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References
2.1 Introduction

Thin film technology has revolutionized in the field of optics, electronics and magnetism, considering new and improved optics, electronics, magnetic devices and photovoltaic solar cell etc. The advantage of thin film devices are low material consumption and possible use of flexible substrates [1]. Recently considerable attention has been given to the preparation of thin metal chalcogenide films for solar cell applications by various techniques [2-7]. Many binary and ternary semiconductors on a variety of substrates have been prepared by the spray pyrolysis technique [8–10]. The thin film deposition can be broadly classified as physical and chemical methods. Physical methods consists vacuum evaporation and sputtering; the material to be deposited has been transferred to a gaseous state either by evaporation or an impact process and then deposited on the substrate. Under chemical methods, we have gas phase, chemical processes such as conventional chemical vapor deposition (CVD), Laser CVD, Photo CVD, Metal organic chemical vapor deposition (MOCVD) and plasma enhanced CVD. The Liquid phase chemical techniques include spray pyrolysis, electrodeposition, chemical bath deposition, successive ionic layer adsorption, anodization and liquid phase epitaxy etc. The broad classification of thin film deposition techniques is outlined in the fig. 2.1. The physical methods are plugged with certain drawbacks and difficulties. A careful and precise control of the boat temperature is an essential requirement for obtaining good stoichiometric films and to obtain the particular composition in alloy films. Chemical methods are relatively economical and easier ones as compared to physical methods. The chemical methods have some drawbacks and advantages over the other methods. However there is no ideal method to prepare the compounds and alloys in thin film form which will satisfy all requirements.

Spray pyrolysis is a simple and low cost technique for the preparation of semiconductor films. The present chapter, therefore, focuses a theoretical aspect of the spray pyrolysis technique, followed by various characterization techniques used for studying the properties of thin film materials.
Fig. 2.1 Broad classification of thin film deposition techniques
Section A

2.2 Thin film deposition technique

2.2. A. 1 Basics of spray pyrolysis technique

Among chemical methods mentioned in the fig. 2.1, solution spraying technique is most popular today because of its applicability to produce variety of conducting and semiconducting materials [11-13]. The basic principle involved in spray pyrolysis technique is that, when droplets of spray solution reach to the hot substrate, owing to the pyrolytic decomposition of solution, well adherent pin–hole free, uniform film is deposited on to the substrates. The other volatile byproducts and excess solvent escape in the form of vapors. The thermal energy for decomposition and subsequent recombination of the species and sintering, recrystallization of the crystallites is provided by the hot substrate. It is different for the different materials and solvents used in the spray process.

Apart from its simplicity, spray pyrolysis technique has a number of advantages.

1) Spray pyrolysis is a simple and low cost technique for the preparation of semiconductor thin films.
2) It has capability to produce large area, high quality adherent films of uniform thickness.
3) Spray pyrolysis does not require high quality targets and /or substrates nor does it require vacuum at any stage, which is a great advantage if the technique is to be scaled up for industrial applications.
4) The deposition rate and the thickness of the films can be easily controlled over a wide range by changing the spray parameters.
5) A major advantage of this method is operating at moderate temperature (100–500°C) and can produce films on less robust materials.
6) It offers an extremely easy way to dope films with virtually any elements in any proportion, by merely, adding it in some form to the spray solution.

7) By changing composition of the spray solution during the spray process, it can be used to make layered films and films having composition gradients throughout the thickness.

Spray pyrolysis technique has been used to prepare the thin film on a variety of substrates like glass, ceramic or metallic. Many studies have been conducted over about three decades on SPT and the mechanism of thin film formation and influence of variables on the film formation process has been comprehensively reviewed in the literature [14]. Due to the simplicity of the apparatus and good productivity of this technique on a large scale, it offered a most attractive way for the formation of thin films of metal oxides [15–19], metallic spinal by oxides [20–22], group I-VI, II-VI, III-VI, IV-VI, V-VI, VIII-VI, binary chalcogenides [23–26], group I-III-VI, II-II-VI, II-III-VI, II-VI-VI and V-II-VI ternary chalcogenides [27-28]. Recently chemical SPT has also been successfully employed for the formation of superconducting oxide films [29–31] etc.

### 2.2. A.2 Steps involved in spray pyrolysis process and growth of thin film

Important parameters involved in spray pyrolysis techniques are precursor solution, evaporation period, thermolysis, and atomization for studying the structural, morphological and crystallinity of thin films. These four process parameters are discussed in the following section.

1) Precursors

A precursor solution plays a vital role in the formation of thin film of various compounds. The true solutions, colloidal dispersions, emulsions and sols can be used as aerosol precursors. Aqueous solutions are usually used due to case of handling safety, low cost and availability of a wide range of water soluble metal salts. The solute must have a high solubility which increases in
particle yield of the process. Increasingly, alcoholic and organic solutions have been studied due to the interest in the synthesis of organic materials from metal organic and undergo polymerization and for the synthesis of non-oxide ceramic solutions.

2) Atomization

A variety of atomization techniques have been used for solution aerosol formation, including pneumatic, ultrasonic and electrostatics. These atomizers differ in droplet size, rate of atomization and droplet velocity. The velocity of the droplet when it leaves the atomizer is important because, it can determine heating rate and residence time of the droplet during spray pyrolysis. The size of the droplets products with pneumatic or pressure nozzles decreases when the pressure difference across the nuclei is increased. For a specific atomizer the droplet characteristics depend on the solution density, viscosity and surface tension.

3) Evaporation period

In first stage of spray pyrolysis, evaporation of the solvent from the surface of the droplet, diffusion of the solvent vapor away from the droplet in the gas phase, change in droplet temperature and diffusion of solute towards the centre of the droplet have important role concerns with the stoichiometry of films. The factors controlling the particle growth and ultimately film formations of well adherent surface is due to

1) evaporation of liquid droplets
2) evaporation from solution droplets
3) temperature of liquid droplets
4) temperature of solution droplets
5) solute diffusion in a droplet
6) solute condensation.

Various steps during pyrolysis of aerosols are shown in fig. 2.2 and summarized below:

A. Aerosol of aqueous solution
B. Solvent evaporation
C. Precipitate formation
D. Pyrolysis of the precipitate
E. Nucleation and growth of thin film
F. Formation of continuous thin layer on to the Substrate

2.2. A.3 Factors governing spray pyrolysis technique (SPT)

Thin film formation by using SPT depends upon various parameters. SPT consists of a thermally stimulated chemical reaction between clusters of liquid or vapour atoms of different chemical species. Every sprayed droplet reaching the surface of the hot substrate undergoes pyrolytic decomposition.
and forms a single crystallite or cluster of crystallites as a product on the substrate. The substrates provide thermal energy for the thermal decomposition and subsequent recombination of the constituent species, followed by sintering and crystallization of the clusters of crystallites and thereby resulting in coherent film. The number of factors governing the film formation mechanism depends on,

1) The automation of the spray solution into a spray of fine droplets which depends on the geometry of the spraying nozzle and pressure of a carrier gas.

2) The properties of thin films depend upon the anion to cation ratio, spray rate, substrate temperature, ambient atmosphere, carrier gas, droplet size and also on the cooling rate after deposition.

3) The film thickness depends on the distance between the nozzle and substrate, solution concentration, quantity and substrate temperature.

4) The film formation depends upon the process of droplet landing, reaction and solvent evaporation which are related to droplet size and its momentum.

An ideal deposition condition is that when a droplet approaches the substrate just as the solvent is completely removed. Lampkin [14] showed that depending on droplet velocity and flow direction, a droplet would be either flattens, skip along the surface. The details of the SPT are discussed in the chapter III.
Section – B

2.3 Photoelectrochemical (PEC) solar cell

2.3. B.1 Introduction

There are several methods of collecting and converting solar energy viz. photovoltaic, photoelectrochemical, photothermal and photosynthetic. Out of these routs the photoelectrochemical system is easiest one. A PEC effect is defined as one in which irradiation of electrode/electrolyte system produce a change in electric potential (on open circuit) or in the current flowing in external circuit (under short circuit conditions) [32].

Thin films of II-III-VI group compounds are promising for utilization in solar cells, out of which the polycrystalline cadmium indium selenide have been attracting, increasing attention of researchers by virtue of their various promising technical features and potentials applicability in the field of solar energy conversion.

Solar energy conversion by photovoltaic cells is well known. These devices essentially use p-n junctions between similar or dissimilar semiconductors termed as homo or hetero junction solar cells respectively. Early semiconductor electrochemistry studies [33] have shown that the distribution of potential at the semiconductor – electrolyte interface is almost similar to that at a simple p-n junction. A direct conversion of solar energy into electrical energy using a semiconductor electrolyte interface was demonstrated by Gerischer [34]. These are generally known as photoelectrochemical solar cells.

Semiconductor/liquid junction cells have several advantages over solid state junction cells which make them attractive. Simple immersion of the semiconductor into the liquid forms the junction. Another feature is that the electron–hole pairs are created in a region of high field, producing efficient charge separation. These cells can in principle much cheaper than the traditional solid – state junction solar cells.
2.3 B.2 Semiconductor–electrolyte (S-E) interface

When an appropriate semiconductor is immersed in an appropriate electrolyte the excess charge residing on the electrode surface must be exactly balanced by an equal charge of opposite sign on the solution side. This can happen by charge transfer across the electrode – electrolyte system.

2.3 B.3 Space charge region in the semiconductor

When a semiconductor is dipped into an electrolyte, the junction is characterized by the presence of a space charge layer in the semiconductor adjacent to the interface with the electrolyte. For semiconductors, the chemical potential of electrons is given by the Fermi level in the semiconductor. For liquid electrolytes, the chemical potential of electrons is determined by the redox potential of redox couples present in the electrolyte. If the initial Fermi level in n-type semiconductor is above the initial Fermi level in the electrolyte, then equilibration of the two Fermi levels occurs by transfer of electrons from semiconductor to the electrolyte. This produces a positive space charge layer in the semiconductor. As a result, the conduction and valence band edges are bent upwards, establishing a potential barrier against further electron transfer into the electrolyte. A reverse effect will occurs with p-type semiconductors having an initial Fermi level below that of the redox potential.

Fig 2.3 shows the energy band diagram for n-type semiconductor and an electrolyte (a) before and (b) after establishing the contact between them. Fermi levels, $E_{f_{\text{semi}}}$ and $E_{f_{\text{redox}}}$ are at different levels resulting in electron transfer from semiconductor to electrolyte which establishes the equilibrium. This flow of electrons results in the accumulation of ions in the semiconductors to form the space charge region near the interface in the semiconductors. A strong local electric field is developed and band bending takes place. The potential drop in the semiconductor space charge layer depends on the difference between the Fermi levels of semiconductor and the redox electrolyte, if the former is free from excess charge.
2.3. B.4 Helmholtz double layer

Helmholtz double layer is a dense layer of ions stuck to the electrode. In this region, the potential varies linearly with distance. This dense layer is divided into inner and outer Helmholtz planes. The inner Helmholtz plane (IHP) is adjacent to the electrode surface and consists of completely oriented water dipoles and specifically adsorbed (or contact-adsorbed) ions. The orientation of water dipoles depends on the specific interaction with the electrode surface as well as the electric field. Large ions with negative free energy of contact adsorption are expected to be contact-adsorbed. In aqueous system, the cations react rather strongly with the water molecule and their inner hydration sphere is retained. This limits their closest distance of approach to the electrode. They are thus separated from the electrode by approximately one or two water molecules. On the other hand, anions interact weakly with water; hence hydration sheath is not covered on them. Thus the closest distance of approach could correspond to direct contact; they can be a part of IHP. The
outer Helmholtz plane (OHP) consists of solvated ions (usually cations) at the closest distance approach from the electrode interface. The OHP thus consists of partly ionized water dipole layers. Bockris et al. [35] developed a model of electrode-electrolyte interface and is shown in fig. 2.4 (a). In absence of contact adsorbed ions the potential distribution is as shown in fig. 2.4(b). In presence of contact adsorbed ions, it can be seen from fig. 2.4(c) that the potential distribution changes across the double layer. OHP \((X=X_2)\) is the site at which non-specifically adsorbed ions arrive to take part in the charge transfer processes.

### 2.3. B.5 Gouy-Chapman diffuse layer

The size of the ions forming the outer Helmholtz plane (OHP) is such that the sufficient number of them cannot neutralize the charge on the electrode. Therefore, the remaining charges are held with increasing disorder as the distance from the electrode surface increases and the electrostatic forces become weaker and dispersion by thermal motion is more effective. These less ordered charges forcing opposite to that on the electrode constitute the diffuse part of double layer. Thus all the charges, which neutralize that on the electrode, are held in a region between OHP and the bulk of the electrolyte. The additional charges required to neutralize the total charge on the electrode forms the Gouy-Chapman layer or diffuse layer.
Fig. 2.4 (a) Electrode Electrolyte Interface, (b) Potential Distribution across the double layer & (c) The schematic of electrodes immersed in electrolyte.
2.3. B.6 Stern model

Stern presented a synthesis of the Helmholtz and Gouy–Chapman model of the double layer. Stern theory suggests that the ions being of finite size, keep a minimum distance of approach of the electrode surface. Thus, the electrolyte side of the double layer is neither abrupt nor diffuse but a combination of the two. In this situation, the electrolyte side of the interface is divided into two regions:

1) A dense layer of ions stuck to the electrode: In this region the potential varies linearly with distance.

2) A diffused layer of ions: This is formed as a result of opposing tendencies of the attractive Columbic force and dis Ordering thermal fluctuations. The potential decays exponentially. The Stern model does not tell explicitly how the ions are stuck to the electrode.

2.3. B.7 Photoinduced charge transfer across S-E junction

The region of the photo-potential can now be understood by considering the changes that occur at such an interface by the absorption of band gap radiation. Irradiation of the semiconductor electrolyte interface is produces electron hole pairs, the electrons being promoted to the conduction band. The potential difference across the space charge layer causes the electrons to move towards the bulk of the semiconductor at this is downhill path for the electrons in a n-type semiconductor. The minority carriers h⁺ moves towards the surface of the electrolyte. This movement of the charge carriers in the field of the space charge layer counteracts the band bending, causing as partial return to the charge carrier distribution as before band bending and is shown in figure 2.5.
Fig. 2.5 The position of bands under illumination responsible for photo induced charge transfer

The result is the development of a Fermi level in the semiconductor called the photon Fermi level which is no longer equal to the redox potential of the electrolyte $E_{F\text{(Photo)}} - E_{F\text{(redox)}}$ goes up as the photo-potential on illuminating the interface with light ($h\nu \geq E_g$). A photocurrent can now be observed by connecting the photoanode to a suitable counter electrode. The photocurrent depends on the absorption coefficient of the semiconductor, width of the space charge region, hole diffusion length, area of illuminated electrode, photon energy and radiation intensity. Under short circuit conditions the Fermi levels of the semiconductor and the potential of the redox couple of the solution are equalized and a net charge flows during the illumination.

2.3. B.8 Some efficiency considerations

Physical theories describing the characteristic of PECs (i.e. I-V characteristic for electrochemical photovoltaic cell or hydrogen evolution for photoelectrolysis cells) are likely to be complicated since they have to encompass the following considerations.
a) Physical behavior of the semiconductor electrode involving carrier generation and their transport, mobility, diffusion length, life time, role of traps, recombination center etc.

b) Physical and chemical behavior of the electrolyte: This would include ionic transport in the electrolyte, chemical nature of the ionic species present, their redox potential etc.

c) Any modification in the charge transfer reactions as a consequence of (a) & (b) and potential barrier at the interface. The surface states, non-uniform doping of the semiconductor, over potentials for redox reactions and relative position of energy levels at the interface.

d) Electrode decomposition: The following two approaches of solid-state semiconductor junction theory have also been adopted for a semiconductor electrolyte junction of PEC.

   i) Schottky barrier theory of PEC: The electrolyte semiconductor junction is linked to a metal semiconductor junction. The charge transfer reactions are assumed to be governing by the drift and diffusion components of photocurrent in the depletion layer.

   ii) Bockries theory of PEC: This includes the quantum mechanical tunneling of photogenerated carriers towards the electrolyte region and associated reaction kinetics.
Section-C

2.4 Heterojunction solar cells

Various models proposed for heterojunction are, i) Diffusion model (Anderson model), ii) Emission model, iii) Emission-recombination model, iv) Tunneling model and v) Tunneling-recombination model. The models have been proposed to study the junction from the point of view of ideality factor obtained from current-voltage (I-V) analysis and to estimate carrier concentrations, flat band potential and depletion layer width. Salient features of various models are mentioned below.

2.4.C.1 Diffusion model (Anderson model) - Anderson developed first [36] by neglecting the presence of defects at the interface states. It is considered that there are no dipoles present at the interface. The model helps to predict the transition width for electron and hole and to confirm conduction mechanism whether by electrons or holes. Using this model the difference in conduction band edges of two semiconductors gives difference in electron affinity ($\chi_1 - \chi_2$) and difference in work function gives flat band potential i.e. $\phi_1 - \phi_2$ is equal to $V_{fb}$. Here $\Delta E_c = E_{c2} - E_{c1}$ is the difference in conduction band edges of two semiconductors and $\Delta E_v = E_{v1} - E_{v2}$ is that in valence band edges. Equilibrium energy band diagram before and after the formation of abrupt n-p heterojunction is shown in Fig. 2.6 and Fig. 2.7, respectively.

2.4.C.2 Emission Model - Perlman and Feutch [37] stated emission model for semiconductor heterojunction by considering interface states i.e in the presence of impurity levels. Transmission coefficient increases than in the diffusion model. Effect of spike is considered.

2.4.C.3 Emission-recombination Model - Dolega [38] considered the presence of thin layer at the interface that disturbed the lattice. The electrons or holes reach the interface via thermal emission. Fast recombination takes place in the interface layer and no rectification is possible till space charge region is wider than thin layer.
2.4.C.4 Tunneling-recombination Model - This model was proposed by Van Ruyven [39]. The interface in this model is similar to two semiconductors having own surface states separated by free surface.

2.4.C.5 Tunneling Model - Rediker Stopek and Ward [40] proposed this model for describing tunneling mechanism of I-V characteristics of an abrupt heterojunction. Electrons have to penetrate to flow from n-type to p-type material with wide band gap. The carriers penetrate the barrier in wider band gap material. Threshold voltage decreases with increase in temperature.

![Equilibrium energy band diagram before the formation of abrupt n-p heterojunction](image)
Fig. 2.7 Equilibrium energy band diagram after the formation of abrupt n-p heterojunction

**Current-Voltage (I-V) studies**

The I-V analysis of heterojunction helps to explain electrical conduction mechanism of heterojunction. The mechanism of charge transport through interface is decided by the nature of I-V characteristics obtained. Depending upon polarity of applied voltage, the characteristics can be classified as forward or reverse. When polarity of applied voltage reduces the barrier potential the characteristic is forward otherwise it is reversed. In heterojunction, current flow can be either due to an applied electric field which is drift current or due to carrier concentration gradient i.e. diffusion current. The dependence of current density (current per square cm) on voltage for heterojunction is exponential and is given by ideal diode equation as,

\[
J = J_s \exp \left( \frac{qV}{nkT} \right) - 1
\]

where \(J_s\) is the reverse saturation current density, \(n\) is the junction ideality factor, \(K\) is Boltzmann’s constant and \(T\) is the absolute temperature. The formation of quality junction is decided by junction ideality factor value and
rectification ratio which is given by ratio of forward current to reverse saturation current which is measure of rectifying behavior of junction. For ideal diode the value of junction ideality factor approaches to unity. As for junction charge transport takes place by various current mechanism the nature of I-V characteristics deviates from ideality. The thermal treatment also affects the ideality factor. Based on the junction ideality factor (n) and rectification ratio, the I-V characteristics consist of following regions [41].

1) **Generation-Recombination current region** - In this region the junction ideality factor has value in between 1 to 2. Due to impurities generation recombination of electrons- holes take place. Hence the electron-hole current is not constant throughout the depletion layer. Depletion layer width gets modified and gives surface leakage current.

2) **Diffusion current region** - In this region the junction ideality factor is close to unity. Due to absence of interface states charge carriers directly flow through barrier.

3) **High injection condition** - At high current densities in forward – bias region injected minority carrier density is comparable with majority concentration both diffusion and drift component of current are important and current is roughly proportional to $J_s (e^{qV/2KT})$ with ideality factor equal to 2 .

4) **Series resistance effect** - At high current densities in forward-bias region effective series resistance become appreciable that absorbs voltage drop between the diode terminals and hence the ideality factor increases.

5) **Reverse leakage current due to generation (Recombination and surface effect)** - Surface leakage current increases due to the modification of depletion layer width because of generation and recombination of carriers. This affects rectification. In short, the current transport mechanism of heterojunction varied as per the value of ideality factor. The ideality factor is strongly dependent on the thickness of film. The current transport mechanism depends upon the ideal factor value (n) as follows:

i) If forward bias transport is limited by diffusion n=1.
ii) If it is limited by recombination at depletion region $n=2$. Exact value of $n=2$ obtained only when a single recombination level is located at midgap is assumed.

iii) When the continuous trap distribution is assumed the value of $n$ is in the range 1 to 2.

2. Capacitance-Voltage (C-V) studies

The electrical parameters of heterojunction such as carrier concentration, flat band potential, depletion layer width can be obtained with the capacitance-voltage studies.

It is a practice to use theoretical expressions of junction capacitance with or without interface with experimental results to fix the junction capacitance model. There are essentially two capacitances associated with the junction. One of them is due to the charge dipole at the depletion layer (depletion capacitance) and another is the diffusion capacitance. Bound charges exist in the region in vicinity of heterojunction if bias is applied or not. Hence near the n-p heterojunction interface net positive charge develops on n-side due to ionized acceptor and negative charge develops on p side due to ionized donors. These bound charges set up a potential across the junction though external potential is not applied. The effective capacitance is non-linear function of the voltage developed. For this it is imperative to study the effective capacitance associated with junction. The junction capacitance is defined as differential flow of charge per unit change in voltage. When voltage across junction is changed depletion layer width changed as a nonlinear function of voltage and the capacitance is called depletion layer capacitance and is given by,

$$C = \frac{dq}{dv}$$

(2.2)

Just like depletion layer the voltage developed changes the number of minority carriers on either side of junction. The capacitance developed due to contribution of minority carrier density is called diffusion capacitance and is given by,
\[ C = \frac{1}{4} K_c \frac{N_d N_a}{N_d + N_a} (V - V_{fb}) \]  \quad (2.3)

where \( N_d \) and \( N_a \) are donor and acceptor charge density, \( V \) is voltage developed and \( V_{fb} \) is the flat band potential. Diffusion capacitance is associated with rearrangement of minority carrier density when junction voltage is changed. This capacitance is significant in forward bias and has small contribution in reverse bias whereas depletion capacitance is significant in reverse bias [42]. Anderson obtained expression for heterojunction assuming absence of interface state. Junction capacitance per unit area of an abrupt anisotype heterojunction is given by,

\[ C = \frac{q \varepsilon_n \varepsilon_p N_a N_p}{2(\varepsilon_n N_a + \varepsilon_p N_p)} (V_{fb} - V)^{-1/2} \]  \quad (2.4)

\( N_p \) and \( N_n \) are donor and acceptor concentrations and \( \varepsilon_n \) and \( \varepsilon_p \) are dielectric constants of n- and p-type semiconductors respectively. \( V_{fb} \) is flat band potential, \( V \) is the applied voltage and \( q \) is the electronic charge. When \( C \propto V^{-1/2} \) the abrupt anisotype heterojunction is formed. For graded junction, \( C \propto V^{-1/3} \) [42].
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