nanoclusters in the ablation plume and their deposition onto the substrate have been recognised by these authors as the main process leading to the formation of nucleation sites for subsequent nanocluster growths. It has also been proposed that a combination of SK-mode nucleation followed by NAPLD assisted growth can occur [16].

### 2.4 Wet Chemical Method

Nanostructured materials can be made by attrition of parent coarse grained materials using the top-down approach from the macroscale to the nanoscale or conversely by assembly of atoms or particles using the bottom-up approach. The control of arrangement of atoms from the nanoscale to the macroscale is indeed the strength of materials chemistry. Therefore, it is not surprising that increasing attention has been paid to the chemical synthesis and processing of nanostructured materials [17-24]. Chemical reactions for material synthesis can be carried out in the solid, liquid, or gaseous state [25].

Chemistry is based on the manipulations of atoms and molecules and indeed has a very long history in the synthesis of materials comprising nanostructures. The fields of colloids and catalysts are such examples. The recent popularity of ‘nanoscience’ not only revitalized the use of many old chemical methods, but also motivated many new and modified ones to be continually developed for the synthesis of nanostructured materials. The scope of chemical synthesis and processing of nanostructured materials is very wide spanning structural, optical, electronic, magnetic, biological, catalytic and biomedical materials. However due to the fact that many advanced materials are hybrid and are prepared using multidisciplinary techniques, clear distinction is not always possible.
The more conventional solid-state synthetic approach is to bring the solid precursors (such as metal oxides or carbonates) into close contact by grinding and mixing, and to subsequently heat treat this mixture at high temperatures to facilitate diffusion of atoms or ions in the chemical reaction. Compared to solid-state synthesis, diffusion of matter in the liquid or gas phase is typically and advantageously many orders of magnitude larger than in the solid phase, thus the synthesis of nanostructured materials can be achieved at lower temperatures. Lower reaction temperatures also discourage detrimental grain growth. Many materials can be synthesized in aqueous or nonaqueous solutions. For example, water is one of the best known and most common solvent. There are three general classes of aqueous reactions: acid/base reaction, precipitation and reduction/oxidation (redox). In basic chemistry terms, starting materials of a chemical reaction are called the reactants and the material to which the reactants are converted the products. The reactants can be solids, liquids or gases in any combination, in the form of single, elements or multi-component compounds. A multi-element compound is usually called a precursor. In a precursor, the components of the final product are in a mixture with atomic scale mixing. Many precursors can be prepared by precipitation reactions. In precipitation reactions, solutions of two or more electrolytes are mixed and an insoluble precipitate or a gelatinous precipitate forms.

In chemical synthesis of materials, one should always use caution when handling reactants and precursors, reaction by-products and post-reaction wastes, particularly when complex and hazardous chemicals are involved. Special procedures may be required to remove any entrapped impurities from the products and post-reaction wastes, particularly when complex and hazardous chemicals are involved. Special procedures may be required to remove any entrapped impurities from the products and to avoid post-synthesis contamination. Although many laboratory-scale reactions can be scaled up to
economically produce large quantities of materials, the laboratory-scale reaction parameters may not be linearly related to that of large-scale reaction. The synthesis parameters such as temperature, pH, reactant concentration and time should be ideally correlated with factors such as supersaturation, nucleation and growth rates, surface energy and diffusion coefficients in order to ensure the reproducibility of reactions.

- **Nucleation and growth of particles**

  The synthesis of particles in a solution occurs by chemical reactions that result in the formation of stable nuclei and subsequent particle growth. The term precipitation is often used to describe this series of events. The reactants are introduced frequently as solids or liquids, and sometimes as gases, in aqueous or nonaqueous solvents that can have a wide range of dielectric constants. The phenomenon of precipitation of solids in solution has been well studied [26, 27]. Elemental or multicomponent particles can be precipitated. When a multicomponent material is desired, special attention is required to control co-precipitation conditions in order to achieve chemical homogeneity of the final product. This is because different ions often precipitate under different conditions of pH and temperatures, and have different solubility product constants.

  Upon addition of reagents such as reducing or oxidizing agents to the solution containing the reactants, chemical reactions occur and the solution becomes supersaturate with the product. The supersaturating drives the chemical system to a far departure from the minimum free energy configuration. The thermodynamics equilibrium state of the system is restored by condensation of nuclei of the reaction product. Two types of nucleation can occur. Homogeneous nucleation does not involve any foreign species as nucleating aids. Homogeneous nucleation, on the other hand, allows the formation of nuclei on foreign species.

  Kinetic factors compete with the thermodynamics of the system in a growth
process [28]. Kinetic factors such as reaction rates, transport rates of reactants, accommodation, removal and redistribution of matter compete with the influence of thermodynamics in particle growth. The reaction and transport rates are affected by concentration of reactants, temperature, pH, the order in which the reagents are added to the solution and mixing. The structure and crystallinity of the particle can be influenced by factors such as supersaturating, nucleation and growth rates, colloidal stability, recrystallization and the aging process. Generally, supersaturating has a predominant influence on the morphology of precipitates. At low supersaturating, the particles are small, compact, and well-formed, and the shape depends on crystal structure and surface energies. At high supersaturating levels, large and dendritic particles form. At even larger supersaturating, smaller but compacted, agglomerated particles form [26]. The growth in solution is interface-controlled when the particle is small; after reaching a critical size, it becomes diffusion-controlled [29].

- **Stable dispersion and agglomeration**

  In a supersaturated solution when the nuclei form at nearly the same time, subsequent growth of these nuclei results in formation of particles with a very narrow size distribution, provided that secondary nucleation does not occur later [30]. Homogeneous nucleation as a single event requires the use of proper concentrations of reagents. Foreign nuclei should be removed before reaction to prevent heterogeneous nucleation that may otherwise result in a wide size distribution of particles. This narrow size distribution can be maintained as long as agglomeration and Ostwald ripening of particles in solution does not occur. The formation of stable colloids and dispersion of agglomerated particles have been extensively investigated [31]. It should be noted that random agglomeration between particles may still occur by Brownian motion. Agglomerates or particles larger than 100 nm tend to settle out of solution.
In aqueous solvents, particles that possess a surface oxide layer or a hydrated surface may become charged under appropriate conditions. Electrostatic repulsion, with a force proportional to the inverse of second power of separation distance, occurs between two particles carrying the same charge. The attractive Vander Waals force is proportional to the inverse of the distance with an exponent of 3–6. The net attractive or repulsive force between the particles in such a suspension is the sum of the electrostatic repulsion and the attractive Vander Waals forces. The DLVO theory (Derjaguin, Landau, Verwey and Overbeek) describes the effects of attraction and repulsion of particles as a function of separation distance [32]. In an appropriate solvent, an electric double layer is formed surrounding the particle. The stable distance of particle separation depends not only on the charges of the particles, but also the concentration of other ions in the diffuse region of the double layer. When there are a sufficient number of such ions or ions with multiple charges in the diffuse layer, the charge repulsion will be neutralized. The collapse of the double layer leads to particle contacts and agglomeration [33, 34].

Nanostructured particles possess large surface areas and often form agglomerates as a result of attractive Vander Waals forces and the tendency of the system to minimize the total surface or interfacial energy. Agglomeration of particles can occur during any of the following stages: synthesis, drying, handing, and processing. In many applications and processing where dispersed particles or stabilized dispersions are required, undesirable agglomeration in each synthesis and processing step must be prevented. To produce unagglomerated particles, surfactants can be used to control the dispersion during chemical synthesis, or disperse as-synthesized agglomerated fine particles.

A surfactant is any substance that lowers the surface or interfacial tension of the medium in which it is dissolved. A surfactant is surface active agent that needs not be completely soluble and may decrease surface on interfacial tension by spreading over the
surface. It has an amphipathic structure in that solvent, i.e., a lyophobic (solvent repulsive) and lyophilic group (solvent attractive). Surfactants are classified as anionic, cationic, zwitterionic (bearing both positive and negative charges), or non-ionic (bearing no charges). Surfactant effectiveness is measured by the maximum reduction in surface or interfacial tension by the surfactant, whereas, surfactant efficiency refers to the surfactant concentration that is needed to reduce the surface or interfacial tension by a certain amount from that of the pure solvents. For example, water and oil can be dispersed in each other if a suitable surfactant is used to stabilize the microemulsion. The surfactant establishes itself at and defines the boundary between the two liquids. The relative quantity of a surfactant determines the amount of surface that can be covered and therefore the extent to which the size and number of droplets of one liquid is dispersed in the other. When the major component is a polar (oil), the dispersion is one in which the water (polar) phase forms the droplets or reverse micelles. The polar head group of the surfactant is pointing inward toward the water phase while the hydrocarbon tail is pointing outward into the oil phase. The radius of the water droplet is related to the amount of water and surfactant.

In most nonaqueous solvents without significant ionization, electrostatic repulsion has a lesser contribution to stabilization of particles. Another stabilization approach involves the steric forces produced by adsorbed surfactant on particle surfaces. The lyophilic, non-polar chains of surfactant molecules extend into the solvent and interact with each other. The interactions of non-polar chains have much less Vander Waals attraction and provide a steric hindrance to interparticle approach. For optimized steric stabilization, the size of surfactant molecules must be large enough to be a barrier without entangling each other. When the particles approach one another, the streched-out lyophilic chains of the adsorbed surfactant are forced into a smaller spatial confinement.
This interaction leads to a thermodynamically unfavorable decrease of the entropy of the system, thus, the particles will be prevented from approaching each other by this entropic repulsion. Entropic stabilization becomes even more stable when the temperature of the dispersion is increased. Steric stabilization can occur in the absence of electric barriers and is effective in both aqueous and nonaqueous media. It is also less sensitive to impurities or trace additives than electrostatic stabilization and is particularly effective in dispersing high concentrations of particles.

Dry, high surface area powders agglomerate by Vander Waals forces and hydrogen bonds. When these agglomerates need to be used in a dispersed form during subsequent processing, deagglomeration can be achieved by breaking the agglomerates using methods such as milling or ultrasonication in an appropriate solvent containing a suitable surfactant for dispersion [31, 34]. The deagglomerated powders may then be carried out in a liquid for further processing such as injection molding and polymer-based casting.

2.5 Vapor Liquid Solid Method

The VLS method is a 1D crystal growth mechanism that is assisted by a metal catalyst [35]. It results in the creation of whiskers, rods and wires 1D crystal growth was initially developed nearly 50 years ago in the Si industry and the mechanism was suggested for wider use by Wagner in 1964 [36]. Figure 2.7 shows a schematic growth of 1D structure by VLS mechanism. In this mechanism, the metal catalyst forms liquid alloy droplets at a high temperature by adsorbing vapor components. For some reason, e.g. temperature or vapor pressure fluctuation, the alloy is further supersaturated, i.e. it becomes a solution in which the actual concentration of the components is higher than the equilibrium concentration. It then drives the precipitation of the component at the liquid–solid interface to achieve minimum free energy of the alloy system. Accordingly, the 1D
crystal growth begins and it continues as long as the vapor components are supplied. Because vapor (carries solid components), liquid (catalyst alloy) and solid (precipitated one-dimensional structures) phases are involved, it is known as the VLS mechanism. At a glance, one can know that the size and position of the catalyst are related to the diameter and position of the 1D structure, as the liquid phase is confined to the area of the precipitated solid phase.

![Figure 2.7: Schematic growth of 1D structure by VLS mechanism [35].](image)

The mechanism works at a high temperature at which the metal catalyst forms a liquid alloy. Therefore, chemical processes that occur at high temperatures such as chemical vapor deposition (CVD), molecular beam epitaxy (MBE), laser ablation (LA) and carbothermal reduction (CR) are generally used in conjunction with the mechanism. Occasionally, metal catalysts sometimes work in a solid state in a vapor or liquid phase environment in a process termed the VSS (vapor–solid–solid) or LSS (liquid–solid–solid) mechanism.
The VLS mechanism is used for the growth of many 1D structures, from the nm to even the mm scale. It also shows the rising of new technology from old technology as a good example of the progress of science and technology from previous studies. Some fundamental aspects which are essential for growing 1D structure using a catalyst are discussed below.

2.5.1 Requirements for Metal Catalyst

Metal catalysts are essential in the VLS mechanism, but not all metals can work. These meet the following requirements: (1) It must form a liquid solution with a component of the solid phase. (2) The solubility limit of the catalyst component in the liquid phase must be much higher than that in the solid phase (i.e., $K_D C_s = C_l < 1$, where $C_s$ is the solubility limit in the solid phase and $C_l$ is the solubility limit in the liquid phase). Under this condition, the catalyst easily leads to the formulation of the liquid alloy with little contamination in the solid phase. (3) The vapor pressure ($V_p$) of the catalyst component over the liquid alloy should be small. Otherwise, the catalyst will evaporate and eventually disappear in the course of growth. (4) It must be inert to chemical reactions. Otherwise, a reaction could deprive it of its catalytic function. (5) It must not make an intermediate solid. Otherwise, the intermediate solid will also deprive it of its catalytic function [36].

Generally, noble and transition metals work well with the VLS mechanism. For example, Au works well for the growth of a 1D structure of group IV materials (e.g., Si and Ge), oxides (e.g., ZnO) and III–V semiconductors. Transition metal such as Ni and Fe also work for the growth of group IV materials (e.g., Si, Ge and SiC) and III–V semiconductors. Naturally, many studies have focused on these metals to grow 1D structures. However, it should be noted that many other metals can also be developed as a catalyst for the VLS mechanism [37].
2.5.2 Phase Diagram

Because the adsorption, dissolving, mixing, diffusion and precipitation in the liquid phase are thermodynamic processes that work toward equilibrium, a phase diagram is useful to predict how a catalyst will work. Figure 2.8 Phase diagram of Au–Si system with indication of the composition of liquid alloy catalyst in the course of growth of 1D structures by VLS mechanism [35]. It should be noted that the currently available phase diagrams are constructed from bulk systems. Because the thermodynamic properties of a nanosystem are wholly different from those of a bulk system, the phase diagram of the type of nanometal catalyst should differ from that of the bulk system. Regardless of the cause of the deviation, it should be considered that the different thermodynamic equilibrium of the nanosystem causes discrepancies between the actual growth behavior of nanowires through a nanometal catalyst and predictions on the basis of a diagram of the bulk system.

![Phase diagram of Au–Si system](image)

*Figure 2.8: Phase diagram of Au–Si system[35].*

2.5.3 Kinetics and Rate-Determining Step

Three phases (gas, liquid and solid) and two interfaces (gas/solid and liquid/solid) are involved in the VLS mechanism. In these complex system, the kinetics of the VLS
mechanism consists of four steps: (1) mass transport in the gas phase; (2) chemical reaction at the vapor–liquid interface; (3) diffusion in the liquid phase; and (4) incorporation of atoms in a crystal lattice (figure 2.9) [38-41]. Identification of the rate-determining step among these is important to control the overall kinetics of the VLS mechanism. However, this is complicated, as three phases, two interfaces and chemical reactions are involved [38].

![Figure 2.9: Kinetic steps in VLS mechanism](image)

2.5.4 Size of the Metal Catalyst

As described earlier, nanowires can be grown using a nanometer-sized metal catalyst because the diameter of a 1D structure is confined by the size of the catalyst. However, it is difficult to decrease the size of the catalyst and in turn the diameter of nanowires in an unlimited manner. Thermodynamically, the minimum radius of a liquid metal droplet is given as [42].

$$R_m = \frac{2V_1}{RT\ln(s) \sigma_{lv}}$$

(2.3)
Where \( V_l \) is the molar volume of the droplet, \( \sigma_{lv} \) is the liquid vapor surface energy and \( s \) is the degree of supersaturation of the vapor. According to this equation, using a smaller catalyst requires a higher degree of supersaturation. However, the chemical potential of the component in the metal alloy catalyst becomes high as the size of the catalyst decreases due to the Gibbs Thompson effect:

\[
\Delta \mu = \frac{2\gamma}{r}
\]  

(2.4)

Here, \( \Delta \mu \) is the chemical potential difference of the component species in the liquid droplet, \( \gamma \) is the surface energy and \( r \) is the radius of curvature of the droplet. Therefore, dissolving a vapor component into a liquid alloy becomes increasingly difficult as the size decreases, making it difficult to reach supersaturation states that sufficiently induce the growth of nanowires. Indeed, it is known that the growth of 1D structures with diameters of several tenths of nm is feasible; however, ensuring a smaller diameter (e.g., sub-10 nm) is difficult due to the thermodynamic limitations associated with the use of a nanocatalyst.

An additional difficulty that arises when downsizing a catalyst comes from the manipulation of metal nanoparticles or droplets. It is well known that nanoparticles have strong van der Waals attractive forces and thus agglomerate into larger particles. Furthermore, Ostwald ripening occurs between nanoparticles at high temperature. Ostwald ripening is a spontaneous process that occurs because larger particles are more energetically favorable. Accordingly, nanoparticles tend to transform into large particles to attain a lower energy state if the temperature is high enough to induce diffusion of the metal component. Because the van der Waals attractive forces and Ostwald ripening lead to the formation of larger droplets, larger diameter 1D structures are often grown from a nanometal catalyst. Thus, metal nanoparticles have to be carefully separated from each
other in the course of the preparation, positioning on the substrate and heating for the growth of 1D structure.

2.5.5 Structural Modulation

To realize novel optical properties and newly fabricated devices, structural modulation of nanowires, such as control of the diameter, alignment and growth-position is needed. Creating heterostructures in the radial or longitudinal direction is also crucial.

- **Diameter Control:** The optical properties of nanowires are dependent on their diameter. For example, the band gap, which determines the wavelength of luminescence, of semiconductor nanowires is renormalized by the diameter. The optical properties of nanowires with both indirect and direct band gaps can be tuned by decreasing their diameter down to their Bohr exciton radius.

- **Vertical growth:** A vertical array of nanowires provides novel optical properties that are advantageous for many applications, including nanolasers, LEDs, photovoltaic cells and field emitters. For example, theoretical analysis indicates that vertical nanowire arrays have much lower reflectance compared to thin films. In a high-frequency regime, nanowire arrays have higher absorption than their thin film counterparts. In low-frequency regime, nanowire arrays absorb less but can be designed to approach the level of the film by changing the filling ratio [43]. Due to the low reflectance, it is possible to develop highly efficient photovoltaic devices. Other novel functions, such as direct conduction paths for photogenerated carriers, the creation of natural waveguiding cavities and field emissions from arrayed atomic scale sharp tips can also be expected from the vertical nanowire array. The use of this type of array also enables the preparation of three dimensional optoelectronic architectures.
2.6 Sputtering

We have used metal deposited substrates in VLS method. The metal (Au/Ni) is deposited on Si substrates by sputtering technique therefore here we discussed about sputtering. Sputtering is a physical process whereby atoms in a solid target material are ejected into the gas phase due to bombardment of the material by energetic ions. Sputtering is largely driven by momentum exchange between the ions and atoms in the material, due to collisions. The process can be thought of as atomic billiards, with the ion (cue ball) striking a large cluster of close-packed atoms (billiard balls). Although the first collision pushes atoms deeper into the cluster, subsequent collisions between the atoms can result in some of the atoms near the surface being ejected away from the cluster as shown in figure 2.10.

![Figure 2.10: Schematic view of sputtering technique](image)

The sputtered atoms, those ejected into the gas phase, are not in their thermodynamic state. Therefore, they tend to condense back into the solid phase upon colliding with any surface in the sputtering chamber. This results in deposition of the sputtered material on all surfaces inside the chamber. Since substrate is the most nearer surface to them so most of the ejected or sputtered atoms condense on it to form a thin film. Other processes associated with the bombardment of a target by highly energetic ions include:
(i) Secondary electrons

(ii) Ion reflection at the target surface

(iii) Ion implantation with the ion permanently buried into the target surface

(iv) Radiation damage in the structural rearrangement varying from simple vacancies and interstitial to gross lattice defects and

(v) Emission of X-rays and photons.

These processes can be summarized as illustrated in Figure 2.11

Figure 2.11: Processes generated by the impact of highly energetic particle on a target surface.

To obtain sputtering as a useful thin film deposition process some criteria have to be met. First, ions of sufficient energy must be created and directed towards the surface of a target to eject atoms of the surface of the material. To achieve this, a low pressure argon gas for example, can be present in a chamber and by application of a sufficiently large voltage between the target and the substrate; a glow discharge is set up in a way to accelerate the positive ions towards the target to cause sputtering. Secondly, the ejected materials must be able to get to the substrate with little impedance to their movement.
The pressure $P$ determines the mean free path of the sputtered particles which according to the Paschen relation is proportional to $1/P$. In addition to pressure, the target substrate distance determines the scattering of the sputtered particles on their way to the substrate and hence also the amount of energy with which they deposit on the substrate.

The number of atoms ejected from the surface per incident ion is called the sputter yield and is an important measure of the efficiency of the sputtering process. Sputter yield depends on the energy of the incident ions, the masses of the ions and target atoms, and the binding energy of atoms in the solid. One important advantage of sputtering as a deposition technique is that the deposited films have the same concentration as that of the target material. This might be surprising, since as we mentioned before the sputter yield depends on the atomic weight of the atoms to be sputtered. Therefore, one might expect one component of an alloy or mixture to sputter faster than the other components, leading to a higher concentration of that component in the deposited film. It is true that the components are sputtered at different rates, however, since only surface atoms can be sputtered, the faster sputtering of one element leaves the surface enriched with the other element, which effectively counteracts the difference in sputter rates resulting in deposited films with the same composition as the target.

There are many types of the sputtering technique some of which are:

1. **Diode sputtering:** Diode sputtering uses a plate of the material to be deposited as the cathode (target) in a glow discharge. Material can thus be transported from the target to a substrate to form a film. Films of pure metals or alloys can be deposited when using noble gas discharges (typically Ar) with metal targets.
2. **Reactive sputtering:** A compound is synthesized by sputtering a metal target (e.g.: Ti) in a reactive gas (e.g. O\textsubscript{2} or Ar-O\textsubscript{2} mixtures) to form a compound of the metal and the reactive gas species (e.g. TiO\textsubscript{2}).

3. **Bias sputtering:** Bias sputtering or ion plating is a variant of diode sputtering in which the substrates are ion bombarded during deposition and prior to film deposition to clean them. Ion bombardment during film deposition can produce one or more desirable effects, such as re-sputtering of loosely bound film material, low-energy ion implantation, desorption of gases and modification of a large number of film properties.

4. **Magnetron sputtering:** Another variant in sputtering sources uses magnetic fields transverse to the electric fields at sputtering-target surfaces. When the transverse B is superposed on E, the electrons are accelerated vertically by E but at the same time force sideways by B. The net motion is a drift around the circle of the target in the E × B direction. Therefore the electrons are trapped until they lose their energy in collisions with gas atoms or cross the magnetic field lines as a result of being elastically scattered from gas atoms.

5. **RF sputtering:** RF sputtering uses a 13.56 MHz sinusoidal wave to drive the source. It enables the use of non-conducting materials as targets and allows direct or reactive deposition of dielectric films. Using this approach, the charge that builds up on a dielectric target is dissipated through the second half of the cycle.

### 2.7 Characterization Techniques

It is very important to systematically characterize the samples (nanomaterials), for making them functional in various device fabrications. Nanomaterials may be characterized via their structural, optical and electrical properties. In the present research
work, we have characterized the samples via their structural and optical properties using X-ray diffraction (XRD), optical spectroscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM). The detailed description (theory and instrumentation) of these techniques employed in this research work is given below.

2.7.1 X-Ray Diffraction (XRD)

X-Ray diffraction (XRD) is a useful technique not only for the phase identification but also for the identification of the lattice structure and for the modeling of the basic unit cell [44]. This technique is applicable to solids or film grown on a substrate. It is also useful in providing information about the crystallinity of the material, lattice parameter, phase present and grain size. The variation of peak position with sample orientation can be utilized to deduce the information regarding the internal strain of the sample. For X-ray Diffraction, only short wavelength X-rays in the range of a few angstrom to 0.1 Angstrom (1 keV - 120 keV) are used. Because the wavelength of the X-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials [45-47].

When X-ray radiation passes through matter, the radiation interacts with the electrons in the atoms, resulting in scattering of the radiation. If the atoms are organized in planes (i.e. the matter in crystalline) and the distances between the atoms are of the same magnitude as the wavelength of the X-rays, constructive and destructive interference will occur. These results in diffraction where X-rays are emitted at characteristic angles based on the spaces between the atoms organized in crystalline structures called planes. In an X-rays diffractometer, X-rays are generated within an evacuated tube and exit through a window composed of a light element, usually beryllium. Inside the tube, a current is passed through a filament (usually tungsten) to generate electrons. These electrons are the accelerated through a potential difference
towards a metal target, such as copper. When the incoming electrons have sufficient energy to eject electrons from the core-shell (K-shell) of copper, a characteristic spectrum is created. The characteristics spectrum is composed of discrete energies, which occur due to X-rays emitted by the de-excitation of electrons to replace the ejected electrons [48]. Electrons de-excited from the L-shell into the K-shell give rise to Copper Kα peaks, electrons from the M-shell give Kβ peaks and electrons from the N shell give Kγ peaks. Kα and Kβ peaks are the most prominent peaks in the characteristic spectrum and since the Kγ peaks are weak component they can be neglected.

The Kα and Kβ peaks are doublets owing to the difference in energies of electrons de-excited from different L and M sub-shells respectively. Electrons will not decay from the L1 sub-shells, but will fall in from the L2 and L3 subshells. Electrons that ‘fall in’ from the L2 sub-shell give rise to Kα2 peaks and electrons the de-excited from the L3 sub-shell give rise to Kα1 peaks. Due to the small difference in energy between the Kα2 and Kα1 peaks, the Kα peak is a closely spaced doublet. A Similar process occurs from electrons de-excited from two of the five M sub-shells to give a Kβ doublet. For experiments where monochromatic radiation is required, Kα radiation is of interest and a filter is used to remove the Kβ radiation. A block diagram of powder diffraction unit is shown in figure 2.12. An X-ray powder diffractometer containing Cu target which is used for the structural studies, in present work, are shown in the figure 2.13. This provides us the X-rays of wavelength 1.54 Å.
Figure 2.12: A typical block diagram of powder X-ray diffraction unit.

Figure 2.13: Photograph of X-ray powder diffractometer (Bruker AXS, D8 Advance).
• **Bragg’s Law**

Since all atoms arranged periodically in a lattice, X-ray scattered from a crystalline solid can constructively interfere, producing a diffracted beam through these atoms.

In 1912 W.L. Bragg recognized a predictable relationship among several factors that is given below in figure 2.14, as Bragg’s law diffraction condition

\[ n\lambda = 2d \sin\theta \]  

(2.5)

Where

- \( n \) = an interger-1, 2, 3….etc \([n=1 \text{ for our calculations}]\)
- \( \lambda \) = the wavelength of the incident X-radiation, symbolized by the Greek letter lambda and, in our case, equal to 1.54 angstroms.
- \( d \) = the distance between similar atomic planes in a material (the interatomic spacing) which we call the d-spacing and measure in angstroms.
- \( \theta \) = the diffraction angle in degree

![Figure 2.14: Bragg’s Diffraction Condition.](image-url)
• **Scherrer’s Formula**

Scherrer’s formula [49] is used to estimate the size of very small crystals from measured width of their diffraction curves and given by

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

(2.6)

Where \( \lambda \) is the X-ray Wavelength (1.54 Å), \( \theta_B \) is the Bragg diffraction angle, and \( B \) is the FWHM of the peak respectively.

**Determination of Lattice Parameter**

One can easily determine the values lattice constant ‘a’ of (100) plane and ‘c’ of (002) plane of wurtzite structures of ZnO from the equation given below [50].

\[
a = \sqrt[3]{\frac{1}{3} \frac{\lambda}{\sin \theta}}
\]

(2.7)

\[
c = \frac{\lambda}{\sin \theta}
\]

(2.8)

Where \( \lambda \) is the X-ray Wavelength (1.54 Å), \( \theta \) is the Bragg diffraction angle,

**2.7.2 Spectroscopic Studies**

Investigations of optical properties of semiconducting materials are essential for proper application in semiconductor devices. The fundamental optical properties, which have been investigated, are reflectance, transmittance and absorption of light at various wavelengths. Figure 2.15 is the photograph of Hitachi spectrophotometer model U-3400. The optical layout of the spectrophotometer, which is used for the spectroscopic studies of the optical properties of the samples, is shown in figure 2.16 in this model of Hitachi spectrophotometer, the prism/grating double monochromatic system is used. The lenses, which were conventionally used in monochromatic system, have been all replaced with mirrors. This is done to eliminate an image deviation due to chromatic absorption. The
PbS detector converges the light beam with a toroidal mirror located below the photo multiple. This permits to replace PbS symmetrically against the sample and reference beam, whereby two beams are completely balanced. A mechanical chopper place before the first monochromatic chops the light beam emitted from the light source, with which a deviation in zero signals can be minimized. The visible wavelength light source is long life WL lamp that can be attached easily. The instrument incorporates the Hitachi microcomputer exclusive for it to control the mechanisms data processing and so on [51].

Figure 2.15: Photograph of Hitachi Spectrophotometer Model U-3400.
Figure 2.16: Optical layout of Hitachi Spectrophotometer Model U-3400.
M₁: Concave mirror
M₂: Toroidal mirror
M₃: Concave mirror
M₄: Plane mirror
M₅: Plane mirror
M₆: Concave mirror
M₇: Cylindrical mirror
M₈: Rotating mirror
M₉: Cylindrical mirror
M₁₀: Plane mirror
M₁₁: Cylindrical mirror
M₁₂: Plane mirror
M₁₃: Plane mirror
M₁₄: Toroidal mirror
M₁₅: Toroidal mirror
M₁₆: Toroidal mirror
P: Prism
S₁: 1ˢᵗ monochromatic slit
S₂: 2ⁿᵈ monochromatic entrance slit
S₃: 2ⁿᵈ monochromatic exit slit
PMT: Detector for UV-VIS (R928)
PbS: Detector for near infrared ray
W₁: Lamp for visible wavelength
D₂: Lamp for ultra violet
G₁: Plane grating 1440 lines/mm (190~ 850 nm)
G₂: Plane grating 600 lines/mm (1800~ 2600 nm)
CH: Mechanical chopper.
The function of the spectrophotometer can be classified into:

2.7.2 (a) Control of mechanisms (function)

Wavelength scan, light source switching, grating switching, detector switching etc.

2.7.2 (b) Signal processing functions

Data averaging, base line correction, calculation of transmittance, reflectance and absorbance, wavelength display, protection against disoperation alarming of abnormal condition etc.

The computer has the ability to process data at a rate of one byte/8 bits, and is connected to input – output devices such as A/D converter and memories through a signal line. A 8K bytes ROM (Read Only Memory) arranged in CPU store in program for starting the floppy disk and a RAM (Random Access Memory) is used in CPU. Variable data such as program and baseline are read from the floppy disk into the RAM and read out for execution during measurement. Photometric output from the detector is fed through the preamplifier, immediately subjected to A/D conversion and input into the computer, where it is discriminated into reference signal R, sample signals and zero signals Z or storage by gate signals obtained in synchronization with rotation of the sector mirror for splitting the light beam. Now the reference signal is compared with a predetermined standard value and used for controlling the voltage applied to the dynode of the photomultiplier.

On the other hand stored photometric value is used for determining transmittance (%T) by the calculation of (S-Z)/(R-Z) and absorbance (ABS) can be obtained by the log conversion of the transmittance.

2.7.2 (c) Optical Absorption

The measurement of absorption spectra is the direct method for probing the band structure of semiconductors. In the absorption process a photon of known energy excites
an electron from a lower to a higher energy state. In other manner we can say that absorption is also resulted from interaction between atoms and electromagnetic radiations. The specific microscopic interactions between a light wave and a real semiconductor, which are important in various part of the spectrum:

- Electron transition from the upper part of the valence band to the lower part of conduction band are responsible for the shape of absorption spectrum near fundamental absorption edge.
- Electron transition from deep states in valance band or states high up in the conduction band, govern the optical properties in the short wave length (ultra violet part of the spectrum).
- The interaction of light with lattice vibration governs the absorption in the far infrared region.

The absorption spectra, with a rapid rise in absorption at shorter wavelength can be used to determine the energy band gap of the semiconductor. Every solid has its own characteristics energy band structure. The conduction and valence band are the regular features of all the solids. Only difference is upto which they are occupied and the vertical separation between them i.e. energy band gap. Thus energy band gap may be defined as the gap of region between the valence and conduction band, in which there is no level of energy. The band gap may be classified as direct and indirect band gap depending upon the electron transition as shown in figure 2.17.
Figure 2.17: Representation of (a) Direct band Gap, (b) Indirect band Gap.

2.7.2 (d) Direct and Indirect Band Gap

As the material absorbs the photon of incident light, an electron is excited from lower to upper energy level or state. This transition of electron can be direct (without photon participation) or indirect (in which the interaction with a phonon takes place). In a direct transition an electron in the conduction band can fall (figure 2.16) to an empty state in the valence band, giving off the energy difference $E_g$ as photon of light. On the other hand, if an electron in the conduction band cannot fall directly to the valence band, but must undergo a momentum change as well as changing its energy. The difference between direct and indirect band structure is very important for deciding that which semiconductor can be used in device requiring light output.

2.7.2 (e) Determination of the Energy Band Gap $E_g$

The absorption spectrum of the material is an important technique, which is used
for measuring the energy band gap ($E_g$) of a semiconductor. An important feature of this method is that it is applicable for any range i.e. narrow or wide band gap material. In this experiment photons of selected wavelength are incident on the sample and the relative transmission of the various photons is observed.

Let a photon beam of intensity $I_o$ (photons/cm$^2$ sec) is incident at the sample of thickness $t$ and the intensity of light transmitted is $I_t$ (Beer-Lambert Law) then,

$$I_t = I_o e^{-\alpha t} \quad (2.9)$$

Where $\alpha$ is the absorption coefficient and has unit cm$^{-1}$. The coefficient varies with photon wavelength and also with the materials. The difference between direct and indirect transition is possible on the basis of the dependence of absorption coefficient on the photon energy.

To determine the energy band gap from absorption spectra the Tauc relation is used [52].

$$\alpha h\nu = A(h\nu-E_g)^n \quad (2.10)$$

where, $h\nu = $ Photon energy

$E_g = $ Band gap

$\alpha = $ Absorption coefficient

$n = 1/2, 2, 3/2, 3$

$A = $ Constant

$n = 1/2$, Allowed direct transition

$n = 3/2$, Forbidden direct transition

$n = 2$, Allowed indirect transition

$n = 3$, Forbidden indirect transition

In case of direct band gap the allowed transition are giving by using the equation (2.10) as,
\[ \alpha \ h\nu = A(h\nu - E_g)^{1/2} \] 

(2.11)

A plot of \((\alpha \ h\nu)^2\) versus photon energy \((h\nu)\) when extrapolated to zero absorption gives the value of energy band gap \((E_g)\).

While in case of indirect band gap the allowed transitions are given by using equation (2.10) as,

\[ \alpha \ h\nu = A(h\nu - E_g)^2 \] 

(2.12)

A plot of \((\alpha \ h\nu)^{1/2}\) versus photon energy \((h\nu)\) when extrapolated to zero absorption gives the value of energy band gap \((E_g)\) of indirect band gap materials.

2.7.2 (f) Determination of Optical Constants

The optical behavior of materials is generally utilized to determine the optical constant \(n\) (refractive index), \(k\) (extinction coefficient), \(\epsilon\) (dielectric constants) and \(t\) (thickness). The thin films are ideal specimen for reflection and transmission measurements. Several of these methods actually determine the effective optical thickness of the film can be derived, provided to the optical constant are known and vice versa. We have used transmission method for determination of \(n\) and \(k\).

- **Transmission Method for Determination of Optical Constants \(n\) & \(k\)**

  The measurement of the transmission \(T\) of light through a parallel-faced dielectric film in the region of transparency is sufficient to determine the real and imaginary parts of the complex refractive index \(\eta = n - ik\), as well as the thickness ‘t’. J.C. Manifacier et.al (1976) derived the expressions to calculate the optical constants of thin film material by using transmission spectra (envelope method) as given below [53].

- **Theory**

  Figure 2.18 represents a thin film with a complex refractive index \(\eta = n-ik\), bounded by two transparent media with refractive indices, \(n_o\) and \(n_i\). Considering unit
Synthesis and Characterization of Zinc Oxide (ZnO) Nanostructures

Figure 2.18: Reflection and transmission of light by single film.

amplitude for the incident light, in the case of normal incidence the amplitude of the transmitted wave is given by:

$$A = \frac{t_1 t_2 \exp(-2\pi \eta t/\lambda)}{1 + r_1 r_2 \exp(-2\pi \eta t/\lambda)}$$  \hspace{1cm} (2.13)

in which $t_1$, $t_2$, $r_1$, $r_2$ are the transmission and reflection coefficients at the front and rear faces. The transmission of the layer is given by:

$$T = \frac{n_s}{n_0} |A|^2$$  \hspace{1cm} (2.14)

The exact expression is given in the appendix. In the case of weak absorption (see appendix) with $k^2 \ll (n - n_0)^2$ and $k^2 \ll (n - n_1)^2$,

$$T = \frac{16 n_0 n_1 n^2 \alpha}{C_1^2 + C_2^2 \alpha^2 + 2C_1 C_2 \alpha \cos\left(\frac{4\pi n t}{\lambda}\right)}$$  \hspace{1cm} (2.15)

Where $C_1 = (n+n_0)(n_1+n)$, $C_2 = (n-n_0)(n_1-n)$ and

$$\alpha = \exp(-4\pi k t/\lambda)$$  \hspace{1cm} (2.16)

$\alpha$ is absorption and $k$ is the extinction coefficient of the thin film.
Generally, outside the region of fundamental absorption \((h\nu > E_G, \text{ thin film gap})\) or of the free-carrier absorption (for higher wavelengths), the dispersion of \(n\) and \(k\) is not very large. The maxima and minima of \(T\) in equation (2.15) occur for

\[
\frac{4\pi nt}{\lambda} = m\pi \quad \text{(2.17)}
\]

Where \(m\) is the order number. In the usual case \((n > n_i, \text{ corresponding to a semiconducting film on a transparent nonabsorbing substrate, } C_2 < 0)\), the extreme values of the transmission are given by the formula

\[
T_{\text{max}} = \frac{16n_0n_1n^2\alpha^2}{C_1 + C_2\alpha} \quad \text{(2.18)}
\]

\[
T_{\text{min}} = \frac{16n_0n_1n^2\alpha^2}{C_1 - C_2\alpha} \quad \text{(2.19)}
\]

By combining equations (2.18) and (2.19), Lyashenko and Miloslavskii (1964) developed an iterative method allowing the determination of \(n\) and \(\alpha\) and, using (2.16) and (2.17), \(k\) and \(t\). They propose an important simplification of this method, they consider \(T_{\text{min}}\) and \(T_{\text{max}}\) as continuous functions of \(\lambda\) through \(n(\lambda)\) and \(\alpha(\lambda)\). These functions which are the envelopes of the maxima \(T_{\text{max}}(\lambda)\) and the minima \(T_{\text{min}}(\lambda)\) in the transmission spectrum. The ratio of equations (2.18) and (2.19) gives

\[
\alpha = \frac{C_1[1 - (T_{\text{max}}/T_{\text{min}})^{1/2}]}{C_2[1 + (T_{\text{max}}/T_{\text{min}})^{1/2}]} \quad \text{(2.20)}
\]

Then, from equation (2.18),

\[
n = \left[N + (N^2 - n_0^2n_1^2)^{1/2}\right]^{1/2} \quad \text{(2.21)}
\]

where

\[
N = \frac{n_0^2 + n_1^2}{2} + 2n_0n_1 \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}}T_{\text{min}}}.
\]
Equation (2.21) shows that \( n \) is explicitly determined from \( T_{\text{max}}, T_{\text{min}}, n_1 \) and \( n_0 \) at the same wavelength. Knowing \( n \), we can determine \( \alpha \) from equation (2.20). The extinction coefficient ‘k’ is given by

\[
k = \left( -\frac{\lambda}{4\pi t} \right) \ln \alpha \quad (2.22)
\]

The thickness \( t \) of the layer can be calculated from two maxima or minima using equation (2.17).

\[
t = \frac{M \lambda_1 \lambda_2}{2(n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1)} \quad (2.23)
\]

Where \( M \) is the number of oscillations between the two extrema (\( M=1 \) between two consecutive maxima or minima); \( \lambda_1 \), \( n(\lambda_1) \) and \( \lambda_2 \), \( n(\lambda_2) \) are the corresponding wavelengths and indices of refraction. It is worthwhile noting those expressions (2.20), (2.21), (2.22) and (2.23) can be easily calculated using a programmable pocket calculator.

We have used the same method for determination of optical constants for Plused laser deposited ZnO thin film and discussed variation of ‘n’ and ‘k’ with wavelength [54].

### 2.7.3 Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. Some advantages of the SEM are the large depth of field, which allows a large amount of the sample to be focus at a given time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since, most SEM only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most widely used instruments in research areas today [55].

The Scanning Electron Microscope (SEM) is one of the most versatile and widely used...
tools of modern science as it allows the study of both morphology and composition of a large range of materials. The schematic diagram of the main frame of SEM is shown in figure 2.19.

**Figure 2.19: Schematic diagram of the main frame of SEM.**

Different signals are used by the corresponding detectors for image formation:

- Secondary electrons: image of the surface and topography.
- Backscattered electrons: contrast arising from the average atomic number.

X-rays with energies characteristic of the atoms in the specimen: qualitative and quantitative information about the elemental composition. Thus detailed maps of elemental distribution can be produced from multi-phase materials or complex materials.
In scanning electron microscopy (SEM) an electron beam is scanned across a sample's surface. When the electrons strike the sample, a variety of signals are generated, and it is the detection of specific signals which produces an image or a sample's elemental composition. The three signals which provide the greatest amount of information in SEM are the secondary electrons, backscattered electrons, and X-rays. Secondary electrons are emitted from the atoms occupying the top surface and produce a readily interpretable image of the surface. The contrast in the image is determined by the sample morphology.

A high resolution image can be obtained because of the small diameter of the primary electron beam. Backscattered electrons are primary beam electrons which are 'reflected' from atoms in the solid. The contrast in the image produced is determined by the atomic number of the elements in the sample. The image will therefore show the distribution of different chemical phases in the sample. Because these electrons are emitted from a depth in the sample, the resolution in the image is not as good as for secondary electrons. Interaction of the primary beam with atoms in the sample causes shell transitions which result in the emission of an X-ray. The emitted X-ray has an energy characteristic to the parent element an electron beam is used to produce SEM images. The beam of electrons is produced by heating the filament at the top of the microscope assembly. The electron beam follows a vertical path through the column of the microscope. It makes its way through electromagnetic lenses which focus and direct the beam down towards the sample. By using electromagnets one can have more control over the magnification. Once the electron beam hits the sample, other electrons like backscattered or secondary are ejected from the sample. Detectors collect the secondary or backscattered electrons, and convert them into a signal that is sent to a viewing screen similar to the one in an ordinary television, producing an image.
2.7.4 Atomic Force Microscopy

Atomic Force Microscope (AFM) is a powerful tool to probe the surface of the material. A small hook at the end of the cantilever is pressed against the surface while the sample is scanned beneath the tip. The force between tip and sample is measured by tracking the deflection of the cantilever. An atomically sharp tip is scanned over a surface with feedback mechanisms that enable the piezo-electric scanners to maintain the tip at a constant force (to obtain height information), or height (to obtain force information) above the sample surface.

Tips are typically made from Si$_3$N$_4$ or Si, Pt and Ir extended down from the end of a cantilever. The nanoscope AFM head employs an optical detection system in which the tip is attached to the undesired of a reflective cantilever. A diode laser is focused onto the back of a reflective cantilever. As the tip scans the surface of the sample, moving up and down with the contour of the surface, the laser beam is deflected off the attached cantilever into a dual element photodiode. The photodetector measures the difference in light intensities between the upper and lower photodetector, and then converts to voltage [55]. Feedback from the photodiode difference signal, through software control from the computer, enables the tip to maintain either a constant force or constant height above the sample. In the constant force mode, the piezo-electric transducer monitors real time height deviation. In the constant height mode, the deflection force on the sample is recorded.

The latter mode of operation requires calibration parameters of the scanning tip to be inserted in the sensitivity of the AFM head during force calibration of the microscope. The block diagram of AFM is shown in figure 2.20. According to the interaction of the tip and the sample surface, the AFM can be classified as repulsive or contact mode and
attractive or noncontact mode. For the present work, Atomic force microscope (AFM) has been used is shown in figure 2.21.

Figure 2.20: The block diagram of AFM.
The Common AFM Modes

Many AFM modes have appeared for special purpose while the technique of AFM is becoming mature. Three commonly used modes: Contact Mode (left), Non-contact Mode (middle) and Tapping Mode (right) are shown and discussed as below:
Contact Mode

The contact mode where the tip scans the sample in close contact with the surface is the common mode used in the force microscope. The force on the tip is repulsive with a mean value of $10^{-9}$ N. This force is set by pushing the cantilever against the sample surface with a piezoelectric positioning element. In contact mode AFM the deflection of the cantilever is sensed and compared in a DC feedback amplifier to some desired value of deflection. If the measured deflection is different from the desired value the feedback amplifier applies a voltage to the piezo to raise or lower the sample relative to the cantilever to restore the desired value of deflection.

The voltage that the feedback amplifier applies to the piezo is a measure of the height of features on the sample surface. It is displayed as a function of the lateral position of the sample. In addition, a large class of samples, including semiconductors and insulators, can trap electrostatic charge (partially dissipated and screened in liquid). This charge can contribute to additional substantial attractive forces between the probe and sample. All of these forces combine to define a minimum normal force that can be controllably applied by the probe to the sample. This normal force creates a substantial frictional force as the probe scans over the sample. In practice, it appears that these frictional forces are far more destructive than the normal force and can damage the sample, dull the cantilever probe and distort the resulting data. Also many samples such as semiconductor wafers can not practically be immersed in liquid. An attempt to avoid these problem is the Non-contact Mode.

Non-contact Mode

A new era in imaging was opened when microscopists introduced a system for implementing the non-contact mode which is used in situations where tip contact might alter the sample in subtle ways. In this mode the tip hovers 50 - 150 Angstrom above the
sample surface. Attractive Van der Waals forces acting between the tip and the sample are detected, and topographic images are constructed by scanning the tip above the surface. Unfortunately the attractive forces from the sample are substantially weaker than the forces used by contact mode. Therefore the tip must be given a small oscillation so that AC detection methods can be used to detect the small forces between the tip and the sample by measuring the change in amplitude, phase or frequency of the oscillating cantilever in response to force gradients from the sample. For highest resolution, it is necessary to measure force gradients from Van der Waals forces which may extend only a nanometer from the sample surface [56].

In general, the fluid contaminant layer is substantially thicker than the range of the Van der Waals force gradient and therefore, attempts to image the true surface with non-contact AFM fail as the oscillating probe becomes trapped in the fluid layer or hovers beyond the effective range of the forces it attempts to measure.

**Tapping Mode**

Tapping mode is a key advance in AFM. This potent technique allows high resolution topographic imaging of sample surfaces that are easily damaged, loosely hold to their substrate or difficult to image by other AFM techniques. Tapping mode overcomes problems associated with friction, adhesion, electrostatic forces and other difficulties that an plague conventional AFM scanning methods by alternately placing the tip in contact with the surface to provide high resolution and then lifting the tip off the surface to avoid dragging the tip across the surface. Tapping mode imaging is implemented in ambient air by oscillating the cantilever assembly at or near the cantilever's resonant frequency using a piezoelectric crystal.
The piezo motion causes the cantilever to oscillate with a high amplitude (typically greater than 20 nm) when the tip is not in contact with the surface. The oscillating tip is then moved toward the surface until it begins to lightly touch, or tap the surface. As the oscillating cantilever begins to intermittently contact the surface, the cantilever oscillation is necessarily reduced due to energy loss caused by the tip contacting the surface. The reduction in oscillation amplitude is used to identify and measure surface features.

In AFM, the height of the (unbiased) tip is controlled by the tip-sample interaction force and a structural surface image is obtained directly. However, the intrinsic lateral resolution is poorer than for scanning tunneling microscope (STM) and significant processing of images may be necessary to give useful information. Furthermore, for both STM and AFM [57] the overall dimensions of the conical tip are generally larger than the crystallite size so that the vertical scale can be significantly distorted. When the tip is moved sideways it will follow the surface of the samples are obtained and the height and roughness evolution can be estimated. For many studies, AFM is applied together with another optical characterization or morphological technique.
References


