CHAPTER 1

INTRODUCTION

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1.1 INTRODUCTION

Electrodeposition is a technique that has developed from the fundamental concepts of electrochemistry. Electrodeposition of metals in the past was limited primarily in fulfilling decorative needs and remained a largely empirical technique. Today, it has developed into a highly sophisticated and systematic process and has attained tremendous importance in production of distinct functional properties such as corrosion resistance, heat resistance, electrical conductivity, salvage of worn out components, purification of metals, electrofabrication and electroforming.[1]

Electrodeposition of semiconducting materials has attained remarkable recognition as it is technically simple, economically inexpensive and requires very little sophistication. It also finds several applications in the preparation of materials for semiconductor devices. One such application is the preparation of semiconductor thin films. Such materials have received considerable importance as they form potential solar cell materials. [2]

Of the several established methods of preparation of semiconducting thin films the electrodeposition process is picking up importance as the other methods are often found to be expensive in terms of time and energy. Further the process of electrodeposition is easily reproducible and materials with properties different from that of the substrate and electrolyte material can be obtained. [3]

The preparations of semiconducting materials involve the use of II-VI binary compounds such as ZnS, ZnSe, CdS, CdSe and CdTe [4]. Ternary compounds of III-V and II-VI groups such as $CuInSe_2$, $AgInSe_2$ are also finding several applications in the production of such materials [5,6] .As most of these materials have been often prepared by tedious procedures, a more intense approach to the study of the process of electrodeposition becomes necessary.

This chapter aims at providing an overview of the fundamentals of the electrodeposition technique, the semiconductor thin films, solar cells and the application of electrodeposition in producing thin film solar cells.

A distinctly clear knowledge of the electrodeposition technique is essential before venturing into large-scale application. It is also essential to identify and fix the parameters necessary so as to obtain coatings of desired nature.

1.2 PRINCIPLE AND TECHNIQUES OF ELECTRODEPOSITION

Processes of electrodeposition of metals are carried out for many and diverse purposes. These may be broadly classified under the following headings:

Decorative: To add colour and pleasing appearance to metals, which lack these.

Protective: To increase endurance of metals in a corrosive atmosphere

Reproductive: To reproduce metal surfaces such as in electrotyping and artistic effects

Building up: In building up worn out machine parts or in changing their dimensions

Refining: Refining metals to higher purity states than those achieved by the metallurgical processes.

Extraction: In the recovery and extraction of low metal concentration from their ores.

Electroplating: To obtain relatively thin adherent films.

Electrodeposition is carried out through the processes of decomposition of suitable selected chemical compounds by the passage of electric current. These chemical compounds are salts, which possess definite chemical features and are normally complex substances. They contain their constituting elements in very definite proportions by weight, which may be a metal or a nonmetal.[7]

1.2.1 Principle:

The electrolytic decomposition of substances is carried out in a set up involving a electrolytic cell. The features of a simple electrolytic cell include two metal plates one to serve as a cathode and the other as an anode. A dc/ac source and an electrolyte form the other necessary components.

On passing electricity the ionization of the electrolyte takes place at the electrodes leading to the formation of oppositely charged ions. The ions migrate towards the oppositely charged electrodes under the influence of an applied field. At the electrodes ions get neutralized either by the loss or gain of one or more electrons and form free states which are either liberated or deposited at the electrodes. A schematic diagram is given in **Fig .1.1. Table 1.1** gives the reactions taking place at the electrodes.

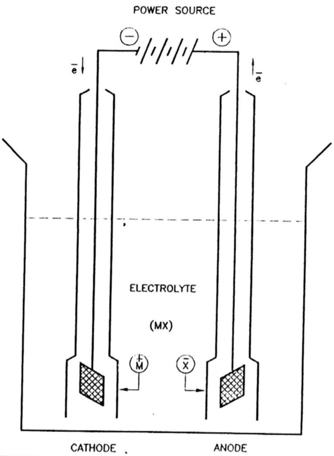


FIG 1.1 ELECTROLYTIC CELL - SCHEMATIC DIAGRAM

[Ref.1]

Cathodic Reactions	Anodic Reactions
1.**Reduction** of ions ; 2. formation of complexes or molecules with lower oxidation state ; 3.deposition of metals or elemental forms on the electrode after their discharge.	1.**Oxidation** of ions ; 2.formation of complexes or molecules to species in a higher oxidation state; 3. ionization of electrode material to form soluble ions or complexes.

Table. 1.1 Cathodic and Anodic reactions

The migration of ions under the influence of the applied field involves the actual transfer of matter in the form of ions and is termed electrolytic conduction. This differs from the electronic conduction in terms the nature of conduction, which does not involve any transfer of matter. The latter involves conduction through free electrons in the lattice.

The amount of matter transferred depends on several factors with relation to the ions such as its rate of mobility i.e., its velocity per unit electric field. The total conductivity of a solution of the electrolyte is proportional to the sum of the mobilities of its ions. This is especially so in dilute solutions. The mobility of various ions differ considerably, with the result that in a given solution the cations carry more current than the anions. The total current carried by a given ion is proportional to its transport number or transference number.

The ions having highest mobilities have the highest conductivity in aqueous solution. Since hydrogen and hydroxyl ion share the highest mobilities, the solutions of acids and alkalis are found to be very good electrolytic conductors.

Although migration of ions accounts for the overall conductivity of electrolytic solutions, this migration has little to do with actually bringing the ion to be discharged to the face of the cathode. Diffusion usually plays an important role.

The measure of amount of chemical change produced is obtained by measuring the quantity of electricity that is passed. This is propounded by the Faraday's laws [1833], which have remained perfectly valid till date.

They may be stated as,

1. The amount of chemical change produced by an electric current is proportional to the quantity of electricity that passes.

2. The amounts of different substances liberated by a given quantity of electricity are proportional to their chemical equivalents.

Accordingly, the amount of substance liberated can be calculated by a given number of coulombs from the electrochemical equivalent, given by the equation,

$$G = I \times e \times t / 96500,$$

where , **I** is the current , **e** the electrochemical equivalent and **t** the time in sec. [8,9].

1.2.2 Factors affecting the nature of electrodeposits:

The nature of electrodeposits obtained is always to a specified requirement. The specified nature of the deposits is dependent on several factors. The most important of these are:

a. Current source: An AC or a DC source can be applied to the process. The preference of DC over AC source is basically to maintain a unidirectional current and polarity of the electrodes.

b. Current density: Current density or current per unit area of the deposited surface is important as it affects the thickness of the deposit, nature and distribution of the deposit on the substrate. As current density increases the hardness of the deposit is also found to increase. A low current density is found to result in irregular grain size and eventually a rough surface and lesser brightness. An increase in the current density is also found to decrease the adhesion of the deposit to the surface as it may lead to a spongy deposition. [10]

c. Current efficiency: Although according to the Faraday's laws the total amount of chemical change produced by a given quantity of electricity can be exactly calculated, in plating and similar processes such as electrorefining and electrotwinning, often the weight of the material deposited is less than the predicted values. The percentage ratio of the weight deposited to the weight expected of the deposit is called the current efficiency, i.e.,

$$\textbf{Current Efficiency} = W_1 / W_2 \times 100$$

When it is applied to the cathodic reaction it is called cathodic efficiency and when applied to the anode it is called anodic efficiency. It differs from one process to another and depends on factors such as bath concentration , temperature, degree of agitation , pH, and current density In case of Cu and Ni plating the current efficiency is found to be 100%

d. Potential: The electrode potential of the electrode as well as the deposition potential of the bath solution play an important role in electrodeposition.

The concept of the reduction potential of the electrode employed and the Electro chemical series is of some importance in this regard. However, the hydrogen overvoltage is to be considered apart from these while selecting the electrode materials to form a cell. **[11]**

When two or more type of materials is to be codeposited or the compound form is to be obtained a codeposition potential is identified. . Obtaining the voltammogram of the chemical compounds used in obtaining the deposits normally attains this.

e. Concentration and nature of the electrolyte: The conducting nature of the electrolyte is an important factor in determining the rate of deposition. The conducting nature is improved by adding small amounts of acids or alkalis.

The concentration of the bath is also an important factor in the determination of the thickness of the deposit. Often a high metal concentration is employed for a better coating as it provides a higher current density. This objective can however be achieved even using lower concentration especially in order to obtain thin films, by employing cathode rod movement or agitation of the electrolyte solution so that the supply of ions is commensurate with their discharge.

f. pH : Control of pH during electrodeposition is necessary in order to obtain the desired physical properties of the deposits and to operate the bath with optimum efficiency.

g. Temperature: Though deposition can be carried out at a normal temperature an increase in temperature is found to hasten the supply of ion to the cathode. Further a raise in temperature is found to lower the hydrogen overvoltage and the rate of growth of the nuclei.

h. Nature of the electrode: The choice of suitable cathode and anode is necessary to use them efficiently together during the electrodeposition. The choice of the electrodes is normally done using their reduction potential and the electrochemical series. The shape and distance between the electrodes is another major parameter to be considered.

i. Addition agents: The addition agents are the small amounts of complexing agents added normally during deposition such as EDTA, sulfuric acid, gelatin etc., which lead to the formation of fine grained deposits.

j. Time duration: The thickness of the deposit is directly related to the duration of deposition. The longer the duration more is the thickness and consequently greater is the amount deposited. The weight of the deposit is directly proportional to the duration or time of deposition as can be seen from the Faraday's equation, mentioned under section 1.2.1.

k. Diffusion rate: Diffusion is the result of random motion of particles of the solution, which tends to produce a uniform distribution of dissolved species throughout the solution. The region next to the electrode, where the concentration of a species differs from that of the bulk of the solution, is called the diffusion layer. The boundary between this layer and solution is not a sharp one but is somewhat arbitrary. The rate of diffusion, say, R is related to the difference in concentration of the bulk, C_O and the concentration at the electrode, C_e, and the effective thickness of diffusion layer dN as ,

$\mathbf{R = D[C_o - C_e] / dN}$, where D is the diffusion constant

The rate of diffusion increases on decreasing the thickness of the diffusion layer dN, which can be achieved by agitation. The diffusion rate is important in determining the limiting cathode current density that may be employed, and, consequently, the deposition rate. If the limiting current density increases no deposit may form. **[7,10]**

1.2.3 Based on the above factors it is possible to summarize that, the desired nature of the electrodeposit can be obtained by,

i. maintaining high current density

ii. maintaining high concentration of metal ions

iii. using addition agents and complex salt solutions

iv. maintaining optimum pH, temperature and electrode materials

v. providing suitable agitation during the process

vi. providing a larger area on the electrode and maintaining a suitable distance between the electrodes.**[11]**

1.2.4 The process of electrodeposition has the following advantages :

* Being a low temperature process it allows the use of inexpensive equipment and instrumentation.

* It enables the fabrication of thin films of the order of 5-1000 microns. The thickness of the film can be varied and controlled by the charge passed during deposition and deposition time.

* The technique provides for the possibility of large surface area deposition

* Being a simple electrochemical process it can be scaled up for mass production at a practical cost.

*The wastage of materials is minimum as the deposition is carried out only on the required substrate section and bath dimension can be adjusted suitably.

* It is also possible to obtain p- and n-type materials by changing the deposition potential. **[12]**.

It is observed that though the process appears to be simple at the outset, it needs sufficient care and expertise to obtain desired nature of the electrodeposit. The technique involves basic principles and interplay of electrochemistry, surface chemistry, solid state chemistry and metallurgy.

1.3 SEMICONDUCTORS AND SEMICONDUCTOR THIN FILMS

The observation that metals are good conductors and nonmetals are poor conductors is a consequence of the measurement of their electrical conductivity. Metallic conductivity is between 10^6 and 10^4 ohm $^{-1}$cm^{-1}while insulators have conductivity less than 10^{-10}ohm^{-1} cm^{-1}. Semiconductors have conductivity between those of metals and insulators, which falls between 10^4and10^{-10}ohm $^{-1}$cm $^{-1}$. This feature is due to the energy or band gap Eg between the valence band and the conduction band.

Fig 1.2[18] illustrates a simple version of the band diagram of a semiconductor. While the Eg of insulating materials is about 6eV, that of the metals is about 3eV. The semiconductors have a convenient band gap of 0.5 to 3.0eV. **[13]**. **Fig 1.3[18]** illustrates a comparison between the Eg of conductors, insulators and semiconductors.

Semiconductor may be identified by the following properties

a. In a pure semiconductor, conductivity rises exponentially with temperature. At lower temperatures a smaller concentration of impurities is required in order to ensure this behavior.

b. In an impure semiconductor the conductivity depends strongly on the impurity concentration. In the doped material, i.e., materials with added impurities, the conductivity changes only slightly with temperature, just as in a metal

c. The conductivity is changed by irradiation with light or high energy electrons or by injection of carriers from a suitable metallic contact.**[14]**.

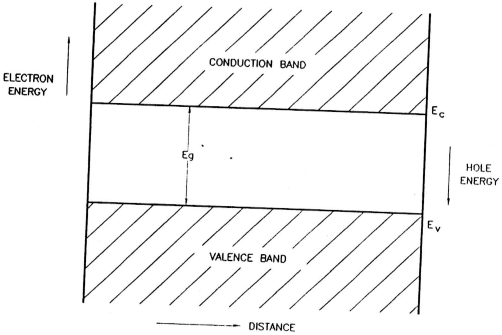


Fig 1.2 SIMPLIFIED BAND DIAGRAM OF A SEMICONDUCTOR

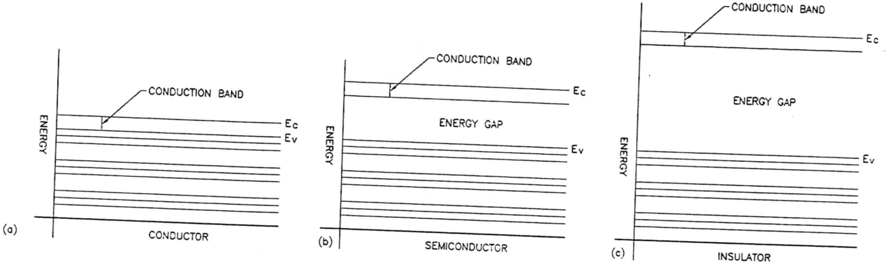
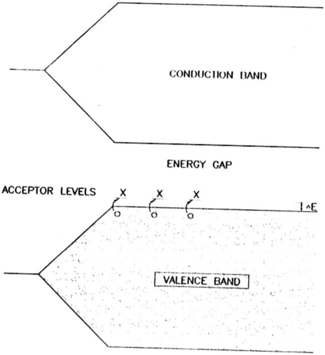


Fig 1.3 COMPARISON OF ENERGY BANDS

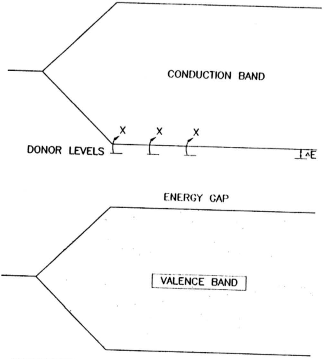
1.3.1 p-Type and n-Type semiconductors and formation of p-n junctions

Typical elemental semiconductors are germanium, silicon and gray tin of the fourth group of the periodic table, boron of the third group and selenium and tellurium of the sixth group. Their semiconducting property is due to the electrons, which overcome the band gap and go over to the conduction band. They are called intrinsic semiconductors. When an impurity belonging to the third or the fifth group is added to an element like silicon it forms an extrinsic semiconductor, p- or n-type. Such impurities introduce acceptor levels above the valence band and donor levels below the conduction band respectively, thereby making the element an extrinsic semiconductor **[Fig. 1.4]**. **[16]** When such n- and p- type materials are in contact they form p-n junctions.

When an n- type and p-type semiconductor material such as germanium is put together to form a single unit, a junction diode with very useful properties is made. Some of the electrons in the valence band receive thermal energy, and as a result electrons and holes move about. As a result they diffuse onto the opposite side of the junction and recombination takes place. This leads to the accumulation of positive charges at the border on the n-side and of negative charges at the border on the p-side. This forms the depletion region. When a Pd is applied to the junction such that the p- side has a positive polarity it forms the forward bias and when the polarity of the applied potential is reversed it forms a reverse bias. **[Fig.1.5]** .**[13]**

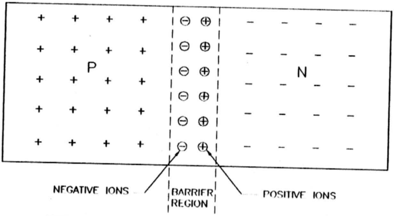


1.4a CONDUCTION BY HOLES p–type SEMICONDUCTOR

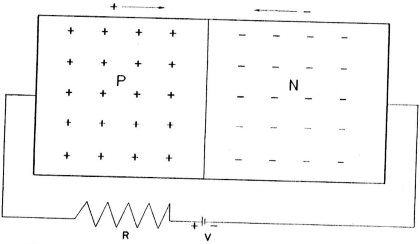


1.4b CONDUCTION BY ELECTORN IN A n–type SEMICONDUCTOR

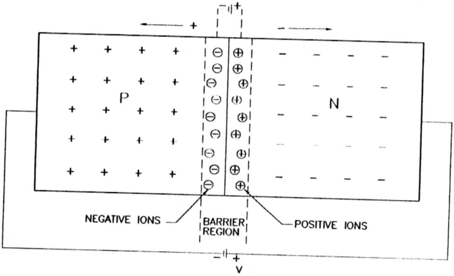
Fig. 1.4



(a) P-N JUNCTION GERMANIUM



(b) FORWARD-BIASED P-N JUNCTION



(c) REVERSE -BIASED P-N JUNCTION

Fig. 1.5

Typical compound semiconductors are GaSb, InSb[III-V compounds] and ZnS[II-VI compounds]. Semiconducting behavior is not restricted to solids and there are liquid semiconductors too.**[30]** Recently, attention has been paid to glassy and amorphous semiconductors, which find technical application such as the solar cells.

Compound semiconductors with nonstoichiometric composition are of n- or p-type depending on one of the components of the compound which is found in excess. Cadmium sulphide is one such compound, which is of interest in the present study. The importance of compound semiconductors such as CdS and CdTe is due to their good potential of producing low cost photovoltaic devices with large surface areas, infrared detectors, p-n junctions, hetero junctions and gamma-ray detectors. Thin films of such materials have found vivid applications currently as they are finding a lot of application in electronic industry. **[14,15]**

1.3.2 Semiconductor thin films:

Thin film preparation techniques: A review

The thin film technology consists in depositing on substrate a thin film of desired materials of thickness from 50 Å to 20,000 Å . The thin film is grown from either vapour or liquid, by a process involving individual atoms and molecules. This growth process determines the properties of the film so formed. The thick film formation on the other hand consists in, depositing on a substrate by screen -and - fire method, a film of desired material of thickness in the range of 1,25,000 Å to 6,25,000 Å. **[13]**

Thin film technology is used for interconnection of components in IC, for making resistors and capacitors either on the some substrate as the active elements or a separate substrate and of late in developing photovoltaic cells

There are over forty types thin film deposition techniques used widely in the preparation of thin films. These processes or techniques can be generally categorized as

- Physical methods
- Chemical methods
- Hybrid methods
- Patterning techniques **[11]**

Only the first two techniques are discussed in detail as they are relevant to the present study. A quick glance at these processes and their advantages and disadvantages are provided in **Table 1.1**

Table 1.1: Thin film deposition techniques: Advantages and Disadvantages

DEPOSITION TECHNIQUE	ADVANTAGES	DISADVANTAGES
1. Electron gun evaporation	Applies to most metallic and semiconductor elements. Produces amorphous elemental semiconductors	Formation of refractory metals. Carbon di oxide difficult to evaporate.
2. Sputtering	Produces amorphous and metallic semiconductor. Easy to apply a biased field	Sputtering gas atoms get incorporated in the film
3.Chemicalvapour deposition	Deposits device quality epitaxial layer with electrical activity and also poly crystalline layers.	Needs elaborate set up, high substrate temperature and critical gas flow rate adjustment.
4.Molecular beam epitaxy	High quality compound films can be obtained	Elaborate set up including very high vacuum
5.Electro deposition	Wide range of film and large area of uniform thickness	Useful mostly to metallic films. Contamination and impurity content possible.
6.Liquid Phase epitaxy	Good compound films	Difficult to produce reproducibility
7.Ion beam techniques	Precision control of deposition parameters	Slow deposition rate

1.3.1 a Physical Methods of deposition

Vacuum deposition, various types of sputtering and vapour plating are classified as physical methods of film deposition.

i. Vacuum deposition: In this process, thin films are evaporated into a substrate in a container such as a bell jar. A filament is brought in contact with the material to be vapour deposited and heated to a suitably high temperature causing the material to vaporize. The material so vaporized then condenses on the substrate, which is also heated, but to a temperature considerably lower than that of the filament. High temperature of the substrate helps in adhesion of the deposited film. The container is kept evacuated in order to avoid collisions of the vaporized atoms in their movement towards the substrate. A mask is generally placed on the substrate to determine the thin film pattern on the substrate. Several different materials such as gold, aluminum and silicon dioxide may be vacuum deposited in the form of thin films or ceramics providing good adhesion.

ii. Cathode sputtering: In this method, a thin stream of an inert gas such as argon, is permitted in to an evacuated container. Simultaneously electrons are made to emit from a cathode made of material to be sputter deposited on the substrate. These electrons collide with the atoms of the gas ionizing them thus resulting in glow discharge. The positive gas ions are attracted to the cathode and they bombard the cathode with sufficiently high kinetic energy so as to release atoms of the cathode material which ultimately hit the substrate placed at the anode with enough velocity to cause good adhesion. Some of the materials so deposited are nichrome, tantalum and silicon dioxide. Other materials such as magnesium oxide, aluminum oxide and barium titanate may be sputter deposited using radio frequency techniques.

iii. E-beam sputtering: In electron - beam evaporation, electrons are used as a source of sputtering. Electron beams generated by a tungsten filament are directed towards the target to sputter the material under a high vacuum condition. 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 which condenses 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 and in cases where the desired material simply cannot be deposited any other way.

iv. Vacuum plating: In this case a volatile metal compound is heated in a plating chamber to a suitably high temperature causing its vaporization and thermal decomposition or hydrogen reduction. Metal than gets deposited on a substrate, forming a thin film. Only such metal compounds are used which get decomposed or reduced at temperatures below the melting points of the substrate and the film.

1.3.1 b Chemical methods of deposition

Films may be deposited on either metallic or non-metallic substrates by chemical or electrochemical means from solutions or by chemical vapour deposition

i. Electrochemical deposition: Deposition by electrochemical reactions involves electroplating , which is defined as the electrodepositon of an adherent metallic coating upon an electrode for the purpose of securing a surface with properties different from those of the basal metal. This method is only described briefly as the process is discussed in detail earlier and is the basis of the present study.

ii. Chemical vapour deposition: The growth of thin films by chemical vapour deposition has become one of the important methods of film formation and constitutes a corner stone for modern technologies. CVD can be defined as a material synthesis method in which the constituents of the chemical reaction are essential characteristics of the CVD method. The type of chemical reactions and the extent of reactions to take place must be understood in a CVD process.

iii.Physical-chemical methods : Plasma deposition and glow discharge polymerization are two major physical-chemical hybrid deposition techniques in application at present. 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.

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. Polymer formation that occurs in such a process is generally referred to as plasma or flow discharge polymerization.

Electrochemical deposition is the object of interest in the present study as it has the advantages of simplicity and low cost as well as effectiveness.[**17,30**]

1.3.2 Growth and structural properties of thin films: The formation of thin films on a substrate by deposition is basically a phase change phenomenon involving nucleation and growth with the constraint of substrate. By controlling the nucleation and growth on the substrate any of the thin films can be obtained and the film structure and composition can be confirmed by characterization studies. The mechanisms involved in the formation of crystalline or non crystalline states primarily depend on the time duration the atoms or clusters of atoms require in order to interact to form bonds in metastable and stable structures. Crystallization 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 thin film material. Amorphous, and in general, polycrystalline thin film possesses no unique directionality or axis in a macroscopic planes. Microscopically amorphous state is a state with only short-range ordered densely packed atoms or micro crystallites, while polycrystalline materials are crystalline but with random grain size, shape and orientation packing.

The grains or crystallites in a thin film are formed by independent nucleation and growth process randomly oriented 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. Rapid quenching, by seeding with additives or rounding the grains controls the grain size. Annealing which reduces the grain boundary surface area may induce recrystallization by diffusion.

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

1. the growth of either state is independent of the substrate

2. an amorphous material can be transferred to a polycrystalline state, but not the reverse. This is because the crystalline state has lower lattice energy.

The polycrystalline state can transform to a single crystal state by reducing the internal surface energy. [17]. Most thin films are obtained as polycrystalline and single crystal form.

1.3.3 Special semiconductor devices: Photoelectric devices:

Photoelectric devices form one of the several semiconductor devices with innumerable applications such as satellite systems, military armaments, computer systems and many more. The input signal of these devices is a light beam.

They can be classified into three groups:

1. Photoemissive devices: The principle of operation of these devices is that when light strikes the surface of these materials, the photons have sufficient energy to knock electrons out of the material which form the primary feature of the devices. Photomultiplier tubes, vacuum and gas diodes are some of the examples.

2. Photoconductive devices: This category includes the devices which have the primary feature of increase in the conductivity of the material., when light beam strikes them. The Photocell is one of them. This includes a broad category of devices fabricated from cadmium sulphide, selenium, germanium and silicon.

3. Photovoltaic devices: They involve the property of generation of electrical energy on being exposed to light. The **solar cells** fall under this category. The incident beam of light generates an electromotive force. Single crystal materials such as silicon are more commonly used. However, large area solar cells have been fabricated from polycrystalline materials. **[18]** More details about the solar cells are given in the following discussion

1.4 PHOTOVOLTAIC CELLS OR SOLARCELLS:

1.4.1 General introduction:

Solar cells or more accurately photovoltaic cells are the simplest of junction devices. Strictly the action of these devices do not necessarily require light from the solar spectrum. Any photon that is sufficiently energetic will generate excess carriers and activate photovoltaic activity. Several device structures can function as PV cells viz., p-n junctions, Schottky barriers or hetero junction structures. Though the precise device physics is different for each type of structure, the photovoltaic action is similar. **[19]**.

As world wide energy demand increases, conventional energy resources, such as fossil fuels, will be exhausted in the near future. Therefore, the development and use of alternative energy sources becomes a necessity. The importance of the solar cell is felt as it can directly convert sunlight to electricity with high conversion efficiency can provide a permanent power at low operating cost and free of pollution. **[20]**

1.4.2 Physical source of sunlight and solar constant

The temperature near the center of the sun, is nearly 2E07 K. This temperature does not determine the characteristic electromagnetic radiation emission from the sun. Most of the intense radiation from the sun's deep interior is absorbed by a layer of negative hydrogen ions near the sun's surface. These ions act as continuous absorbers over a great range of wavelength. The accumulation of heat in this layer sets up convective currents that transport the excessive energy through the optical barrier **[Fig 1.6]**.

The energy passing through this layer is reradiated into the relatively transparent gases above. The sharply defined level where connective transport gives way to radiation is referred to as photosphere. Temperature within the photosphere is much cooler than at the sun's interior, and is around 6000K. The photosphere radiates an essentially continuous spectrum of electromagnetic radiation, closely approximating that expected from a black body at this temperature.

Solar constant: The radiant power per unit area perpendicular to the direction of the sun outside the earth's atmosphere but at the mean earth- sun distance is essentially constant. This radiation intensity is referred to as solar constant or Air Mass Zero [AM0] radiation. There is a great deal of difference between the solar spectrum as measured at the earth's surface and in space. The difference arises due to the effect, which the earth's atmosphere has on the light passing through it.

[18, 22].

The intensity of radiation as measured at the sea level with the sun directly over head is referred to as Air Mass One [AM1]. The solar spectrum as it would be measured at the earth's surface [AM1] and in space [AM0] is illustrated in **Fig 1.7** The solar cells are usually tested on the earth's surface although the end application is concerned with power generation in space. Hence these aspects of solar spectrum becomes important in the production of quality solar cells.

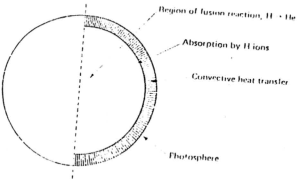


FIG 1.6 PRINCIPLE FEATURES OF SUN

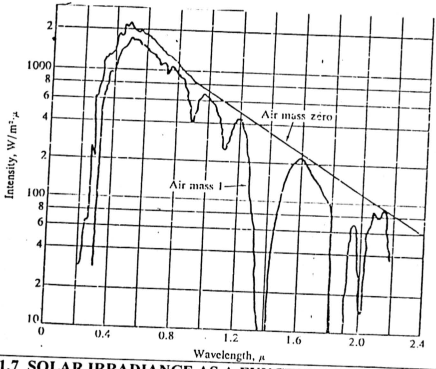


FIG 1.7 SOLAR IRRADIANCE AS A FUNCTION OF WAVELENGTH

[ref.22]

1.4. 2 Discovery and development of the solar cells:

The origin of solar cells can be traced back to 1839 and Becquerrel's discovery of photo voltage. When light was shown on an electrode in an electrolyte solution photo voltage was developed. Adams and Day reported a similar effect in solid selenium material in 1867. Subsequent work in selenium and copper oxide led to the development of the selenium solar cell and its wide use in photographic exposure meters. By 1914 selenium solar cells had reached about 1% efficiency in directly converting sunlight to DC electricity. The modern semiconducting solar cell was first developed by Chaplain, Fuller and Pearson in 1954 using a diffused silicon p-n junction. There after a notable increase in the research and development of such materials have been achieved.

Solar cells at present furnish the most important long-duration power supply for satellites and space vehicles. Solar cells have also been successfully employed in small -scale terrestrial applications. Research and development of low -cost, flat - panel solar cells, thin-film devices, concentrator systems and many innovative concepts have been attracting attention ever since. **[20,21]**.

1.4.3 Thin film solar cells: In thin film solar cells, the active semiconductor layers are polycrystalline or disordered films that have been deposited or formed on electrically active or passive substrates, such as glass, plastic, ceramic, metal graphite or metallurgical silicon. A thin film of CdS, Si, GaAs, InP, CdTe and so on , can be deposited onto the substrate by methods such as, vapour growth, evaporation plasma , and plating.

If the semiconductor thickness is larger than the inverse of the absorption coefficient, most light will be absorbed. If the diffusion length is larger than the film thickness, most photo-generated carriers can be collected. The main advantage of thin film solar cells is their promise of low cost, which is due to low cost. processing, and the use of relatively low cost materials **[15,31]**.

1.4.4 PRINCIPLE OF SOLAR CELL OPERATION

A simple approach to the understanding of the principle of the solar cell operation is to consider a simple p-n junction with the depletion region drawn in. There exists a local field (E), due to the redistribution of the charges at the depletion zone. When photons of sufficiently high energy, say > 1.1 eV enter the depletion zone of the junction, electron-hole pairs are generated. Due to the presence of the local field, the carriers generated will flow; the electrons flowing to the n-side and the holes to the p-side of the device. This segregation creates a charge imbalance with more electrons on the n-side and more holes on the p- side compared to the thermal equilibrium condition (with no light shining on the junction). This is the forward bias for the device. **Fig 1.8 illustrates** the energy band diagram depicting photovoltaic action

The idealized circuit equivalent for a PV cell or a solar cell is given in **Fig 1.9**

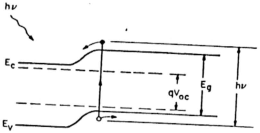


FIG. 1.8 ENERGY BAND DIAGRAM OF p-n JUNCTION SOLAR CELL

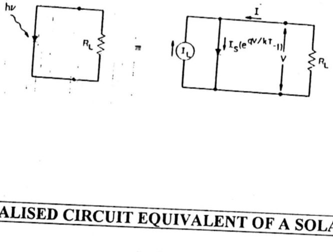


FIG. 1.9 IDEALISED CIRCUIT EQUIVALENT OF A SOLAR CELL

[ref.22]

The typical I-V characteristics of an illuminated PV cell shows current and voltage in the fourth quadrant with opposite signs. The significance of this is that power can be drawn from the device [**Fig.1. 10**].

The power conversion efficiency for a solar cell is defined as,

$\eta = P_m / Pin = I_m . V_m / Pin$, where Pm- is the maximum power that can be extracted from the device, I_m and V_m the current and voltage level which gives the maximum power. Alternately, it can be written as,

$\eta = FF. I_l. V_{oc} / Pi$, where, FF is the fill factor , I_l is the diode current under a short circuit condition , V_{oc} is the open circuit voltage and P_{in} is the incident power.The fill factor is defined as , $FF = I_m . V_m / I_l. V_{oc}$

The fill factor provides a convenient comparison between the maximum deliverable power and the maximum power that can be extracted . The larger the FF value , higher is the efficiency expected.[**19**].

1.4. 5 Applications of solar cells

Photovoltaic energy conversion is used today for both space and terrestrial solar energy conversion. Solar cells have found immense application orientation in communication satellites and in manned space laboratories as solar batteries. The usefulness such cells in devices such as calculators, watches and heaters, air conditioners, solar air planes, airships and solar cars makes it a more lucrative pursuit. The solar energy as a future source of energy makes the study purpose all the more emphasized. [**21,22**]

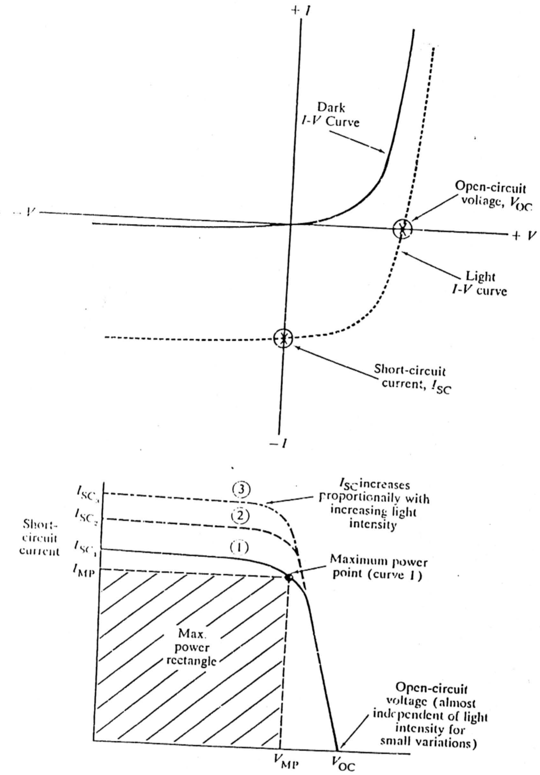


FIG. 1. 10

I-V CHARACTERISTICS OF A SOLAR CELL UNDER ILLUMINATION

[ref.21]

1.5 Aims and Objectives of the present study

Considerable work has been done on the formation of thin films of binary and ternary compounds of cadmium such as CdS [24], CdSe [25], CdTe [26] and CdSTe [27], CdSeTe [28], CdMnS [29] to list a few by different materials. The choice of the cadmium based thin films is basically due to the convenient band gap Eg which is usually between 1.7eV and 2.6 eV. Further these films have excellent absorption coefficient and good stability. The compounds of cadmium are less expensive, are easily available and have no notable toxicity. This makes the material handling easier.

Chemical deposition methods of preparing the solar cells have been attracting attention for some time. The disadvantage normally faced during preparation of such films is the impurity content. The problems encountered include the selection of the substrate material, selection of counter electrodes and electrolytes.

The present study aims at an attempt to use different substrate materials such as n-Silicon wafers and ITO/glass films and to obtain thin film deposit of CdS using simple electrolyte combinations. Further an attempt has been made to develop ternary CdSeS thin films and to optimize the conditions of deposition so as to obtain relatively good solar cells. Characterization studies of the developed materials have been made by the techniques of XRD, SEM and EDAX and optical measurements. The detailed procedures of these techniques are reported in the next chapter.