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References
3.1 Introduction

The interest in semiconductor-liquid junction has evolved parallel to the development of solid state junctions [1-5]. Although there have been both academic advances and market growth in photovoltaic technology in recent years, there remains a need for increased efficiency, lower cost processing and increased process yields. Many binary and ternary semiconductors on variety of substrates have been prepared by the spray pyrolysis technique [6-8]; the more important examples being CdS, CdSe, CdTe, CuInS$_2$, CuInSe$_2$, Bi$_2$CdS$_4$, CdIn$_2$Se$_4$ etc. The ternary chalcogenide materials have been studied for the development of photoelectrochemical solar cells for the sustained and efficient capture of solar energy conversion [9]. Cadmium Indium Selenide (CdIn$_2$Se$_4$) has received very little attention as a prospective material for photoelectrochemical solar cells [10]. The growth and structural, optical and thermoelectric properties of deposited CdIn$_2$Se$_4$ are reported by Hady et al. [11]. The optical absorption, photoelectric properties, photoluminescence study, vibrational scattering of CdIn$_2$Se$_4$ thin films have been reported by several authors [12-18].

In this chapter, experimental arrangement of spray pyrolysis technique is described in detail. The optimized preparative parameters for the deposition of CdIn$_2$Se$_4$ thin films from aqueous medium are reported. The structural, optical and electrical properties of the films are studied and discussed.

3.2 Experimental

3.2.1 Thin film deposition

3.2.1.1 Spray pyrolysis technique

The schematic diagram of the spray pyrolysis technique is shown in fig. 3.1. It mainly consists of spray nozzle, rotor for spray nozzle, liquid level monitor, hot plate, gas regulator valve and air tight fiber chamber.
a) Spray nozzle

It is made up of glass and consists of the solution tube surrounded by the glass bulb. With the application of pressure to the carrier gas, the vacuum is created at the tip of the nozzle and the solution is automatically sucked in the solution tube and the spray starts.

b) Rotor for spray nozzle

Stepper motor based microprocessor controller is used to control the linear simple harmonic motion of the spray nozzle over the required length of the hot plate.

c) Liquid level monitor

The spray rate at a fixed air pressure depends upon the height of the solution measured with respect to the tip of the nozzle. The arrangement for the change in height of the solution forms the liquid level monitor.

d) Hot plate

The iron disc, with diameter 16 cm and thickness 0.7 cm to which 2000 Watt heating coil is fixed is used as a hot plate. Maximum temperature of 500 ± 5°C can be obtained with this arrangement. The chromel-alumel thermocouple is used to measure the temperature of the substrates and is fixed at the center of the front side of the iron plate. The temperature of the hot plate is monitored with the help of temperature controller (Aplab made Model No. 9601).

e) Gas regulator valve

The gas regulator valve is used to control the pressure of the carrier gas flowing through the gas tube of the spray nozzle. A glass tube of length 25cm and of diameter 1.5 cm is converted into gas flow meter. Since air pressure depends upon the size of the air flow meter, the air flow meter should be calibrated from nozzle to nozzle.

f) Air tight fiber chamber
Since the number of toxic gases is evolved during the thermal decomposition of sprayed solution, it is necessary to fix the spraying system inside with air tight fiber chamber. An air tight fiber chamber of the size (8 feet³) was fabricated. The fiber avoids the corrosion of the chamber. The outlet of chamber is fitted to exhaust fan to remove the gases evolved during thermal decomposition.

![Schematic diagram of spray pyrolysis technique](image)

**Fig. 3.1 Schematic diagram of spray pyrolysis technique**
3.2.1.2. Substrate cleaning

Substrate cleaning is the process of breaking bonds between substrate and contaminant without damaging the substrates. In thin film deposition process substrate cleaning is an important factor to get reproducible films as it affects the smoothness, uniformity, adherence and porosity of the films. The substrate cleaning process depends upon the nature of substrate; degree of cleanliness required and nature of contaminate to be removed. The common contaminates are grease, adsorbed water, air born dust, lint, oil particles etc. The micro slides supplied by Blue Star of dimensions 7.5 cm \times 2.2 \text{ cm} \times 0.1 \text{ cm} have been used as substrates. The following process has been adopted for cleaning of substrates:

1) The substrates were washed with detergent solution ‘Labolene’ and then with water.
2) These substrates were boiled in chromic acid for five minutes.
3) Substrates were cleaned with double distilled water.
4) These substrates were kept in NaOH solution to remove the acidic contaminations.
5) The substrates were again washed with distilled water and cleaned ultrasonically.
6) Finally substrates were dried in alcohol vapours.

3.2.1.3 Preparation of solutions

I) Ingredients used to deposit fluorine doped tin oxide thin films

Initial ingredients used to deposit FTO thin films are as follows

i) Stannic chloride pentahydrate (SnCl\(_4\). 5H\(_2\)O), A. R. grade supplied by Himedia Pvt. Ltd. Mumbai.


iii) Oxalic acid ((COOH)\(_2\).2H\(_2\)O) supplied by s. d. fine chem., Ltd. Mumbai.

iv) Propane 2-ol (Iso-propyl alcohol) (CH\(_3\)CHOHCH\(_3\)) A. R. grade supplied by Merck Ltd. Germany.
II) Ingredients used to deposit CdIn$_2$Se$_4$ thin films

Initial ingredients used to deposit CdIn$_2$Se$_4$ thin films in aqueous medium are as follows:

i) A. R. Grade cadmium chloride (CdCl$_2$) supplied by s. d. fine chem., Ltd. Mumbai.

ii) A. R. Grade indium trichloride (InCl$_3$) supplied by Merck chem. Ltd. Germany

iii) A. R. Grade selenourea [CH$_4$N$_2$Se] supplied by Merck chem. Ltd., Germany.

III) Ingredients used to deposit CdTe thin films

Initial ingredients used to deposit CdTe thin films in aqueous medium are as follows:

i) A. R. grade cadmium chloride (CdCl$_2$) supplied by s. d. fine chem., Ltd. Mumbai.

ii) A. R. grade tellurium dioxide (TeO$_2$) supplied by s. d. fine chem., Ltd. Mumbai.

3.2.1.4 Deposition of fluorine doped tin oxide thin films (FTO)

100 cc of 2 M stannic chloride solution was prepared in doubled distilled water and 14.285 gm of ammonium fluoride was dissolved in it, to obtain the 20% doping concentration of fluorine. A few drops of oxalic acid were added in it for removal of whitish precipitate from the above mixture, 10 cc solution was taken as a precursor solution and 10 cc of propane 2-ol was added in it which gives the 20 cc spraying solution. The final solution was sprayed through the specially designed glass nozzle at the spray rate of 5 cc per minute. The substrate temperature was maintained at 475$^\circ$C. It is found that, the conducting glasses have 10-20 $\Omega$/cm$^2$ sheet resistance and about 90% transparency.

3.2.1.5 Deposition of CdIn$_2$Se$_4$ thin films

Thin films of CdIn$_2$Se$_4$ were deposited by spraying equimolar solutions of (CdCl$_2$), (InCl$_3$) and CH$_4$N$_2$Se onto preheated amorphous and FTO coated
glass substrates in appropriate volumes so as to obtain Cd:In:Se ratio as 1:2:4. The spray rate was kept constant at 2cc min\(^{-1}\) and 28 cm nozzle to substrate distance for each deposition. Ambient air was used as a carrier gas to atomize the spraying solution. The films were allowed to cool to room temperature and taken out of the deposition chamber to preserve them in dark dessicator. The variation of different substrate temperatures (240-300\(^\circ\)C) and solution concentrations (0.005-0.02 M) were studied.

**3.2.1.6 Deposition of CdTe thin films**

Thin films of CdTe were deposited by spraying equimolar solutions of (CdCl\(_2\)) and (TeO\(_2\)) onto preheated amorphous and FTO coated glass substrates in appropriate volumes of Cd:Te in stoichiometric proportion as 1:1. The precursor solution to be sprayed was prepared by appropriate volumetric proportion of CdCl\(_2\) and TeO\(_2\) dissolved in hydrazine hydride, NH\(_4\)OH and HCl being used to form clear spraying solution with optimized pH value. Hydrazine hydride served as reducing agent to obtain Te\(^{2-}\) ions. When the droplets of spraying solution reach to the preheated substrates, well adherent and pale brown colored films of CdTe are formed. The spray rate was kept constant at 1.5 cc min\(^{-1}\). Influence of substrate temperature (225-300\(^\circ\)C), solution quantity (20-40 cc), pH (10-11) and solution concentrations (7.5-15 mM) on to their physico-chemical properties of CdTe thin films.

**3.2.2 Fabrication of photoelectrochemical (PEC) solar cell**

The construction of practical photoelectrochemical cell (PEC) for the conversion of sunlight into electricity (or chemical energy), the most important fact is the long-term stability of cells that show reasonable conversion efficiency. PEC cell consists of a semiconductor photoelectrode, an electrolyte and a counter electrode as shown in fig. 3.2. The distance between photoelectrode and counter electrode is 0.5cm. When both electrodes are immersed in the electrolyte, band bending of semiconductor photoelectrode may occur. The transfer of electrons from the electrolyte can takes place only in the energy region of conduction band, while hole transfer can take place in
the region of the valance band. Such a transfer can occur between two states of the same energy, one empty and other filled. Under illumination, electron-hole pairs are generated in the depletion layer and separated by the electric field present at the interface. The incident energy of photon should be greater than the band gap energy of the semiconductor. The electron-hole pairs generated in the bulk of the semiconductor are essentially lost through recombination. If a positive potential is applied to the n-type semiconductor photoelectrode and illuminated, electron-hole pairs are generated and separated electrons rise to the top of the conduction band and holes in the valence band. This process sets up a counter field under open circuit conditions. The counter field is at its maximum and is the open circuit voltage; $V_{oc}$ is given by the equation

$$V_{oc} = \left( \frac{nKT}{e} \right) \ln \left[ \frac{I_{ph}}{I_o} + 1 \right]$$

(3.1)

On the other hand, the counter electrode is being in the same electrolyte, the photovoltage acts as a driving force for electrons to move under short circuit conditions from semiconductor electrode to the counter electrode and a regenerative cell is formed and is shown in fig 3.3.

Short-circuit current is given by the equation.

$$I_{sc} = \int_0^\infty Q_c (1 - R_n) (1 - e^{-\alpha \omega}) e \times n_{ph} EdE$$

(3.2)

where, $Q_C$ is collection efficiency of a semiconductor material,

$R_n$ is reflectance of a semiconductor photoelectrode,

$\alpha$ is absorption coefficient of semiconductor photoelectrode,

$\omega$ is thickness of semiconductor photoelectrode,

$e$ is electronic charge,

$n_{ph}$- number of photons in the energy range $E$ and $E+dE$

Thus $I_{sc}$ is dependent on many semiconductor photoelectrode parameters.

The electrons promoted to the conduction band drift towards the interior, while the holes, the minority carriers, come to the surface of semiconductor. Here, they encounter the reduced form of redox couple in the solution. The
component is oxidized by holes, transported to the counter electrode and therefore gets reduced. This reduction is driven by the external connection from the semiconductor.

![Diagram](image)

**Fig. 3.2 A typical electrochemical photovoltaic cell**

![Diagram](image)

**Fig. 3.3 Current flow and energy level diagram for n-semiconductor PEC cell**
3.2.2.1 Requirements of photoelectrochemical (PEC) cells

Following are the requirements, expected for achieving good performance of the PEC cell:

a) Semiconductor photoelectrode

One of the important factors in developing a PEC solar cell is the selection and preparation of semiconducting material which reflects the changes in the electrical properties of a cell. Semiconductor photoelectrode used in PEC cell for the achievement of good performance should satisfy the following basic requirements.

(a) The band gap of the material should be such that maximum part of solar spectrum is used. Most of the visible part of solar energy reach the earth’s surface is centered in the range 1.65-3.5 eV. Therefore, very wide band gap semiconductors are not suitable.

(b) The efficiency of the cell should be high which depends upon absorption coefficient, band gap, diffusion length, conductivity, recombination, surface states etc.

(c) The electrode must be stable against corrosion when placed in the specific redox electrolyte. Low band gap semiconductors generally get easily corroded. Therefore, the choice of semiconductor materials is a very important for PEC solar cells.

(d) Thickness should be large enough to absorb all the incident radiation.

(e) Series resistance $R_s$ should as small as possible and shunt resistance $R_{sh}$ should be large enough, ideally $R_s = 0$ and $R_{sh} = \infty$.

(f) Cost of manufacturing and efficiency should be acceptable.

b) Electrolyte

Another important parameter in the PEC cell is the electrolyte. Electrolyte consists of oxidized species and reduced species. These species are
ionic species which helps to transfer the photogenerated holes from photoelectrode to counter electrode. The energy levels in the electrolyte are similar to the concept of energy states in the solid and $E_{\text{f-redox}}$ is equivalent to the Fermi energy level of the semiconductor. When the semiconductor electrode is immersed into the electrolyte, the equilibrium situation is achieved by the electron exchange at the surface; the Fermi level of the semiconductor adjusts with each other which produces a barrier height depends on the nature of the solution species and particular semiconductor.

Electrolyte properties requisite for the PEC cells are:

(a) Reduction–oxidation reactions should occur appropriate to the semiconductor band edges.
(b) Charge transfer rates of oxidized and reduced species at both semiconductor and counter electrode should be high or effective.
(c) Oxidized, reduced species and supporting electrolyte concentration in solvent should be adequate to reach required current densities.
(d) The electrolyte should have minimum optical absorption.
(e) It should be non-corrosive to electrodes.
(f) Toxicity, reactivity and cost should preferably below.

\section*{c) Counter electrode}

The counter electrode must satisfy regenerative processes, the electrolyte species are oxidized at counter electrodes giving no net chemical change in the composition of electrolyte. The requirements of counter electrode for better performance in the PEC cell are:

a. The counter electrode should be chemically inert.

b. The charge transfer between the counter electrode and redox species in the electrolyte must be fast.
c. When a counter electrode is immersed into the electrolyte, the half cell potential of the electrode should match with that of the half cell potential of the semiconductor electrode.
d. The counter electrode must be cheaper; platinum and graphite are the most commonly used.

### 3.2.2.2 Butler-Volmer relation

The dependence of the current density, across metal solution interface, on the potential $V$ can be explained by well known Butler-Volmer relation [19],

$$ I = I_0' \left[ e^{\beta F / RT} - e^{-\beta F / RT} \right] $$

(3.3)

where, $I_0'$ is the equilibrium current density,
- $V$ is the over voltage,
- $R$ is the universal gas constant,
- $F$ is Faraday constant, and
- $\beta$ is symmetry factor

The same relation is applicable to semiconductor electrolyte junction. The important parameter in equation 3.3 is the symmetry factor $\beta$. In an electrode electrolyte system, there is hill shaped potential energy barrier even in the absence of an electric field, as shown in the fig. 3.4.

**Fig. 3.4 Construction of potential-energy-distance profile by consideration of the potential energy changes produced by varying $X_1$ and $X_2$**
This barrier has to do with the atomic movements in bond stretching which are a prerequisite of processes such as chemical reactions and diffusion of atoms and ions. An electrical field modifies the existing potential barriers. The modification is such that only a fraction \((1- \beta)\) of the input electrical energy \(qV\) turns up in the change of activation energy and hence in the rate expression. This is because the atom movements necessary for the system to reach the barrier peak are only a fraction of total distance over which potential difference extends.

### 3.2.3 Development of n-CdIn\(_2\)Se\(_4\)/p-CdTe heterojunction solar cells

A high quality thick layer of p-CdTe were grown on to FTO coated glass substrates by taking equimolar solutions of cadmium chloride and tellurium dioxide by spray technique. The optimized preparative parameters were 250°C substrate temperature, 0.01 M solution concentration, 1.5 cc/min spray rate, 30 cc quantity of solution and pH 10.5. FTO layer acts as a back contact. Over this layer appropriate thin layer of n-CdIn\(_2\)Se\(_4\) with optimized parameters (substrate temperature=280°C, solution concentration=0.0125M, spray rate=2 cc/min, quantity=56 cc) was grown by spray pyrolysis technique. Then antireflecting coating of zinc oxide was applied on to the n-CdIn\(_2\)Se\(_4\) layer. FTO layer acts as a back contact. Front contacts were made with the help of silver paste. This developed heterojunction solar cell was further tested for their current-voltage, capacitance-voltage, power output characteristics and spectral response.
References