CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION TO THIN FILMS

Smaller and faster is the technological imperative of our times and so there is a need for suitable materials and processing techniques. Thin films play an important role in fulfilling this need. Besides, they have been used for device purposes over the past 50 years. Thin film is a two dimensional structure, i.e. it has a very large ratio of surface to volume, and created by the process of condensation of atoms, molecules or ions (Halstead and Aven 1965). They do the same function with the corresponding bulk material and their material costs are smaller. Most of the electronic devices require reliable ohmic contacts for electrical signals to flow into and out of the device and highly stable metal-semiconductor rectifying contacts as the active region (Nair et al 1994). In both cases, one must know how to fabricate reliable and efficient metal contacts which have high yield and stability. Thus, it is clear that knowledge of these devices can be used for the development of future technology.

1.2 PROPERTIES OF CDS THIN FILM

Cadmium Sulphide is a II-VI compound semiconductor. Bonding in these compounds is a mixture of covalent and ionic types. Group VI atoms are considerably more electronegative than group II atoms and it introduces iconicity (Noblanc et al 1970). This character has the effect of binding the
valence electrons rather tightly to the lattice atoms. Thus, each of these compounds has a higher melting point and larger band gaps than those of the covalent semiconductors of comparable atomic weights. Structure type of the deposited thin film depends on the substrate thickness, polycrystalline in nature and shows the hexagonal structure (Doty et al 1992). CdS has 2.42 eV direct band gap at room temperature. CdS has numerous applications in photoconductive cells, because of its wide band gap (an n-type window layer within the heterojunction photovoltaic cells), which converts the optical radiation into electrical energy, thin film FET transistors, X-ray detectors, photodiodes for solar-meters and recently photoelectrolytical and photocatalytical solar energy stocking (Lozada Morales et al 1998). CdS thin films can be prepared by several different deposition techniques such as, spray pyrolysis, thermal evaporation, close space sublimation (CSS), sputtering, electrolysis, molecular beam epitaxy (MBE), screen printing, chemical deposition, etc. The vacuum evaporation and chemical bath deposition is among the least expensive methods in terms of energy (Norris and Zanio 1982). Deposition techniques and substrate temperature has a strong effect on the electrical and structural properties of CdS thin films (Gracia Jimenez et al 1992). The current transport behavior of metal CdS is explained with existence of interface states.

Pure CdS crystals have a high resistivity about $10^{12} \ \Omega\text{-cm}$. Polycrystalline CdS thin films resistivity can be reduced by In, Sn, Al, Cr or Br doping or by some growth techniques (Johnson et al 1991). For example, $10^{-3} \ \Omega\text{-cm}$ resistivity was reported for the films grown by close-space vapor transport. The grain sizes of CdS films are usually around 0.3-0.5 μm. As the film thickness is increased, larger crystallites are formed in the films.

Studies on the transport properties of Schottky barrier diodes with CdS show that there is no linear correlation between barrier height and metal
work function. In general, it is believed that differences are caused by interface defect formation. Earlier studies showed that there are significant changes in the degree of reactivity between CdS and different metals (Chopra et al 1983b). To investigate chemical composition and bonding at the metal CdS interfaces, X-ray photoelectron spectroscopy (XPS) analysis is performed on clean and oxidized CdS.

1.3 CRYSTAL STRUCTURE

Generally, solids can be classified into two types, crystalline solids which include single and polycrystalline solids (where the atoms are arranged in such a way that the positions are exactly periodic) and non-crystalline solids which also called amorphous solids (where the atoms appear to be randomly arranged). Knowledge of the crystal structure is important in solid state physics because these structures usually influence the physical properties of solids.

Most of the III-V compounds are crystalline in the zincblende structure and many semiconductors including some of the III-V compounds are crystallize in the wurtzite or rock-salt structures as shown in Figure 1.1. The wurtzite structure has a tetrahedral arrangement of four equidistant nearest neighbors, similar to a zincblende structure (Reno and Jones 1992). The figure shows the rock-salt lattice, which can be considered as two interpenetrating face-centered cubic lattices. In the rock-salt structure each atom has six nearest neighbors. Some compounds, such as zinc Sulphide and cadmium Sulphide, can crystallize in both zincblende and wurtzite structures (Boudreau and Rauh 1983, Oliva et al 2001, Espinosa et al 1983 and Kaur et al 1977).
1.4 VACUUM EVAPORATION DEPOSITION

Vacuum evaporation is a simple method in which the material is created in vapour form by means of resistive heating. On heating a material in vacuum, sublimation takes place and the atoms are transported and get deposited onto cleaned substrates held at suitable distances at desired temperatures. The material for deposition is supported on a source, which is heated, to produce desired vapour pressure (Matsukawa et al 1999). The requirements for the source are that it should have a low vapour pressure at the deposition temperature and should not react with the evaporant. The shape of the source is designed and fabricated in such a way to hold the evaporant material. Tungsten baskets and tungsten helix are used as the sources of heating electrodes (Bramley 1955). The evaporant material in the powder form is deposited using a molybdenum boat. The low tension (LT) supply for evaporation source is obtained from a 230 V input transformer by means of parallel or series connections in the secondary side of the transformer.
1.5 CHEMICAL BATH DEPOSITION

Methods of preparing thin films may be divided into two main groups, namely chemical methods and physical methods. Among chemical and electrochemical methods the most important are electrolytic deposition, anodic oxidation, chemical vapour deposition and chemical bath deposition (Perna et al 2004a). A thin film may be prepared by a process as simple as hammering or rolling down a piece of bulk material. For practical use, however, thin films are prepared by depositing the film material, atom by atom, onto a substrate.

Chemical bath deposition is a widely used method in semiconductor technology for the preparation of thin monocristalline films of high purity. Chemical bath deposition technique is the most efficient polycristalline thin film deposition technique (Rablau et al 1998). However, it appears to be relatively simple, inexpensive and convenient for large area deposition of polycristalline thin films (Franc et al 2000). CBD technique has been intentionally employed in this work, so as to see if our modification techniques are competent or not.

1.6 SEMICONDUCTOR

Every atom has a set of discrete electron energy levels. As several atoms are brought closer to one another, the original energy levels spread into energy bands. The highest energy band containing electrons is defined as the valence band, and the conduction band is defined as the energy band where electrons can conduct net current by moving through the unoccupied energy states (Bruder et al 1993). The gap in energy between the lowest energy of the conduction band $E_C$ and the highest energy of the valence band $E_V$ is the forbidden band, where in the ideal case, no energy states are allowed. Doping impurities and unintentional defects, however, exist in the forbidden band and
are responsible for most semiconductor applications. The energy defining the forbidden band is the band gap, $E_g = E_C - E_V$. The Pauli Exclusion Principle says that each quantum state can only be occupied by two electrons with one spin up and one down (Savadogo and Mandal 1993). Therefore, in the ground state, electrons start filling the energy levels from the lowest energy. The energy of the top most filled level from the ground state is defined as the Fermi energy $E_F$. At finite temperature, however, the system is no longer in the ground state, and some electrons will fill higher energy states (Francombe and Vossen 1982). The probability of the occupation of an allowed energy state at a given energy $E$ is given by the Fermi-Dirac distribution function:

$$F(E) = \frac{1}{1 + \exp \left[ \frac{(E - E_F)}{kT} \right]}$$ \hspace{1cm} (1.1)

Where $k = \text{Boltzmann constant} = 1.38 \times 10^{-23} \text{ J/K}$ and $T = \text{absolute temperature}$.

The band structure governs the characteristics of solids. Figure 1.2. shows the band diagrams of different solids. A solid with either a partially filled conduction band or overlapping conduction and valence bands has a zero band gap. In this solid, electrons subject to a small applied field are free to move. Therefore, this solid is a conductor shown in Figure 1.2 (a). In an insulator from Figure 1.2 (b), the band gap is so large that essentially no electrons can be excited to conduction band to contribute to the current flow. In a semiconductor, the band gap is relatively narrow shown in Figure 1.2 (c). At low temperatures, a semiconductor material behaves like an insulator. At higher temperatures, however, there is a reasonable probability of electron excitation from the valence band to the conduction band, so electrons can contribute to the current in the conduction band. In the valence band, electrons also conduct net current through the unoccupied energy states, which are referred to as holes. Instead of considering the motion of electrons
in the valence band, it can be more simply described as the motion of a hole in the opposite direction.

![Diagram of energy bands]

**Figure 1.2** Schematic energy bands of (a) a conductor, (b) an insulator and (c) a semiconductor

### 1.7 POLYCRYSTALLINE THIN FILMS

The current high production cost of conventional solar cells is a major barrier to large-scale deployment of solar energy. The price of the active material and the manufacturing methods are the main elements determining the total price of solar energy conversion technologies. Researchers are required to explore new processes for producing low-cost methods and material suitable for solar energy conversion. In recent years, there has been considerable interest in the application of semiconductor (SC) electrodes to photoelectrochemical (PEC) solar cells for solar energy
conversion. Single crystal SC electrodes are known to give the highest efficiency for such purposes. But due to the prohibitive cost of single crystal SC materials, a necessity to develop less expensive, but stable PEC cells based on thin film materials has emerged. Thin film SC materials have a major advantage over single crystalline, since most of them have direct band-gap, resulting in higher optical absorption. This allows typical thin film solar cells to use very thin layers of active materials (~1 m) that can thus be of lower quality.

1.8 TRANSPORT MECHANISM OF POLYCRYSTALLINE SEMICONDUCTORS

The polycrystalline material is composed of random sized, shaped and oriented crystallites or grains separated by grain boundaries. Inside each crystallite the atoms have nearly perfect periodicity and so it is considered as if a single crystal (Cody et al 1984). The grain boundary consists of a few atomic layers of disordered atoms which cause the large number of defects. This results in formation of trapping states.

Several models have been proposed to explain the polycrystalline semiconductor transport properties and the grain boundaries between grains play an important role in determining these properties. In general, there are three types of conduction mechanisms depending on temperature region in polycrystalline thin films. They are thermionic emission, tunneling and hopping and are explained in the following sections.

1.9 GENERATION AND RECOMBINATION PROCESS IN SEMICONDUCTOR THIN FILMS

Generation is the process of elevating an electron from a state in the valence band to one in the conduction band producing electron-hole pairs.
Recombination is the reverse of this process and it annihilates these pairs. In thermal equilibrium these two processes must balance (i.e. their rates must be equal). The released energy that results from the recombination process can be emitted as a photon (radiative recombination) or dissipated as a heat to the lattice (auger or nonradiative recombination). When a bond between two neighboring atoms is broken due to the thermal vibration of lattice atoms, an electron-hole pair is generated (Ashour El-Kadry and Mahmoud 1999). If electron in the conduction band makes a transition downward to the valence band, an electron hole pair is annihilated (recombination).

Different recombination process can occur in semiconductor materials depending on the band structure. Direct recombination is occurring in the direct-bandgap semiconductor. The probability of that the electrons and holes will recombine directly is high (Francou et al 1990). That is because the bottom of the conduction band and the top of the valence band are lined up and no additional crystal momentum is required for the transition across the bandgap.

Indirect recombination is occurring in the indirect - bandgap semiconductor. Because the electrons at the bottom of the conduction band have nonzero crystal momentum with respect to the holes at the top of the valence band, the dominant recombination process is indirect transition via localized energy state at the forbidden energy gap. These states act as stepping stones between the conduction band and the valence band. These states, also called as recombination centers and they can substantially enhance the recombination process. The indirect recombination can be due to single or multiple levels (states) in and across the bandgap. Impurities are also efficient recombination centers.
1.10 APPLICATIONS OF SEMICONDUCTOR THIN FILMS

Semiconductor thin films are widely used in a large number of solid state device applications such as photoconduction, Xerography, electroluminescent devices, piezoelectric transducers, communication, laser material, optical detectors, light-emitting diodes, ultrasonic transducers, photovoltaic solar energy conversion, thin film transistor electronics and other optoelectronic devices (Stadler et al 1994). One of the most important applications is the conversion of solar energy into electrical energy by the meaning of the photovoltaic effect. Photovoltaic effect is the production, as a result of the absorption of photons, of a voltage difference across a p-n junction which is caused by the internal drift of holes and electrons. The photovoltaic effect is the basic physical process through which a solar cell converts sunlight into electricity. In 1839, Edmund Becquerel, a French experimental physicist, discovered the photovoltaic effect while experimenting with an electrolytic cell made up of two metal electrodes. Becquerel found that certain materials would produce small amounts of electric current when exposed to light.

1.11 PHOTOELECTROCHEMICAL CELLS VS. PHOTOVOLTAIC CELLS

Both photovoltaic and photoelectrochemical cells are based on using semiconductor materials in solar energy conversion. These semiconductor materials need to be photosensitive in a certain part of the solar spectrum to absorb photons with wavelengths that are equal or shorter than their threshold wavelengths and this will lead to excitation of an electron from the upper valence band to the lowest conduction band and creates excess electrons in the conduction band and excess holes in the valence band.
If this semiconductor contains a p-n junction shown in Figure 1.3, as in photovoltaic cell, electrons will move downhill to n-type through the solid junction and holes move upward towards p-type side (Chen et al 1991). These photogenerated electron-hole (-h^+) pairs are separated with some built-in electric field within the cell resulting in photovoltage / photocurrent.

![Diagram of p-n junction](image)

**Figure 1.3 Energy level diagram for a p-n junction**

The only difference between photoelectrochemical and photovoltaic (PV) devices is that in photo electro chemistry, a semiconductor electrolyte junction is used as the active layer instead of the solid-state junctions in photovoltaic. In both cases, a space charge region is formed where contact formation compensates for the electrochemical potential differences of electrons on both sides of the contact.

Potentially, there are several advantages for the use of PEC cells for solar energy conversion over conventional PV devices:

(a) PEC devices can store energy in the form of conventional fuel and can convert light to electrical energy as well;
(b) PEC devices can be fabricated and modified with considerable ease. Contrary to PV devices, no solid-solid junctions are demanded in PEC. The band bending characteristics of the SC can be conveniently varied by suitable choice of electrolyte and cell variables;

(c) PEC cells do not have problems associated with different thermal expansions of solid-solid junction; and

(d) Unlike PV devices, no antireflection coatings are required in PEC cells.

However, absorption of light by the electrolyte solutions, reflection losses from the cell and the stability of the electrode limit the energy conversion efficiencies in PEC devices in many cases and are shortcomings of PEC systems.

1.12 DARK CURRENT OCCURS IN PEC CELLS

The dark current results from electrons transfer from the Conduction Band to the electrolyte redox couple in n-type semiconductor (cathodic current flow). At equilibrium, the band bending creates an energy barrier for the electrons to overcome before they transfer. For any given SC and electrolyte, there exists a unique potential for which the potential drop between the surface and the bulk of the electrode is zero (Sushilkumar et al 2001). This potential is called the flat band potential ($V_{fb}$), since the band edges do not bend. Thus, for dark current to occur, the n-type semiconductor must be negatively biased to provide the electrons with enough energy to overcome the barrier, equals $E_1$, Figure 1.4.
1.13 PHOTOCURRENT OCCURS IN PEC CELLS

When light absorption generates a population of excited holes and electrons, the majority carrier concentration changes relatively little and the minority carrier concentration is greatly enhanced. Hence, photo-effects are greatest when minority carriers dominate the electrode response. This occurs when the electrode is biased to form a depletion layer and the photo-generated minority carriers migrate towards the electrode/electrolyte interface.

The dependence of the photocurrent or photopotential on excitation wavelength provides information about the band gap energy $E_g$ and nature of optical transition (direct or indirect). Recombination is another important phenomenon of photo-effects in the PEC. Recombination can occur directly with the electron descending from the conduction band edge to the hole at the valence band edge, or indirectly via intermediate energy levels (bulk or surface states). Recombination reduces the magnitude of photoeffect, and consequently lowers the power and the efficiency of PEC cell (Ueno et al.
1987). When n-type SC electrode is biased sufficiently positive of $V_n$, the dark currents are very low, due to the blocking effect of the depletion layer. Upon irradiation of SC through the electrolyte with light ($\lambda$ shorter than $\lambda_g$), large anodic photocurrents appear, Figure 1.5.

![Figure 1.5 Dark and photo current voltammogram for n-type semiconductor](image)

These photocurrents arise from the flux holes (minority carrier) arriving at the surface. The generated electron-hole pairs in the depletion layer are separated by the electric field in the depletion layer, with the electron moving towards the bulk of the crystal and the hole migrating towards the surface (Varshni 1967). Electron-hole pairs generated beyond the depletion layer also diffuse into the electric field and become separated. The shape of the photocurrent voltammogram depends on the energy distribution of the incident photons, the absorption coefficient of the SC, the diffusion distance of the excited holes and electrons, and the recombination rates.
Figure 1.6 Photocurrent generation at n-type semiconductor

As the applied potential approaches $V_{fb}$ the space charge layer thickness decreases. Recombination rate increases because the holes and electrons are no longer being separated by the electric field as shown in Figure 1.6. The photocurrents drop sharply and merge with the dark current near $V_{fb}$, the electrode is no longer blocking, and the dark current increases dramatically, with small cathodic photocurrent sometimes observed.

In the usual model of charge transfer across SC/electrolyte interface, it is assumed that the occurrence of this process is isoenergetic. That is, as shown in Figure 1.7, electrons can be exchanged between the SC and electrolyte due to either of two reasons. The first is when the energy levels of the valence band overlap with the occupied energy levels of the electrolyte redox couple (anodic current flow by hole injection). The other reason is when the conduction band overlaps with the empty energy levels of the electrolyte redox couple (cathodic current flow by electron injection). However, experimental results show that the inverse is generally true. These results are generally explained by involving the existence of surface states (Yoshikawa et al 1973 and Giles et al 1988).
Figure 1.7 Isoenergetic charge transfer of hole from \( n \)-type semiconductor

The surface state, or intermediate trapped charges, exists within the forbidden \( E_g \) of the SC. These states result from different sources, including structural defects, metallic impurities, or bond breaking processing. Surface states are most effective when they are located energetically between the band edges, at the surface. They mediate charge transfer of majority and minority carriers, control surface charge and band bending and catalyze recombination of photo-generated carriers (Lincot and Ortega Borges 1992a). The existence of surface states lowers the resulting photocurrent density. Researchers always try to eliminate or minimize surface state formation.

Surface state may be classified as intrinsic or extrinsic. Intrinsic states arise from the abrupt termination of the crystal lattice at the electrode surface. The dangling bonds in the crystal will dangle long in an electrolyte. The new chemical entity formed by reaction with a solution species may then behave as a surface state.
1.14 OBJECTIVE

The present work is to study and to investigate CdS (SC) thin films grown using Vacuum evaporation technique and Chemical bath deposition technique on to glass substrates. In this work, we expect to enhance the characteristics of CdS (SC) thin films by varying thickness, structural, electrical and optical properties of CdS thin films. All the above studies are reported in detail by means of the following seven chapters:

Chapter 1 of the thesis contains a general introduction to CdS thin films their structural, electrical, optical properties and the related theoretical background in addition to the important applications.

Chapter 2 of the thesis contains a brief literature review on CdS thin films and their properties. The various preparative methods and the experimental results reported in literature on CdS thin films are summarized.

Chapter 3 explains the experimental details of preparation and characterization methods which have been used in the present investigations.

Chapters 4 discusses the structural, Surface morphology and Elemental composition analysis on CdS thin films.

Chapter 5 presents the Optical and photoluminescence properties of CdS thin film prepared by Vacuum evaporation and Chemical bath technique.

Chapter 6 explains the Electrical properties such as resistivity, I-V, C-V and Hall Effect characteristics of CdS thin films.

Finally, chapter 7 deals with the important results arrived from the above studies and scope for further research.