CHAPTER 1 : INTRODUCTION

1.1 Introduction

Thin film preparation and characterisation has gained a lot of attention in recent years due to the increase in the demand for such films in the production of thin film devices. Moreover, the advancement of the techniques employed in the preparation of thin films coupled with new, advanced and accurate characterising instruments has led to the intense research of this field among many researchers.

Semiconductor thin films is one of the major areas that has been studied as these materials currently have a high scientific and technological importance [1]. II-VI semiconductor compounds are gaining a lot of application in electronic industry. The transport properties of the II-VI compounds, particularly CdTe and CdS, is still attracting considerable interest, as a result of their good potential for producing low cost photovoltaic devices with large areas [2,3], infra-red detectors [4], p-n junctions and heterojunctions [5] and gamma-ray detectors [4].

The lack of compounds which exhibit both n-type and p-type conductivity is one of the shortcomings of the II-VI materials [6]. In this regard, it is appropriate to point out that CdTe is unique among the semiconducting II-VI compounds, in its ability to exhibit both n-type and p-type conductivity at relatively high levels [7,8]. CdTe possesses the largest atomic number in the II-VI compound series and gives good absorption characteristics, so that, in theoretical considerations, a nearly ideal solar cell [9] with the highest theoretical efficiency can be constructed. The performance of such devices depends on the physical as well as electronic properties of the material, particularly in thin film form, which depends markedly on the preparation techniques and conditions.

As such it is important here to review some of the thin film preparation techniques used before embarking on the properties of Cadmium Telluride.

1.2 Thin film preparation techniques : a review

There are over forty types of thin film deposition techniques used widely in the preparation of thin films as well as etching [10] depending on the requirements and affordability. These processes or techniques can be generally categorised as

(a) physical methods of film deposition

(b) chemical methods of film deposition

(c) hybrid (physical-chemical) methods of film deposition and

(d) patterning techniques.

1.2.1 Physical methods of film deposition

Vacuum evaporation, various types of sputtering and thermal evaporation are classified as physical methods of film deposition.

In sputtering, a target (a plate of the material to be deposited or the material from which a film is to be synthesised) is connected to a negative voltage supply. The substrate holder faces the target. The holder may be grounded, floating, biased, heated, cooled, or some combination of these.

In glow discharge, a gas is introduced to provide a medium in which glow discharge can be initiated and maintained. Gas pressures ranging from a few to about 100 mTorr are used. The most common sputtering gas is argon. When the glow discharge is started, positive ions strike the target plate and remove mainly neutral target atoms by momentum transfer, and these condense into thin films. There are in addition, other particles and radiation produced at the target (secondary electrons and ions, desorbed gases, X-rays and photons), all of which may effect this film properties.

In electron-beam evaporation, electrons are used as a source of sputtering. Figure 1.1 shows a setup for deposition by electron-beam evaporation [11]. Electron beams generated by a tungsten filament (e-beam source) are directed towards the target to sputter the material under a high vacuum condition (10^{-5} to 10^{-4} torr). These sputtering techniques allows the target to be evaporated without melting the material or in other words without reaching the melting point of the material, as the case in vacuum evaporation. In vacuum evaporation, the filament acting as the target heats the material until it melts and subsequent heating causes the evaporation of the material and condense into thin films at the substrate. This process like e-beam evaporation, requires high vacuum to achieve good quality films.

In general, sputtering processes are found to be most useful in applications requiring rather thin films (generally less than 1 μm because of relatively low deposition rates) and/or in cases where the desired material simply cannot be deposited stoichiometrically any other way [12].

Ion beams are used in physical thin film deposition in two basic configurations. In primary ion beam deposition the ion beam consist the desired material and is deposited at low energy (around 100 eV) directly onto a substrate. In secondary ion

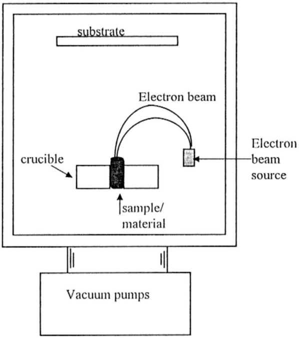


Figure 1.1 : Electron beam evaporation process [11]

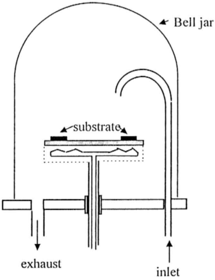


Figure 1.2 : Experimental CVD reactor [11]

beam deposition, or ion beam sputter deposition, the ion beam is usually an inert or reactive gas at higher energy (hundreds to thousands of electron volts). The beam is directed at a target of the desired material, which is sputtered and collected on a nearby substrate [13].

1.2.2 Chemical method of deposition

Films may be deposited on either metallic or non-metallic substrates by chemical or electrochemical mean from solutions or by chemical vapour deposition (CVD). Figure 1.2 shows an example of CVD reactors. Chemical deposition from solution can be divided into chemical and electrochemical reactions. Chemical reactions involved in the deposition are

(a) deposition by homogenous chemical reactions

(b) autocatalytic deposition, similar to (a) except that the reaction takes place only upon certain specific surfaces, called catalytic whereas in (a) reduction takes place throughout the solution [14].

(c) conversion coatings, in which a reagent in solution reacts with the substrate, a metal, to form a compound of the metal having certain favourable properties [15].

Deposition by electrochemical reactions involves electroplating, which is defined as the electrodeposition of an adherent metallic coating upon an electrode for the purpose of securing a surface with properties or dimensions different from those of the basis metal [16].

The growth of thin films by chemical vapour deposition has become one of the most important methods of film formation and now constitutes a corner stone for modern technologies such as solid-state electronics [17]. CVD can be defined as a material synthesis method in which the constituents of the vapour phase react to form a solid film at some surface. The occurrence of the chemical reaction is an essential characteristic of the CVD method. The type of chemical reactions and the extent of reactions to take place must be understood in a CVD process. Fundamental aspects of CVD being the [18]

(a) reaction chemistry; a material synthesis method in which the constituents of the vapour phase react to form a solid film at some surface.

(b) thermodynamics; this is to predict the feasibility of the process under some specified conditions and to provide quantitative calculation, such as give the theoretically obtainable amount of a specified experimental conditions.

(c) kinetics; kinetics play an important role in the determination of rate limiting step.

(d) transport phenomena; understanding of transport phenomena allows the achievement of required thickness and semiconductor doping uniformity by controlling the amounts of reactant gases and dopants delivered to all substrates in system and also to achieve satisfactory growth rates and utilisation of input chemicals.

1.2.3 Physical-chemical deposition of thin films

Plasma deposition and glow discharge polymerisation are two major physical-chemical hybrid deposition techniques in application now. Plasma deposition, depends on the generation of chemically reactive species at low temperature. The films deposited by plasma reactions are usually amorphous in nature, with very little short-range structural ordering . The stoichiometry of the films can be made to vary in a controlled fashion by variation of dominant plasma parameters, such as reactant gas flow ratios [19].

When an organic vapour is injected into a glow discharge of an inert gas such as argon, or when a glow discharge of a pure organic vapour is created, the deposition of polymeric films onto an exposed surface is often observed [10]. Polymer formation that occurs in such a process is generally referred to as plasma or glow discharge polymerisation.

1.3 Growth and structural properties of thin films

The mechanisms involved in the formation of crystalline or non-crystalline (amorphous) states by condensation from vapour and liquid phases primarily depend on the time that the atoms or clusters of atoms interact to form bonds in metastable and stable structures [20]. Crystallisation is the long-range ordering of atoms in a periodic solid-phase lattice near equilibrium conditions.

Amorphous polycrystalline or single crystal are the phases that can be obtained in the preparation of material. Amorphous, and in general, polycrystalline thin film possesses no unique directionality or axis on a macroscopic planes. Microscopically amorphous state is a state with only short-range ordered densely packed atoms or microcrystallites [21], while polycrystalline materials are crystalline but with random grain size, shape and orientation packing [20].

The grains or crystallites in a thin film are formed by independent nucleation and growth process randomly orientated and spaced with respect to one another. There is no epitaxial registration with the substrate lattice other than for nucleation occurring preferentially at defect sites and other surface irregularities. The grain size is controlled by rapid quenching, by seeding with additives or rounding the grains. Recrytallization may be induced by annealing which reduces the grain boundary surface area by diffusion [22].

The shape of the crystallite is determined by the surface orientation favourable for adatom attachment from the solid. This surface is determined by the orientation with the low interfacial energies [23] such as the $\{110\}$ or $\{111\}$ orientation for diamond cubic and zinc blendes and $\{100\}$ orientation for NaCl structures. Deposition of these materials will in general show a high degree of preferential orientation normal to the plane of the substrate.

Major conclusions that can be drawn based on the growth of amorphous and polycrystalline thin films are

(a) the growth of either state is independent of the substrate

(b) an amorphous material can be transferred to a polycrystalline state, but not the reverse.

This letter irreversibility indicates that the crystalline state has a lower lattice energy [23]. Indeed, the polycrystalline state, too, will transform to a single crystal state by the reduction of internal surface energy.

1.4 Optical properties of polycrystalline semiconductor thin films

1.4.1 Optical properties : Theory

Various experimental techniques are usually employed to determine the optical constants (n, k) [24] of thin films, where n is the index of refraction and k is the extinction coefficient of the material.

The complex refractive index, n* is defined as

$$n^* = n - ik \qquad \text{.........} (1.1)$$

and is related to the velocity of propagation by

$$v = c/n^* \qquad \text{.........} (1.2)$$

The absorption coefficient, α is related by

$$\alpha = (4\pi k)/\lambda \qquad \text{.........} (1.3)$$

where λ is the wavelength of the light in a vacuum.

The dielectric constant, ε can be introduced in two ways. One can define the dielectric constant to be real and describe any losses by a conductivity, σ. Then

$$n^2 - k^2 = \varepsilon \qquad \text{.........} (1.4)$$

$$nk = \sigma/\nu, \qquad \text{.........} (1.5)$$

where ν is the frequency. Alternatively one can define ε to be complex

$\varepsilon^* = \varepsilon_1 - i\varepsilon_2$, then

$$\varepsilon_1 = n^2 - k^2 \qquad \text{...........} (1.6)$$

$$\varepsilon_2 = 2nk \qquad \text{.......... (1.7)}$$

Clearly a knowledge of n and k determine ε_1 and ε_2 and vice versa. The quantitative ε_2 is often more convenient to use in theoretical calculation while experimental results often appear in terms of α [25]. A plot of α vs. Photon energies, has generally the same shape as a plot of ε_2, because n usually does not vary strongly with energy [23].

1.4.2 Experimental techniques

Method of calculation employed in the determination of optical properties depends upon the techniques used during the characterisation. Three famous experimental techniques are used in the determination of optical properties. They are

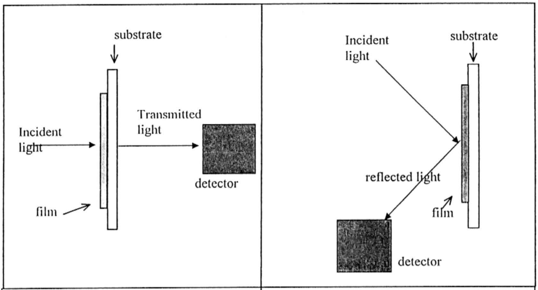
(a) transmission spectroscopy [26, 27]

(b) reflection spectroscopy, or (a) and (b) together [26]

(c) spectroscopic ellipsiometry [28, 29]

Transmittance and reflectance measurements are made using spectrophotometer with an available range of measurement, usually in the UV-VIS-NIR region. Transmittance basically measures the amount of light transmitted through the material while the reflectance measurement involves the measurement of the intensity of the reflected light from a sample as shown in figure 1.3.

In ellipsiometry, the behaviour of light radiated normal to the film is determined using spectrophotometer. When the angle of incidence of the incoming light is not zero (in practice, when it is greater than about 10°), the reflected intensity is polarisation dependent as shown in figure 1.4. The reflectance , R_p of light with the electric field parallel to the plane of incidence is different from the reflectance, R_s with



Transmittance measurement

Reflectance measurement

Figure 1.3 : Transmittance and reflectance measurement

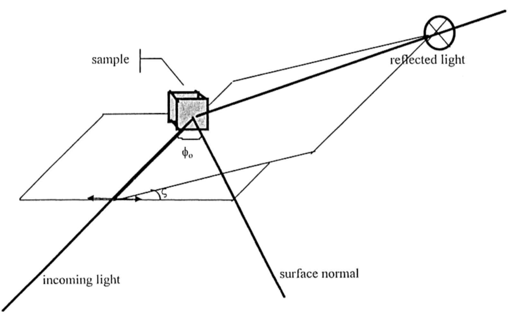


Figure 1.4 : Measurement geometry for ellipsiometry
(ϕ_o = angle of incidence ; ς = the angle between the plane of incidence and plane of polarisation)

the electric field perpendicular to the plane of incidence. In addition there is generally a phase shift, Δ between the two components. In practice R_p and R_s or R_p/ R_s may be measured at various angles or the reflection of the unpolarized light may be measured at various angles.

Ellipsiometry consists of a measurement of the ratio of the reflected amplitude

$$\tan \psi = r_p/r_s \qquad \text{...........} (1.8)$$

together with phase shift, Δ, (the phase difference between r_p and r_s).

Ellipsiometry is generally capable of considerably higher sensitivity and precision then intensity measurements for the determination of optical constants. For example, one can detect the presence of a fraction of a monolayer of an absorbed substance on a substrate [30]. Alternatively one can achieve high precision in the determination of optical properties of bulk material [31].

1.5 Quantum Semiconductor Nanoclusters

Recent developments in the understanding of the size dependency of bulk structural and electronic properties in metals semiconductors have attracted the physical chemistry as well as solid state physics communities [32]. In these materials there is a strong spatial delocalization of valence electrons, and therefore a small crystallite must grow fairly large to achieve the limiting bulk electronic structure [33]. Research has shown that the intermediate-sized clusters can have unique properties, as in the case of semiconductor crystallites exhibiting the bulk unit cell but have only partial band structure development [34]. These crystallites are sometimes called quantum dots or nanoclusters.

Nanoclusters have optical spectra that can be tuned in wavelength simply by varying the crystallite size [32]. They represent, in three-dimensions, an analogy to the quantum well semiconductor heterostructures that show one-dimensional quantum size effect [35]. It is experimentally known that [32] II-VI semiconductor crystallites with approximately 200 or more atoms do exhibit bulk unit cell, with bulk-like lattice and phonon properties. This is the regime of hybrid molecular state (or quantum dot) behaviour where a large, three dimensional quantum size effect occurs in the excited electronic states.

Colloidal synthesis methods [36] and semiconductor doping of glasses and gels [37] are being used widely in the synthesis of nanoclusters which allows the engineering of the size to a great extent.

1.5.1 Electronic properties of quantum semiconductor nanoclusters

The band gap of a semiconductor is by definition, the energy necessary to create an electron (e^-) and hole (h^+), at rest with respect to the lattice and far enough apart so that their Coulomb attraction is negligible [38]. If one carrier approaches the other, they may form a bond state (Wannier exciton) appropriately described by hydrogenic Hamiltonian [39] at an energy slightly below the band gap.

$$\hat{H} = \frac{-\hbar^2}{2m_h}\nabla_h^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{\in |r_e - r_h|} \qquad \text{.......... (1.9)}$$

Here m_h, m_e are the effective mass of hole and electron respectively and ε is the dielectric constant of the semiconductor. This bulk energy level scheme is not valid for sufficiently small crystallites. As the crystallite size approach the size of 1S exciton, electron-hole interaction with the crystallite surfaces will dominate the dynamics.

When the radius of the nanoclusters is much less than the Bohr exciton radius, $R << a_o$ both type of charge carriers are individually confined and with no exciton formation. But when the crystallite size is 2-4 times the Bohr exciton radius a_o, the electrons and holes are weakly confined. Coulombic interaction between electrons and holes are present, hence formation of exciton is possible. Under these conditions the optical transitions of an exciton is quantized and the energy shift of the first optical transition assuming parabolic energy bands is given by [38]

$$\Delta E_{shift} = \frac{\hbar^2 \pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.786e^2}{\in R} - 0.248E_{RY} \qquad \text{..........} \; (1.10)$$

where the first term in the above equation represents quantum energy of localisation of the charge carriers, the second, Coulomb interaction between the charge carriers while the last term represents spatial correlation effects. The presence of exciton in the sample is clearly exhibited in the absorption spectrum as shown in the figure 1.5 for CdS crystallites [34] and had been calculated theoretically [38] A blue shift is observed in absorption edge as the crystallite size reduces.

1.6. Cadmium Telluride

1.6.1 Structural properties

Cadmium Telluride, CdTe, is a II-VI semiconductor compound which has a molecular weight of 240.2. It is usually synthesised as brownish black, cubic crystal

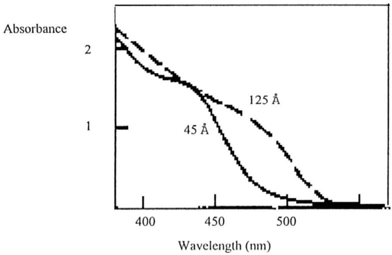


Figure 1.5 : Absorption spectra of CdS quantum dots [33]

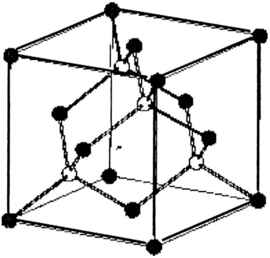


Figure 1.6 : The two equivalent interpenetrating face center cubic lattices of the zinc blende structure.
[● - Tellurium, Te, atom ; ○ - Cadmium, Cd, atom]

[40] with a melting point temperature of 1041°C. CdTe can be oxidised upon prolonged exposure to moist air .

CdTe single crystals are formed by [4] congruent and near congruent melt growth, growth from Te-rich solutions, sublimation, vapour growth and many more. These crystals show a stable form of zinc blende structure. This structure belongs to the cubic space group $F\bar{4}3m(T_d^2)$ and consists of two interpenetrating face centre cubic lattices offset from on another by one-fourth of a body diagonal as shown in figure 1.6.

There are four molecules per unit cell, the co-ordinates of Te atom being 000, 0½½, ½0½ and ½½0 and those of the cadmium atoms being ${}^{1}/_{4}{}^{1}/_{4}{}^{1}/_{4}$, ${}^{1}/_{4}{}^{3}/_{4}{}^{3}/_{4}$, ${}^{3}/_{4}{}^{1}/_{4}{}^{3}/_{4}$ and ${}^{3}/_{4}{}^{3}/_{4}{}^{1}/_{4}$. As a result every atom is surrounded tetrahedrally by four atoms of the other by $\frac{\sqrt{3}a}{4}$, where a is lattice spacing or constant. The best value of the lattice constant is 6.481 Å [4]. This value is subject to change due to deviation from stoichiometry.

Due to greater bond density within the double layers and the lack of symmetry, the crystal exhibits crystallographic polarity and the chemical and physical properties on the {111} Cadmium or Tellurium faces. Although the zinc blende structure is the stable form for bulk CdTe at atmospheric pressure, thin films in both sphalerite and wurzite forms are common. CdTe thin films are obtained either in polycrystalline or amorphous phases from various preparation techniques such as sputtering [41], hot-wall flash evaporation [42] and vacuum evaporation [43]. These phases and orientation can be recognised from the ASTM index which is presented as a plot in figure 1.7.

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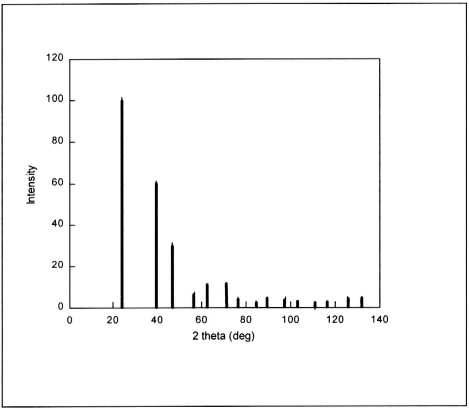
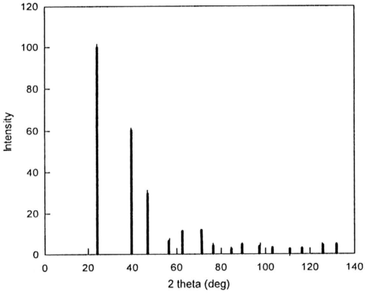


$2\theta^0$	27.4	39.3	46.4	56.8	62.3	71.2	76.3	84.5
hkl	111	220	311	400	331	422	511	440
$2\theta^0$	89.4	97.4	102.4	110.8	116.1	125.6	131.8	
hkl	531	620	533	444	711	642	731	

Figure 1.7: XRD peaks of cubic crystal CdTe at $\lambda = 2\theta^0$ (generated from ASTM index card 15-770 [43])



$2\theta^0$	2.74	39.3	46.4	56.8	62.3	71.2	76.3	84.5
hkl	111	220	311	400	331	422	511	440
$2\theta^0$	89.4	97.4	102.4	110.8	116.1	125.6	131.8	
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1.6.2 Optical and electronic properties

Researchers [44] have investigated the behaviour of optical constants, n and k (refractive index and extinction coefficient) of CdTe thin films prepared via vacuum evaporation. It has been reported that at low absorbing region the refractive index becomes constant, taking a value in the range of 2.6 to 2.9. A rather low value was also observed [46] where for electrochemically deposited thin film of CdTe, n takes a value of 2.0 in low absorbing region. The refractive index were seen to increase near the band edge following the dispersion proposed by Cauchy relationship. The effects of preparation conditions on the behaviour of n were also investigated [6,42, 45, 46]. The refractive index is seen to increase with film thickness [6], which was attributed to the increase in the crystallinity of thin films. Substrate temperature is also known to increase the refractive index [45] for similar reason given above.

Very few researchers have discussed the behaviour of k, as it is quite difficult to compute k since most of the calculation methods involve the low absorbing region (where k = 0). However it has been shown [6]that the variation of k near the band gap, can be obtained by using the Murmann's exact equation. He reported that k varies in the range 10^{-3} to 10^{-2} in the low absorbing region and reduces to zero near absorption edge. Film with different thickness had varying k values but displayed same absorption edge indicating no crystallite size effect.

Several methods of calculation were adopted in the evaluation of band gap of CdTe. One being the theoretical fitting of direct or indirect transitions [47] as used by Thutupalli et.al.,[48] and Ehsan Khawaja et.al., [49] and the other evaluation from the maxima of the first derivative of optical density [50]. A direct band gap was reported by many researches which occur around 1.5 eV [4,42,45,50,51]. But this value is still subject to much debate as Aranda et.al., [52] have reported the presence of both direct and indirect band gap. Moreover Saha et.al., [53] and Chaudhuri et.al., [42] observed an indirect transition at lower energies, 1.3 eV and (0.6-0.7) eV respectively, besides the direct band gap of 1.5 eV. This low energy indirect transition was attributed to the presence of defects and impurities at the grain boundaries giving rise to an electron field at the grain boundaries. This causes an additional absorption through the Franz-Kelydish effect.

Quantum size effects in CdTe thin films have attracted very few researches as we find very few published papers on this subject. This could be due to the difficulties in the preparation techniques of quantum nanoclusters. However CdTe doped glass matrix were characterised by Liu et.al., [54] and it was confirmed that they obey the Brus model discussed in the previous section where the band gap was found to be blue shifted with decrease in the crystallite size.

1.7. Objective of this study

As can be seen from the previous discussion, CdTe is still a centre of attraction to researches as the behaviour of the material varies with the deposition techniques and conditions. Optimising these conditions will allow the mass production of these thin films for use as photovoltaic cells and IR-detectors at very low cost.

With this in mind, in the present study the material was proposed to be prepared by electron-beam evaporation technique as this method requires simple vacuum system and can yield good quality thin films. Moreover this method also allows the evaporation of the material without approaching the melting point of CdTe which is 1041 ^{0}C, thus minimising the power consumption. The e-beam evaporated CdTe will be later characterised in terms of physical and electronic properties.

In the present study, it is also aimed at looking at the quantum size-effect of nanoclusters present in the thin films. Researches have used the colloidal synthesis and chemical precipitation for the preparation of nanoclusters but the effect was not seen in physically evaporated thin films as it requires a coherent, small crystallite sized thin film to exhibit three-dimensional quantum size effect. The Al/CdTe junctions will be studied to see the feasibility of these thin films to be used as photovoltaic cell in the future.