Chapter - II

VARIOUS METHODS OF FILM DEPOSITION AND CHARACTERIZATION
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2.1 Introduction

Modern technology requires thin films on several occasions for variety of applications [1] like solar cell devices, ICS [2], optical coating, display devices etc. Broadly the deposition techniques can be classified into (a) Physical Deposition and (b) Chemical Deposition. In physical deposition, thermal evaporation is one of the most well known techniques. It is simple and one can evaporate a large variety of materials (metals, semiconductors or insulators) on different types of substrate. In thermal evaporation, the evaporation is carried out at low pressure or high vacuum (~ $10^{-6}$ Torr). In our present investigation, we have studied photoconductivity rise and decay of some CdTe thin films prepared by vacuum thermal evaporation method. We have studied the photoconductivity process on unanalyzed data in CdTe thin films provided by our co-workers. The objective was to be acquainted with the process of data analysis and CdTe as an important calcho genide material of II-VI compound together with the physical deposition process.

Our main experimental work in preparation of thin films and nanomaterial was concentrated with CdS as a material of II-VI compound. Thin films of CdS were prepared by chemical bath deposition process (CBD) using tetra-ammine complex method. CBD is a simple, low cost method and large area film can be deposited by this technique. It offers obvious advantages for production of low cost devices without much complexity. Details of CBD technique for preparation of CdS thin film and their characterization have been described in Chapter IV.
For preparing CdS nanocrystalline thin film, we have used chemical route. In chemical route, polymer stabilizer plays a very important role in the synthesis of nanocrystals or quantum dots. In our present investigation, nanocrystalline CdS have been prepared using polyvinyl alcohol (PVA) as the capping agent or matrix. Details of preparation of such film and subsequent characterization have been described in Chapter-V.

Preparation of thin films and synthesis of nanoparticles and their subsequent characterization process provides necessary informations on the growth mechanism, structure, defects and nature of the thin films and nanomaterials. The structural property attained by thin film and nanomaterial is important in determining their properties and applications. In addition to that, compositional analysis is also important for determining stoichiometry of the grown film and nanomaterial. Thus structural characterization and compositional analysis provide useful information about the material property. Success in devising and assembling systems based on thin film and nanomaterial require a deeper understanding of the basic process involved during growth and formation. Hence one of the key objectives is to adopt and develop a range of techniques that can characterize the structural, optical, optoelectronic, electronic and other properties of the grown system. Among the structural characterization techniques, X-ray diffraction using X-ray optics is important for getting a whole range of information about the films and nanomaterials. X-ray diffraction (XRD) supplements electron diffraction in the determination of the crystallographic structure of thin film. X-ray diffraction also can be used for determining the thickness of thin film and nanocrystallite size. Other instruments based on x-ray optics for compositional analysis are wavelength dispersive x-ray fluorescence (WD X-RF), energy dispersive analysis
by X-ray (EDAX) or energy dispersive spectroscopy (EDS) attached with scanning electron microscopy and X-ray photoelectron spectrometer (XPS) or electron spectroscopy for chemical analysis (ESCA).

Optical characterization is also important as a non-contact method of characterizing thin film and nanomaterial. Among the optical characterization, absorption spectrometry, optical emission spectrometry or photoluminescence (PL), Laser-Raman spectrometry are important in determining thickness of thin film, size of the nanocrystallite, nature and width of the band gap, defect etc. In addition Fourier Transform Infra Red spectroscopy (FTIR) represents finger print of a sample with absorption peaks corresponding to the frequency of vibration between the bonds of the atoms making up the material.

Microscopy is another powerful tool which can provide direct imaging of the morphology of thin film and nanomaterial. It is also a means of replacing our eyes and hence in order to “feel and see” thin film morphology and nanostructure. Electron microscopy first developed in 1950 by Ernst Ruska and scanning tunneling microscopy (STM) developed by Gerd Binning and Heinrich Rohrer of IBM’s Zurich Laboratory in 1981 provided stunning insight into the world of single atoms of materials. All of them (Ruska, Binning and Rohrer) were awarded 1986 Nobel prizes in physics for their design of STM and design of first electron microscope. The STM was modified by Binning and his colleague to develop another type of microscope, known as atomic force microscope (AFM) in 1986. AFM provides a significant advantage as an imaging tool compared with electron microscope for making topographic maps of nanostructures of semiconductor material and other non-conducting material in real time. Thus electron microscopy and atomic force microscopy is an indispensable tool in characterizing thin film and nanomaterial.
Among the optoelectronic techniques of characterizing thin films, photoconductivity is important to determine band structure and defect, electron transport properties of material. It also provides basic information relating to physics and chemistry of the material. Photoconductivity growth and decay can be used to determine the excess carrier life time, diffusion length, junction capacitance, depletion layer width etc. of semiconductor devices [3-7].

2.2 Various methods of deposition of thin film

The act of applying a thin layer to a surface is known as thin-film deposition. It is a technique for depositing a thin film of material onto a substrate or onto previously deposited layers. “Thin” is a relative term, but most deposition techniques allow layer thickness to be controlled within a few tens of nanometers, and some (molecular beam epitaxy) allow single layers of atoms to be deposited at a time.

Thin films can be prepared by various methods, which have been reviewed in the literature [8-23] from time to time. Deposition techniques can be divided into two broad categories, depending on whether the process is primarily chemical or physical. In all the deposition techniques the three basic step involved are:

(a) Creation of materials to be deposited in an atomic, molecular or particulate form prior to deposition.
(b) Transport of materials thus created to the substrate in form of a vapour stream, ion or spray etc.
(c) Deposition of the material on the substrate and film grown by a nucleation growth process.
The various techniques as described in wikipidia encyclopedia can be summerised as follows [24].

**Chemical deposition**

Here, a fluid precursor undergoes a chemical change at a solid surface, leaving a solid layer. An everyday example is the formation of soot on a cool object when it is placed inside a flame. Since the fluid surrounds the solid object, deposition happens on every surface, with little regard to direction; thin films from chemical deposition techniques tend to be conformal, rather than directional.

Chemical deposition is further categorized by the phase of the precursor as follows:

1. **Plating** relies on liquid precursors, often a solution of water with a salt of the metal to be deposited. Some plating processes are driven entirely by reagents in the solution (usually for noble metals), but by far the most commercially important process is electroplating. It was not commonly used in semiconductor processing for many years, but has seen a resurgence with more widespread use of chemical-mechanical polishing techniques.

2. **Chemical solution deposition (CSD)** uses a liquid precursor, usually a solution of organometallic powders dissolve in an organic solvent. This is a relatively inexpensive, simple thin film process that is able to produce stoichiometrically accurate crystalline phases.

3. **Chemical vapor deposition (CVD)** generally uses a gas-phase precursor, often a halide or hydride of the element to be deposited. In the case of MOCVD, an organometallic gas is used. Commercial techniques often use very low pressures of precursor gas.
4. Plasma enhanced CVD (PECVD) uses an ionized vapour, or plasma, as a precursor. Unlike the soot example above, commercial PECVD relies on electromagnetic means (electric current, microwave excitation), rather than a chemical reaction, to produce a plasma.

Physical deposition

Physical deposition uses mechanical or thermodynamic means to produce a thin film of solid. An everyday example is the formation of frost. Since most engineering materials are held together by relatively high energies, and chemical reactions are not used to store these energies, commercial physical deposition systems tend to require a low-pressure vapour environment to function properly; most can be classified as physical vapour deposition (PVD).

The material to be deposited is placed in an energetic, entropic environment, so that particles of material escape its surface. Facing this source is cooler surface, which draws energy from these particles as they arrive, allowing them to form a solid layer. The whole system is kept in a vacuum deposition chamber, to allow the particles to travel as freely as possible. Since particles tend to follow a straight path, films deposited by physical means are commonly directional, rather than conformal.

Examples of physical deposition include:

A thermal evaporation uses an electric resistance heater to melt the material and raise its vapour pressure to a useful range. This is done in a high vacuum, both to allow the vapour to reach the substrate without reacting with or scattering against other gas-phase atoms in the chamber, and reduce the incorporation of
impurities from the residual gas in the vacuum chamber. Obviously, only materials with a much higher vapour pressure than the heating element can be deposited without contamination of the film. Molecular beam epitaxy is a particular sophisticated form of thermal evaporation.

An electron beam evaporation fires a high-energy beam from an electron gun to boil a small spot of material; since the heating is not uniform, lower vapour pressure materials can be deposited. The beam is usually bent through an angle of 270° in order to ensure that the gun filament is not directly exposed to the evaporant flux. Typical deposition rates for electron beam evaporation range from 1 to 10 nanometers per second.

Sputtering relies on a plasma (usually a noble gas, such as argon) to knock material from a “target” a few atoms at a time. The target can be kept at a relatively low temperature, since the process is not one of evaporation, making this one of the most flexible deposition techniques. It is especially useful for compounds or mixtures, where different components would otherwise tend to evaporate at different rates.

Pulsed laser deposition systems work by an ablation process. Pulses of focused laser light vaporize the surface of the target material and convert it to plasma; this plasma usually reverts to a gas before it reaches the substrate.

Catholic arc deposition (arc-PVD) which is a kind of ion beam deposition where an electrical arc is created that literally blasts ions from the cathode. The arc has an extremely high power density resulting in a high level of ionization (30-100%), multiply charged ions, neutral particles, clusters and macro-particles (droplets). If a reactive gas is introduced during the evaporation process, dissociation, ionization and excitation can occur during interaction with the ion flux and a compound film will be deposited.
Other deposition processes

Some methods fall outside these two categories, relying on a mixture of chemical and physical means:

In reactive sputtering, a small amount of some non-noble gas such as oxygen or nitrogen is mixed with the plasma-forming gas. After the material is sputtered from the target, it reacts with this gas, so that the deposited film is a different material, i.e., on oxide or nitride of the target material.

In molecular beam epitaxy (MBE), slow streams of an element can be directed at the substrate, so that material deposits one atomic layer at a time. Compounds such as gallium arsenide are usually deposited by repeatedly applying a layer of one element (i.e., gallium), then a layer of the other (i.e., As), so that the process is chemical, as well as physical. The beam of material can be generated by either physical means (that is, by a furnace) or by a chemical reaction (chemical beam epitaxy).

In topotaxy, a specialized technique similar to epitaxy, thin film crystal growth occurs in three dimensions due to the crystal structure similarities (either heterotopotaxy or homotopotaxy) between the substrate crystal and the growing thin film material.

2.3 Methods of deposition of nanomaterials

The methods of deposition of nanomaterials can be classified broadly into two general classes as gas phase methods and condensed phase methods. Often gas phase clusters are produced and studied in the gas phase only, or they are deposited on a solid surface. These methods are used for small quantities of nanostructure. The second class of synthesis is that in which the nanostructure
are obtained in the condensed phase. These methods are mainly divided into two classes as chemical and physical methods. A classification of nanoparticle synthesis techniques is shown in the flow chart of fig. 2.1.

**Fig. 2.1**: A classification of nanoparticle synthesis techniques

Thus for deposition of nanomaterials and nanostructures, a variety of techniques like spray pyrolysis, thermal deposition, molecular beam epitaxy (MBE), vapour phase epitaxy, electrochemical deposition, photo-chemical deposition, rf sputtering, sol gel, chemical vapour deposition, laser oblation etc. have been widely used. Out of these methods, chemical route is an useful one for obtaining nanocrystalline thin films and nanomaterials as it can be performed using a range of precursor and synthesis conditions like temperature, deposition time, stirring rate, concentration of reactants, pH etc. By varying these parameters, one can achieve the size and shape of the nanoparticle of his own choice. The
methods other than chemical route to prepare nanoparticles are complex, costly and need sophisticated instrumentation in some techniques like MBE. Chemical route is a useful method for obtaining CdS nanoparticles both in thin film form and liquid form. Thus chemical method has been given much attention as a low cost, simple and promising technique for deposition of nanomaterials. Again depending upon the starting material and complexing agent used, size, structure, morphology, electronic and optical properties etc. may be different.

In our present investigation we have selected wide and direct band gap CdS material of II-VI compound for fabrication of nanocrystalline film embedded in polyvinyl alcohol (PVA) matrix. Details of synthesis of nanocrystalline CdS/PVA solution and thin film by chemical route have been described in Chapter-V.

2.4 **Substrate selection and substrate cleaning**

The depositions of thin films require certain supporting materials called substrate. The choice of the substrate and substrate cleaning is very important consideration in thin film preparation. Substrate may be amorphous, polycrystalline or single crystal in nature. Glass, mica, quartz, ceramic, etc. are commonly employed substrates in thin film growth. Recently, efficient polycrystalline films are bring deposited on polymer substrates, such as polycarbonate and polyethylene terephthalate as they are light weight, of small volume and can make the obtained devices foldable and also easy to carry. [25]

The idea of selecting proper material as substrate for some particular need, can be obtained from the review given by Brown. [26]

In our experiment, glass was used as substrate because of the following advantages.
1. Well adherent and smooth.
2. It is chemically inactive.
3. It has high electrical resistivity (~$10^{15} \Omega \text{ m}$) compared to our CdS films and hence acts as an insulating substrate.
4. It has a good thermal stability so as to permit heating up to higher temperature (~480 K) and cooling to liquid nitrogen temperature (~77 K).
5. It is easily available and a low cost material.

The glass substrates, used to prepare CdS thin film, were cut into required size for different structural, optical, electrical and morphological analysis and cleaned properly.

The cleaning procedure adopted in the present work has been outlined below:

1. The substrate cut into required size were first washed with mild soap solution and thoroughly washed with distilled water.
2. These were then kept in dilute nitric acid for 10 to 12 hours.
3. The substrates were then properly washed with freshly prepared distilled water and were kept immersed in freshly prepared chromic acid for about 1 hour.
4. These were then removed from the chromic acid, washed with distilled water and kept in very dilute (0.5% w/v) sodium hydroxide solution for about 10 to 15 minutes.
5. After removing from sodium hydroxide solution the substrate were rubbed by clean filter paper using tweezers and then thoroughly rinsed with double distilled water.
6. The substrates were then kept in a properly cleaned corning glass beaker in an inclined position and dried by keeping this arrangement inside a cleaned and closed oven for 15 minutes at 100°C.

7. Finally the substrate to be used for deposition technique of CdS thin films was transferred immediately to a clean desiccators.

2.5 Various characterization methods

For characterization of CdTe thin films, we have applied optoelectronic technique and for characterization of CdS thin films and nanocrystalline films, optical technique has been employed. The various characterization methods adopted in our investigation can be classified as follows:

(a) Optoelectronic technique.
(b) Structural characterization and size determination by X-ray optics.
(c) Characterization by optical absorption spectroscopy.
(d) Characterization by optical emission spectroscopy (Photoluminescence).
(e) Characterization by Fourier Transform Infrared Spectroscopy (FTIR).
(f) Morphological characterization.

2.5 (a) Optoelectronic technique:

By optoelectronic techniques we mean the electronic processes which are directly connected with photoconductivity mechanisms. The phenomenon of photoconductivity occurs when an incident light beam having photon energy \( hv \geq E_g \) impinges upon a semiconductor and causes an increase in its electrical conductivity. The atomic resistance of the photoconductor changes in a definite manner with the intensity and colour of light. This phenomenon of
photoconductivity was first intelligently observed in selenium by Willoughby Smith in 1873. All practical photoconductors have the common property of being semiconductors.

The photoconductivity of a material depends on both intensity and wavelength of the incident radiation. The studies on the dependence of photocurrent on intensity and wavelength of the incident radiation gives information regarding the recombination mechanism, intrinsic and extrinsic band gaps of the material. The rise and decay of photoconductivity provide the additional information about the trap levels, capture cross sections and also about the trap distribution within the band gap.

When a photoconductor is exposed to light radiation, the photocurrent takes some time called the growth time to reach the maximum or steady state. Again when the light is turned off the photocurrent decays to reach the initial dark value within another interval of time which is called the decay time.

The growth and decay processes in a photoconductor are understandable in terms of processes of release of extra electrons and holes and illumination followed by their recombination [27]. When a photoconductor is exposed to radiation having photon energy \( hv \geq E_g \) the intrinsic band gap energy, electron hole pairs are generated and their densities tend to increase with illumination time. However increase of excess carrier density is controlled by the recombination process as it counter balances the generation process. After a lapse of time, a steady state is established when the recombination rate equals the generation rate. As the light is turned off the photocurrent decays due to recombination. Presence of traps plays a significant role in the recombination mechanism. When the material is exposed to radiations, a certain proportion of generated free carriers is captured by these traps. These
filled traps will be emptied after the exciting radiation is switched off, at a rate depending upon their cross-section and ionization energy. Thus the decay time will be different depending upon the trap depth, trap distribution etc.

The time dependence of the growth of photoconductivity \( \sigma_t \) is given by—

\[
\sigma_t = q \mu \alpha \eta J \tau \left\{ 1 - \exp\left( -\frac{t}{\tau} \right) \right\}
\]  

(2.1)

Where \( q \) is the charge of the carriers, \( \mu \) is the mobility of carriers, \( \alpha \) is the light absorption coefficient, \( \eta \) is the photo-ionization quantum yields (efficiencies), which determine the average number of electron-hole pairs generated by a quantum (hv) of radiant energy, \( J \) is the light intensity and \( \tau \) is the growth time. For \( t = 0 \), \( \sigma_t = 0 \) and for \( t \to \infty \), \( \sigma_t = q \mu \alpha \eta J \tau = \sigma_0 \) and hence we get from equation (2.1).

\[
\sigma_t = \sigma_0 \left\{ 1 - \exp\left( -\frac{t}{\tau} \right) \right\}
\]  

(2.2)

The plot of the function given by equation (2.2) for the growth of the current will yield a curve as shown in Fig. 2.2. The tangent to this curve at the origin of the co-ordinate system intercepts the straight line \( \sigma = \sigma_0 \) at \( t = \tau \), corresponding to the photoconductivity growth time.

After a lapse of time when the photocurrent reaches the steady state value the light is turned off and then the photocurrent begins to decrease. The time dependence of the decay of photoconductivity \( \sigma_t \) is given by—

\[
\sigma_t = \sigma_0 \exp\left( -\frac{t}{\tau} \right)
\]  

(2.3)
The second part of the curve in Fig. 2.2 is obtained by plotting the function given by equation (2.3). The decay time is obtained by drawing the tangent to the curve at the point \( t_0 \) and intercepts the time axis at \( t \) gives the decay time \( \tau = t - t_0 \).

![Graph showing photocurrent decay](graph.png)

**Fig. 2.2 :** The growth and decay of photocurrent of a photoconductor after turning on and off the light.

2.5 (b) **Structural characterization and size determination by x-ray optics :**

**Introduction :**

The diffraction of X-ray is an important tool for investigating fine structure of matter. The technique had its beginning in Von Lave’s discovery in 1912 that crystals diffract X-rays. Presently, X-ray diffraction is widely used in many fields of science and in many industries for applications ranging from basic research to routine quality control. It is used to identify new compounds and crystalline structures, unknown materials in terms of its crystalline structure, and to look for deviations from the perfect structure which may indicate the presence of impurities, strain, the size of the crystals and other fine-scale structural defects.

The diffraction of X-ray is of great analytical interest as applied to study crystalline nature of materials. XRD may be regarded as fingerprint of material
for its identification. It can be used for phase identifications, crystallite size, shape and distribution, non-uniform, percentage crystallinity, layer thickness, roughness, density, preferred orientation and also for non-ambient experiments. The XRD technique has also been found to be especially suitable for structural analysis of thin films and nanostructured films. For low scattering and high penetrating power, XRD technique is not suitable for surface structure of thinner films. But for films with thickness ≥ 1000 Å, XRD technique is generally employed to obtain a whole range of information about the crystallographic aspects of samples.

WDXRF spectrometry is now widely accepted as a highly versatile, rapid and potentially accurate method of instrumental elemental analysis [28, 29]. The fluorescent emission of x-ray provide one of the most potential tools available to the analyst for identification and measurement of heavy elements in the presence of each other and in nearly any matrix. The method fails with elements lighter than sodium (At. No. 11, At. Mass 22.990) and is marginal below calcium (At. No. 20, At. Mass 40.078). Though our sample film material CdS contains one heavy element Cadmium (At. No. 48, At. Mass 112.41) and lighter element sulphur (At. No. 16, At. Mass 32.066), an attempt has been made to observe sample composition and inclusion of any other impurities present in the samples using XRF technique.

Here we discuss structural analysis of poly crystalline thin film and nanostructured film by XRD technique.
Theoretical Consideration of Determination of Structural Parameters:

XRD is considered to be a very important experimental technique that has long been used to address all issues related to crystal structure of solid, including lattice constant and geometry, identification of unknown material, orientation of single crystal, defects and stress etc.

When a monochromatic parallel beam of x-ray, with a wavelength ranging from 0.7 Å to 2 Å is incident on a specimen, the constituent atoms which are arranged in a regular manner can diffract the beam to form interference patterns. Thus diffraction takes place from the set of crystallographic planes hkl (Miller indices) and constructive interference can occur only for satisfying the condition given by Bragg’s law [30] (for first order n = 1).

\[ 2d_{hk} \sin \theta = \lambda \]  

(4.01)

Here \( \lambda \) is the x-ray wavelength, \( \theta \) is the glancing angle of incidence of X-ray, \( d_{hk} \) is the spacing between parallel atomic planes from which reflection occurs and \( n \) is any integer corresponding to spectral orders. The intensity of the diffracted X-ray is measured as a function of the diffraction angle (2\( \theta \)) and specimen orientation. This diffraction pattern is used to identify the specimen’s crystalline phases and to measure the structural properties.

II-VI compound semiconductors generally have propensity to exist in two crystalline modifications viz. cubic zinc blende and hexagonal Wurtzite [31]. In general, thin films of most materials assume similar crystal structure as the bulk material. However, the structural order, i.e. size and orientation of the crystallites departs considerably from that of the bulk [32]. Depending upon the growth
techniques and the deposition parameters, the sample changes from hexagonal to cubic phase. Earlier works by various workers [1, 33-35] on chemical bath deposited CdS thin films have shown the formation of both hexagonal and cubic phase. Again the diffraction peak positions shift due to homogeneous or uniform elastic strain present in nanostructured films [30]. From the shift of peak position it is possible to calculate the change in d-spacing.

**Lattice Parameters:**

The interplanner spacing, \( d_{hk\ell} \) for hexagonal and cubic crystal is given respectively by equations 2.5 and 2.6 [36].

\[
\frac{I}{d^2_{hk\ell}} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \left( \frac{\epsilon}{c} \right)^2 \quad (2.5)
\]

\[
\frac{I}{d^2_{hk\ell}} = \left( \frac{h^2 + k^2 + \epsilon^2}{a^2} \right) \quad (2.6)
\]

According to Vegard’s law, the lattice parameters for hexagonal unit cell are nearly exactly related to the cubic lattice parameter of the same compound by [37]

\[
a_{\text{hexa}} = \left( \frac{1}{2} \right)^{\frac{1}{6}} a_{\text{cubic}} \quad (2.7)
\]

\[
c_{\text{hexa}} = \left( \frac{4}{3} \right)^{\frac{1}{6}} a_{\text{cubic}} \quad (2.8)
\]

Therefore, for an ideal hexagonal Wurtzite lattice,

\[
c_{\text{hexa}} = (1.6333) a_{\text{hexa}} \quad (2.9)
\]

For cubic system, the lattice constant ‘a’ can also be determined by combining equation (2.4) and (2.6).
\[ a = \frac{\lambda}{2} \left( \frac{\sqrt{h^2 + k^2 + \ell^2}}{\sin \theta} \right) \]  

(2.10)

For hexagonal system, the lattice constant ‘a’ and ‘c’ can be determined by applying the precision technique of Straumani’s [38]. The lattice constant \( a_0 \) and \( c_0 \) can both be ascertained by solving one or more pairs of simultaneous equations. Combing equations (2.4) and (2.5) we get

\[
\left( \frac{2 \sin \theta}{\lambda} \right)^2 = \frac{4}{3} \left( \frac{h^2 + h k + k^2}{a_0^2} \right) + \left( \frac{\ell}{c_0} \right)^2 
\]

\[
\therefore \sin^2 \theta = \frac{\lambda^2}{4} \left[ \frac{4}{3} \left( \frac{h^2 + h k + k^2}{a_0^2} \right) + \left( \frac{\ell}{c_0} \right)^2 \right] 
\]

(2.11)

Now, applying the above quadratic formula for two Bragg angles \( \theta_1 \) and \( \theta_2 \) for indices \((h_1, k_1, \ell_1)\) and \((h_2, k_2, \ell_2)\) we get

\[
\sin^2 \theta_1 = \frac{\lambda^2}{4} \left[ \frac{4}{3} \left( \frac{h_1^2 + h_1 k_1 + k_1^2}{a_0^2} \right) + \left( \frac{\ell_1}{c_0} \right)^2 \right] 
\]

(2.12 a)

\[
\sin^2 \theta_2 = \frac{\lambda^2}{4} \left[ \frac{4}{3} \left( \frac{h_2^2 + h_2 k_2 + k_2^2}{a_0^2} \right) + \left( \frac{\ell_2}{c_0} \right)^2 \right] 
\]

(2.12 b)

The combination of these equations gives the following expressions for lattice constants ‘a’ and ‘c’ for hexagonal system.

\[
a_0 = \lambda \sqrt{\frac{\ell_1 (h_2^2 + h_2 k_2 + k_2^2) - \ell_2^2 (h_1^2 + h_1 k_1 + k_1^2)}{3 (\ell_1^2 \sin^2 \theta_2 - \ell_2^2 \sin^2 \theta_1)}} 
\]

(2.13)

\[
c_0 = \frac{\lambda a_0 \ell}{2} \sqrt{\frac{3}{3 a_0^2 \sin^2 \theta - \lambda^2 (h^2 + h k + k^2)}} 
\]

(2.14)

The values of lattice constants ‘a’ for cubic and \( a_0 \) and \( c_0 \) for non-cubic system calculated using the above equations are found to vary from one reflection
to another, the variation being of two kinds, random and systematic. Both random and systematic error decreases or tends to a minimum as \( \theta \) approaches 90°. The systematic errors in 2\( \theta \) can be eliminated by extrapolation technique given by Nelson and Riley [39]. The Nelson-Riley curve is plotted between calculated lattice parameter 'a_{cal}' for each line from the diffraction patterns and error function

\[
f(\theta) = \frac{1}{2} \left( \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)
\]

(2.15)

**Grain size**

(a) **For Thin Film**

The mean grain size \( D_{hkt} \) in the (hkt) direction is given by Scherrer formula [40]

\[
D_{hkt} = \frac{K\lambda}{\beta \cos \theta}
\]

(2.16)

Where \( \beta \) is the Full Width Half Maximum (FWHM) and \( \lambda \) is the X-ray wavelength and \( \theta \) is the diffraction angle. The value of the shape factor \( k \) in the Scherrer formula assumes various numerical value ranging from 0.70 to 1.70 depending upon a number of factors, including:

(1) The crystallite shape

(2) The indices, (hkt), of the reflecting planes.

When the shape of the crystallite becomes spherical the value of \( k \) is in the neighbourhood of 0.9, and hence the crystallite size given by equation (2.16) may be written as

\[
D_{hkt} = \frac{0.9\lambda}{\beta \cos \theta}
\]

(2.17)
Although equation (2.17) is generally applied for cubic crystal, it can be used to the peak breaths of non cubic materials also. However, correction for instrumental broadening arising due to slit widths, wavelength widths of $K\alpha_1$ and $K\alpha_2$ line etc. are to be made for acceptable value of $D_{hkt}$.

(b) **For nanocrystalline film**:

Inhomogeneous strains vary from crystallite to crystallite that cause a broadening of the diffraction peaks that increase with $\sin\theta$. Peak broadening is also caused by the small size of crystallite [41, 42]. But if there is no inhomogeneous strain, the crystallite size i.e. mean grain size $D_{hkt}$ is given by Scherrer formula [40].

$$D_{hkt} = \frac{k\lambda}{\beta \cos\theta} \quad (2.18)$$

However, Scherrer formula may produce result different from the true particle sizes because nanoparticles often form twinned structure [18].

2.5 (c) **Characterization by optical absorption spectroscopy**:

The highest energy band occupied by electrons is called valanced band (VB) and lowest unoccupied band is called conduction band (CB). The energy gap between the two level is called band gap energy ($E_g$). II-VI semiconductors have wide variation of band gap as low as $\sim 10^{-2}$ eV (HgTe) and as high as $E_g > 3$ eV (ZnS and ZnO) [43]. An electron hole pair (e⁻-h⁺) can be produced when a photon of energy comparable or more than the energy gap $E_g$ is absorbed in a semiconductor crystal i.e. absorption of light occurs when the energy of a quantum $h\nu > E_g$. 

45
\[ Eg = \frac{hc}{\lambda_g} = \left(\frac{1240}{\lambda_g} \text{ in nm}\right) \text{eV} \quad (2.19) \]

In the experimental observation by spectrophotometer, threshold wave length \( \lambda_g \) is determined at the point where there is an abrupt change in absorbance \( A \) versus wave length \( \lambda \) curve. Semiconductor absorbs light below threshold wave length and transmit light above \( \lambda_g \). For CdS, \( \lambda_g = 512 \) nm, which gives \( E_g = 2.42 \) eV at room temperature (300k) for pure bulk sample [43].

Within the semiconductor, the extinction of light follows the exponential law

\[ I = I_0 \exp(-\alpha t) \quad (2.20) \]

Where \( t \) is the penetration distance of light or thickness of the sample, \( \alpha \) is absorption coefficient, \( I_0 \) is the incident light intensity and \( I \) is the transmitted light intensity. Equation (2.20) is known as Bouger-Lambert law with the absorption coefficient related to concentration of absorption centre \( (N) \) and to the effective absorption crossection for one photon per unit time \( (\sigma) \).

\[ \alpha = \sigma N \quad (2.21) \]

The quantity \( (\sigma N)^{-1} \) or \( \alpha^{-1} \) may be termed as the mean free path \( t_{ph} \) of a photon in an absorbing medium.

\[ t_{ph} = (\alpha N)^{-1} = \alpha^{-1} \quad (2.22) \]
The quantity $\alpha$, is the probability of a photon absorption over a unit path. The absorption coefficient $\alpha$ can be calculated from the absorbance ($A$) or transmittance ($T$) and the sample thickness ($t$) using the relation

$$\alpha = 2.3026 \frac{A}{t} \quad (2.23)$$

The interband transitions are characterized by some variations of the non-linear absorption coefficient ($\alpha$) when plotted with photon energy ($h\nu$). The interband absorption theory shows that near optical absorption band edge the coefficient ($\alpha$) satisfies the relation

$$\alpha h\nu = C (h\nu - E_g)^n \quad (2.24)$$

where $E_g$ is the energy gap and $C$ is a constant. For direct transition $n=1/2$ and in this case $E_{gd}$ is the direct energy band gap. For indirect transition $n=2$ and $E_{gi}$ will be the energy of indirect band gap. The exponential curve linearity for direct transition is

$$(\alpha h\nu)^2 = C d^2 (h\nu - E_{gd}) \quad (2.25)$$

and for indirect transition

$$\alpha h\nu)^{1/2} = C i^{1/2} (h\nu - E_{gi}) \quad (2.26)$$

The absorption data obtained from the spectrometer can be fitted to equation 2.25 & 2.26. The best fit will give the nature of the band gap in the material. The
direct transition is conditional upon the probability of two particles meeting an electron and a photon. An indirect transition involves the meeting of three particles, an electron, a photon, and a phonon. This means that the indirect transition is a less probable process than the direct. Therefore the light absorption coefficient ($\alpha$) should be greater for the direct transitions than for indirect ones. The absorption coefficients for direct transition usually reach $10^4$ to $10^5$ cm$^{-1}$, whereas the absorption coefficient for indirect transition is usually $10^3$ to $10^4$ cm$^{-1}$ [44].

In case of nanomaterials, some unique optical properties arise from quantum size effect. When size of the nanocrystallite is smaller than the deBroglie wavelength, electrons and holes are spatially confined and electric dipoles are formed, and discrete electronic energy level would appear in all materials [45]. The transition between these levels can be generated by photons or phonons. Which means quantum confinement may have optical or vibrational effect. Again by changing the quantum well size (i.e. size of nanoparticle) one may calculate the energy at which the energy absorption or emission occurs.

2.5(d) Characterization by Optical emission spectroscopy (Photoluminescence)

Photoluminescence is a powerful tool that can be utilized for characterizing near band gap transitions in thin semi-conductor films. It is a simple non-destructive technique for the evaluation of semi-conductor optical quality through the analysis of the radiative transitions. The basic principle of photoluminescence involves the photoexcitation of electrons from their ground state in the valence band to the upper reaches of the conduction band. High energy incident photons ($hv \geq E_g$) create free carries with high kinetic energy within a short absorption
length at the surface of the semi-conductor which then diffuse into the sample. These carriers quickly (0.2 - 100 ps) lose energy by the emission of photons. The energy of the emitted photon from a band-to-band transition, an exciton recombination or any of a number of other possible transitions is the characteristic of the energy levels involved. The radiation transitions seen by PL are at or near the semi-conductor band-gap. The width and strength of these detected transitions are indicative of the material quality. But PL observation has also limitations as it is a surface technique, probing only the material within an absorption length of the surface, and that only relative measurements of the emitted intensity are possible. PL also will only reveal near band gap transition such as free bound excitons and those involving shallow impurity levels.

Photoluminescence data can be analysed in two formats. One is based on the real data from the spectrometer in units of wavelength, and the second where the x-axis is converted into energy. The full width-at-half-maximum (FWHM) at the peak of a pL signal in the units of energy can be obtained using the following equation

\[
\Delta E_{\text{FWHM}} = \frac{hc}{\lambda_{\text{peak}}} \Delta \lambda_{\text{FWHM}}
\]  \hspace{1cm} (2.27)

The width of a pL transition is a measure of the semi-conductor quality. For instance, alloy clustering, etc. can shift the discrete energy levels, and since the pL is integrated over a volume of the sample, the FWHM is effectively broadened.

Again an additional observation of interest which intrinsically couples the photoluminescence and absorption spectral profiles in a phenomenon termed as the Stokes Shift. If photons of visible light are scattered with the absorption or
emission of phonons, the frequency shifts are small but observable. An excitonic peak which is apparent in the spectral absorption data of a particular nanocrystal will have a peak absorption located at $\lambda_{\text{Abs}}$. In comparison, spectral photoluminescence content will also typically exhibit a predominant peak wavelength located at $\lambda_{\text{PL}}$. It will always be the case that $\lambda_{\text{Abs}} < \lambda_{\text{PL}}$ for the case of phonon emission. The energy associated with this shift in peak wavelength can be attributed to phonon emission when light is incident on the semi-conducting material. The magnitude of the Stokes shift may vary in magnitude as a function of the energy of the emitted phonon from a few meV.

2.5 (c) **Characterization by Fourier Transform Infrared Spectroscopy (FTIR):**

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular “fingerprint”. One of the unique characters of IR spectra is that no two different compounds will have identical curves. Hence spectrum of a pure compound represents a sure method of fingerprint identification provided the spectrum of known compound is available.

FTIR is most useful for identifying chemicals that are either organic or inorganic in any form of solid, liquid and gases. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. Today’s FTIR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments. FTIR can be used both for qualitative as well as quantitative analysis.
The physical principles involved in FTIR spectroscopy is like this.

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state ($E_0$) and the first excited state ($E_1$)].

The energy corresponding to these transitions between molecular vibrational states is generally 1-10 kilocalories/mole, which corresponds to the infrared portion of the electromagnetic spectrum [46]. The region includes radiation at wavelength between 0.7 and 500µm (or in wave numbers, between 14,000 and 20 cm⁻¹). The spectral range of greatest use is the mid-infrared region, which covers the frequency range from 200 to 4000 cm⁻¹ (50 to 2.5 μm) and provide many useful correlations. Mid-infrared regions is divided again into the “group frequency” region 4000-1300 cm⁻¹ (2.5-8 μm), and the fingerprint region 1300-650 cm⁻¹ (8-15.4 μm).

For a simple case of diatomic molecule, which has only one vibration: stretching of bond connecting two atoms, the energy (in cm⁻¹) associated with the stretching vibration of diatomic atoms which have masses $m_1$ & $m_2$ can be shown to be

$$\nu' = 1/2\pi c(R/\mu)^{1/2}$$

(2.28)
where \( \mu = \frac{m_1 m_2}{m_1 + m_2} \) = reduced mass, and \( R \) is the force constant of the bond.

2.5 (f) **Morphological characterization by SEM and AFM**

The morphological characterization of the deposited CdS thin films and nanocrystalline films were carried out using both scanning electron microscope (SEM) and atomic force microscope (AFM).

**SEM**

Scanning electron microscope is one kind of electron microscopes first developed in 1950. The other being transmission electron microscope developed in 1933 by Earnst Ruska. SEM is one of the most widely used characterization instrument for thin films, nanomaterials and in other branches of material science. The resolution of SEM approaches a few nanometer, and the instrument can operate magnifications that are easily adjusted between \( 10 - 3 \times 10^5 \). However the maximum resolution of 3nm can be achieved only at highest magnification. Again at very high magnification, the image quality deteriorates and the sample damage also occurs. SEM provide not only topographical information, but also provides the chemical composition of the sample near the surface. SEM is also used to extract information pertaining to agglomerate size/shape, particle morphology and surface appearance of nanoclusters. In a SEM, a source of electron is focused into a beam, with very fine spot size \( \sim 5 \) nm and have energy from 100 eV – 50 KeV. The beam is scanned over the surface of the specimen and the secondary electrons ejected from the specimen are used for Z- modulation. The main advantages of SEM are:
(a) A high resolution and high magnification.
(b) Depth of focus in SEM is 500 times greater than an optical microscope. SEM images impressed the observer with a seemingly three dimensional structure.

AFM:

The Atomic Force Microscope, which was invented in 1986, is used to solve processing and materials problems in a wide range of technologies affecting the electronics, telecommunications, biological, chemical, automotive, aerospace and energy industries. The materials being investigated include both conducting and insulating surfaces together with biological samples in real time. By using AFM one can not only image the surface in atomic resolution but also measure the force at nano-newton scale.

The working principle of the instrument involves the measurement of interaction forces between a probe (the AFM tip) fitted on a cantilever (acting as a spring), and the sample surface. In the simplest case, the variation of this interaction force at different points of the sample surface during a raster scan is converted into a topography contrast to obtain the morphology of the surface. A typical AFM system consists of a micro-machined cantilever probe and a sharp tip mounted to a Piezoelectric actuator and a position sensitive photo detector for receiving a laser beam reflected off the end-point of the beam to provide cantilever deflection feedback. Now-a-days, the tip-cantilever assembly typically is microfabricated from Si or Si₃N₄. The advantage of the AFM is that it is applicable to non-conducting samples also. Typical, an AFM can be operated in three modes; contact mode, tapping mode and non-contact mode. The contact
mode acquires sample attributes by monitoring interaction forces while the cantilever tip remains in contact with the target sample. This is the simplest mode capable of obtaining images with highest resolution at higher scanning speed and is ideally suited for hard samples. The tapping mode, on the other hand is widely used for soft samples like polymers, biological samples, self assembled structures like micelles etc., which tend to get damaged in the contact mode, as a cantilever tip oscillating near the natural resonance frequency of it (the cantilever) is used. The change in the amplitude of the oscillating cantilever due to the interaction with the sample surface is tracked to generate the sample topography. In the non contact mode the probe scans the sample from a close proximity, without actually touching it. This mode is rarely used in practice for imaging and is used for probing electric, magnetic, and/or thermal property contrast on a sample surface. Compared with SEM, AFM provides extraordinary topographic contrast direct height measurements and un-obscured views of surface features (no coating is necessary).

Another characterization technique is by Transmission Electron Microscopy (TEM) which is one of the most non destructive methods which can give the information about the particle of size < 1 nm. In addition to the capability of structural and chemical analysis, TEM has also been explored for other application in nanotechnology such as determination of melting point of nanocrystals. Similarly High Resolution Transmission Electron Microscopy (HRTEM) is an imaging mode of the TEM that allows the imaging of the crystallographic structure of a sample at an atomic scale. But as TEM facility was not available during our observation (available at RSIC, NEHU, Shillong was not in the working condition during that period and the one available at IIT, Guwahati was not installed at that time) we could not characterize our samples using TEM.
Reference


56
38. p. 478 in Ref. 1.