## Chapter 3

**PREPARATION OF CuInS\textsubscript{2} THIN FILMS STARTING FROM CBD Cu\textsubscript{x}S AND CBD CdS**

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Chapter 3

PREPARATION OF CuInS$_2$ THIN FILMS STARTING FROM CBD Cu$_x$S AND CBD CdS

3.1 Introduction

It is well known that a major reason that limits popular usage of PV devices today is high cost. Apart from material cost, cost of production is very decisive factor determining the cost of solar cells. As far as thin film solar cells are concerned, material consumption is very low. Hence for lowering the cost, adoption of low cost thin film deposition techniques is inevitable. Also the technique adopted should be simple, reproducible, suitable for large area deposition and should not create any environmental or health problems.

Recently, there has been considerable interest in developing CuInS$_2$ thin films using various techniques. This chapter describes preparation and characterization of CuInS$_2$ thin films prepared using two new techniques developed in our lab.

Although CBD is one of the prominent techniques for the preparation of binary compounds, when we prepare ternary films using this method, it is very difficult to control various parameters and produce films with good stoichiometry. In our lab, we tried to prepare CuInS$_2$ films using CBD technique. We were able to prepare uniform, adherent films. However, XPS and ICP analysis indicated that In content in the film is very low, and hence we concluded that the film was most probably the binary compound Cu$_x$S, with traces of indium.
Hence we selected another route to prepare CuInS\(_2\) thin films and reported the preliminary results of our attempt [1]. For this, Cu\(_x\)S films were prepared using CBD technique and In was introduced into this film by thermal diffusion. For this, 99.999\% pure In was evaporated onto the Cu\(_x\)S film and was subsequently annealed in vacuum. This is quite a new technique and is simple and low-cost as the binary film Cu\(_x\)S is prepared using the low-cost CBD technique at room temperature itself. Moreover, there is no requirement of vacuum for Cu\(_x\)S deposition. Earlier, Yukawa et al. have reported electrodeposited Cu\(_x\)S thin films as the first step for the preparation of CuInS\(_2\) films by two-stage electrodeposition and to the best of our knowledge, this is the only technique similar to ours’ and reported earlier [2].

Brief description of CBD and vacuum evaporation techniques used in the present work is given below.

3.2 Deposition techniques

3.2.1 Chemical bath deposition (CBD)

Although CBD has been used as a technique for preparing films since 1910, utilization of this technique to deposit thin films of semiconductors in photovoltaic devices started very recently. Later CBD became a useful method for the deposition of thin films of compound semiconductor materials, which are sulfides and selenides of some metals. Many of these compound semiconductors were identified as good candidates for PV device fabrication. Many groups started working in this area as this technique involves only low-tech process and is suitable for deposition of large area films.
3.2.1.1 Chemical aspects of CBD

Like any other thin film deposition process, CBD involves three main steps: 1) production of appropriate atomic, molecular or ionic species, 2) their transport to substrate through a medium and, 3) condensation on substrate, either directly or via a chemical reaction, to form a solid deposit. Formation of a thin film takes place via nucleation and growth process [3].

According to solubility product principle, in a saturated solution of a weakly soluble compound, ionic product is a constant at a given temperature. If the ionic product exceeds the solubility product, precipitation occurs. It is necessary to eliminate spontaneous precipitation in order to form a thin film by a controlled ion-by-ion reaction. Concentration of the ions in the solution can be controlled by adding appropriate complexing agents and by adjusting the temperature and pH of the solution. When precipitation is controlled, the compound gets deposited on the substrates, kept immersed in the reaction bath. Growth kinetics depend on concentration of ions, their velocities, as well as nucleation and growth processes on the immersed surfaces. Effect of these parameters on film deposition process is discussed in detail in references [4] & [5].

CBD process has several advantages over other methods of thin film deposition, which can be listed as follows. 1) the technique is simple and requires very low capital investment, 2) the process may be easily adapted to large area processing at low fabrication cost, 3) in many cases, films may be deposited at room temperature itself upon a variety of substrates, 4) thickness of the deposited layers may be readily controlled by variation of deposition time 5) does not require vacuum, 6) does not require high purity materials for film deposition, 7) can be operated by a technition for large scale production 8) no reaction involving gas or vapor.
3.2.2 Vacuum Evaporation

This is probably the most popular technique used for thin film deposition. There are several review articles/books giving detailed descriptions of this technique [6-9].

In this process, material is heated to a high temperature in a vacuum chamber so that a large number of atoms or molecules leaves the surface of the material and gets deposited on the substrate. Because of low pressure in the chamber, most evaporated molecules suffer no collisions with residual gas molecules and travel in straight lines to the substrate. Small amounts of active residual gases can cause contamination and can change significantly the properties of the evaporated film.

Rate of free evaporation of vapor molecules from clean surface of unit area in vacuum is given by

\[ N_e = 3.513 \times 10^{22} \frac{p_e}{\sqrt{MT}} \text{ molecules/(cm}^2\text{)(sec)} \]  

(3.1)

where \( p_e \) is the equilibrium vapor pressure (in Torr) of the evaporant under saturated-vapor conditions at a temperature T, and M is the molecular weight of the vapor species. Rate of deposition of vapor on substrate also depends on source geometry, its position relative to substrate and condensation coefficient.

Thermal evaporation can be achieved directly or indirectly (via a support) by a variety of physical methods such as resistive heating, flash evaporation, arc evaporation, exploding-wire technique, laser evaporation, RF heating, and electron bombardment heating. In the present work, we used resistive heating method for the evaporation of indium.

This method consists of heating the material using resistively heated filament or boat, generally made of refractory metals such as W, Mo, Ta and Nb, with or without ceramic coatings. Choice of supporting material is primarily determined by
evaporation temperature and resistance to alloying and/or chemical reaction with vaporant. Vapor sources of various types, geometries and size can easily be constructed or obtained commercially. Details of dependence of growth, structure and adhesion of evaporated films etc with different deposition parameters are described in many references [7-9].

Part-1 CuInS_2 thin films from CBD Cu_xS

3.3 Experimental Details

3.3.1 Brief review of Cu_xS films

Cu_xS (x = 1-2) thin films have recently received considerable attention due to numerous technological applications in the area of PV devices. At room temperature, Cu_xS in bulk form, is known to exist in five stable phases: chalcocite (Cu_2S), djurleite(Cu_{1.93}S), digenite(Cu_{1.5}S), anilite(Cu_{1.75}S), and covellite(CuS). Mixed phases are also known in the intermediate compositions [10] This material (especially Cu_2S) possesses extremely favorable properties which make it suitable for large-scale photovoltaic applications, particularly in combination with CdS. Low production cost and material availability make this cell suitable for large scale PV applications. Cu_xS/CdS thin film solar cell has been the most extensively investigated thin film photovoltaic system. Main problem regarding this cell is degradation in presence of moisture. Interestingly, Partain et al., observed that degraded Cu_xS/CdS solar cells could be recovered by annealing in presence of H_2 and air [11].

Kimihioko et al. studied electrical conductivity and phase transition of copper sulfide [12]. Various techniques such as vacuum evaporation [13], spray pyrolysis [10], sputtering [14], and chemical bath deposition [15,16], were
employed to prepare Cu$_x$S thin films. Fatas et al. prepared Cu$_x$S from a bath containing 1M CuSO$_4$, 1M sodium acetate, 1M thiourea and 7.4 M TEA. A. J. Varkey reported deposition from bath containing CuCl, NaCl and hydroxylamine hydrochloride solutions, using EDTA as a complexing agent. Rezig et al. prepared Cu$_x$S films by conversion of spray deposited CdS by ion exchange [17].

3.3.2 Preparation of Cu$_x$S films using CBD

In the present work, Cu$_x$S films were prepared using CBD technique. Bath used for this contained 1M Cupric Chloride (10 ml), 2M Thiourea (10 ml) and 5ml Ammonia solution (25%). Here triethanolamine (TEA) was used as complexing agent. pH of final solution was maintained at 9.8. Microscope glass slides (75mm x 25mm x 1.25mm) were used as the substrate. These slides were washed thoroughly first using soap solution and then using chromic acid. Microscopic impurities were removed using ultrasonic cleaning. These cleaned glass slides were dipped vertically in the bath. Four slides were dipped at a time and time of deposition was 15 minutes at room temperature. No stirring was given during deposition. Films obtained were uniform and golden in colour. Multiple dip films were prepared for the present work. Thickness of the double-dip sample, measured using Stylus method, was found to be 0.1 micron.

It is reported that annealing in hydrogen and other reducing atmospheres causes an increase in stoichiometry of Cu$_x$S layers whereas exposure to or annealing in air always causes oxidation, with a deterioration in the stoichiometry and a decrease in the resistivity [13]. Hence, prepared Cu$_x$S samples were dried and were immediately transferred to vacuum chamber of the coating unit to deposit thin films of indium.
3.3.3 Evaporation of indium

The Cu_xS samples were masked 5mm from the four edges using teflon-tape (were having an area ~ 25mmx15mm) and were loaded in the vacuum chamber. Required amount of 99.999% pure indium was weighed accurately using a microbalance and was placed in the Mo boat which was at a distance of 14cm from the substrates. Chamber was evacuated to a pressure of \(<10^{-5}\) torr. The boat was resistively heated until whole In was evaporated and deposited on surface of Cu_xS film. In this case, thickness of the In layer was varied as 200Å, 400Å, and 600Å and for this, 20 mg, 40 mg and 60 mg of indium were used respectively.

3.3.4 Annealing of the bilayer film

The In/Cu_xS bilayer film was then annealed in vacuum at 300 °C for 2 hours. Annealing chamber was made of a glass tube over which nichrome wire was wound uniformly along the entire length. This tube was heated by passing a current through the nichrome wire. Temperature was controlled by adjusting current using a variac. Two samples were placed well inside the tube, at a time to ensure uniform heating. The tube was then placed in the vacuum chamber and was evacuated to a pressure of \(<10^{-5}\) torr. Temperature on the sample surface was measured using chromel-alumel thermocouple, kept in contact with the samples. In all the cases, heating and cooling rate was 3°C/minute.

After annealing, it was found that entire indium diffused into Cu_xS film, forming a uniform film with a dark brown appearance. No indium layer was left behind at the surface after annealing. New preparation method developed for CuInS_2 thin films can be summarized as follows:
I Step: Preperation of Cu₃S

1M CuCl₂ (10 ml) + 2M CS(NH₂)₂ (10 ml) + 5 drops TEA
+ 5ml NH₃ solution (25%) at pH 9.8, time of deposition- 15 mts at room temp

II step: deposition of indium over Cu₃S film by vacuum evaporation

III Step: annealing bilayer Cu₃S/In for 120 mts., in vacuum

3.4 Results and Discussion

3.4.1 XRD Analysis

XRD is one of the most powerful methods for exploring structure of materials. It can be used to determine phase content in many minerals and materials. It requires no elaborate sample preparation and is essentially non-destructive. Generally, it gives a whole range of information about crystal structure, orientation, crystallite size, composition (with the help of standards), defects and stresses in thin films. Experimentally obtained diffraction pattern of sample is compared with Joint Council Powder Diffraction (JCPDS) data for standards. This gives information of different crystallographic phases, relative abundance and preferred orientations. From width of the diffraction peak, average grain size in the film can also be estimated.

Interplanar spacing d was calculated from X-ray diffraction profiles using the formula,

\[2d \sin \theta = n\lambda \]  

(3.2)
where $\theta$ is the Bragg angle and $n$ is order of the spectrum, $\lambda$ is the wavelength of X-rays. Using $d$-values the set of lattice planes $(h \, k \, l)$ were identified from standard data and lattice parameters are calculated using following relations.

For the tetragonal systems,

$$\frac{1}{d^2} = \frac{(h^2 + k^2)}{a^2} + \frac{l^2}{c^2} \quad \text{(3.3)}$$

and for hexagonal systems,

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \quad \text{(3.4)}$$

where $a$ and $c$ are lattice parameters. Grain size ($L$) can be evaluated using Scherrer’s formula,

$$L = \frac{k\lambda}{\beta \cos \theta} \quad \text{(3.5)}$$

where $k$ is a constant, which is nearly equal to one and $\beta$ is “full width at half maximum (FWHM)”, usually measured in radians.

In the present study, XRD analysis was done using Rigaku (D.Max.C) X-Ray Diffractometer, with Cu K\(\alpha\) ($\lambda = 1.5405 \, \text{Å}$) radiation and a Ni filter operated at 30kV and 20mA. XRD studies of as-prepared Cu\(_x\)S sample revealed that films were not crystalline. So these samples were annealed at different temperatures 200°C and 300°C for two hours in rotary vacuum. Even after annealing, there was no improvement in the crystallinity as revealed by the XRD analysis (Fig.3.1a, b & c)

CuInS\(_2\) films obtained after diffusing indium layer thickness of 200Å, 400 Å and 600 Å are named CIII(2), CIII(4) and CIII(6) respectively. All these films were annealed at 300 °C for 120 minutes in order to diffuse indium. Fig.3.2 shows XRD pattern obtained for films after diffusing indium into Cu\(_x\)S film. When indium film
of thickness 200Å was diffused into Cu_xS layer [sample CIII(2)]. 100% intensity peak (112) of CuInS_2 appeared in the spectrum (Fig.3.2a). Second peak corresponding to (220) of CuInS_2 at 2θ = 46° has also become visible. But when thickness of the indium layer was increased to 400Å [Sample CIII(4)], peaks became more prominent as evident from Fig.2b. This clearly indicated that annealing Cu_xS samples after giving a thin layer of indium over the surface improved the crystallinity and lead to formation of CuInS_2 phase in the film. On further increasing the indium layer thickness to 600 Å [sample CIII(6)], there is no appreciable change in the XRD pattern (Fig.3.2c). Hence for latter studies, thickness of the indium layer was fixed at 400 Å, annealing temperature at 300°C and annealing time at 120 minutes. Calculated 'd' values are listed in Table-1. One can see that predominant plane of the CuInS_2 is (112)

Table-3.1
X-ray data of CuInS_2 thin film

<table>
<thead>
<tr>
<th>2θ</th>
<th>D Å</th>
<th>hkl</th>
<th>Standard 'd' Value (Å)</th>
<th>Variation (Δd )</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.8</td>
<td>3.2</td>
<td>112</td>
<td>3.19</td>
<td>+0.01</td>
</tr>
<tr>
<td>32.66</td>
<td>2.74</td>
<td>200</td>
<td>2.74</td>
<td>0</td>
</tr>
<tr>
<td>46.00</td>
<td>1.97</td>
<td>220</td>
<td>1.95</td>
<td>+0.02</td>
</tr>
</tbody>
</table>

Grain size of the film was calculated from peak at 2θ =27.8° using Scherrer’s formula D = 0.9λ /βcosθ where D is diameter of the crystallites forming the film, λ is the wavelength of the CuKα line, β is FWHM and θ is the Bragg angle. Grain size value obtained is 32 nm.
Fig. 3.1 XRD pattern of Cu$_x$S films: a) as-prepared Cu$_x$S; 
b) annealed at 200°C; c) annealed at 300°C

Fig. 3.2 XRD pattern obtained after diffusing indium into the Cu$_x$S film: 
a) CIII(2); b) CIII(4); c) CIII(6)
3.4.2 Optical Absorption Studies

The most direct and the simplest method for probing the band structure of semiconductors is to get optical absorption spectrum. Absorption is expressed in terms of a coefficient $a(hv)$ which is defined as relative rate of decrease in light energy $L(hv)$ along its propagation path: [18]

$$
\alpha = \frac{1}{L(hv)} \frac{d[L(hv)]}{dx} \quad \text{(3.6)}
$$

absorption coefficient $\alpha$ is related to the energy gap $E_g$ according to the equation

$$\alpha h\nu = A(h\nu - E_g)^n \quad \text{(3.7)}
$$

where $A$ is a constant, $h$ is Plank’s constant, $\nu$ the frequency of incident beam and $n$ is equal to $\frac{1}{2}$ for a direct gap and 2 for an indirect gap.

Absorption spectra of samples were recorded using UV-VIS-NIR spectrophotometer (Hitachi 3410) model. Fig.3.3a and 3.3b show variation of the absorption coefficient with photon energy ($h\nu$) of incident light for samples Cu$_x$S and CIII(4). From the plot of $(\alpha h\nu)^2$ against photon energy ($h\nu$) (Fig.3.4a), a direct band gap of 1.86 eV was obtained for the Cu$_x$S film which compares well with published data [19]. But due to the sensitivity of optical properties to the exact structure and composition of layers, there is a wide variation in the reported results regarding the bandgap in Cu$_x$S films.

$(\alpha h\nu)^2$ Vs $h\nu$ plot of the sample CIII(4) (Fig 3.4b) shows a direct band gap of 1.41 eV which can be attributed to p-type CuInS$_2$ films [20]. This is lower than band gap value reported for crystals of CuInS$_2$ [21]. Such lower band gap has been reported earlier for CuInS$_2$ thin films [22-23].
Fig. 3.3. Variation of $a$ with photon energy ($hv$): (a) Cu$_2$S; (b) ClIII(4)
Fig. 3.4. \((\alpha h
\nu)^2\) vs. \(hv\) plot for samples: a) CuS; b) CIII(4)

3.4.3 Electrical properties

3.4.3.1 Sheet resistance

Sheet resistance of CuS and CIII(4) was measured at room temperature using Keithley I-V measurement system. Silver electrodes were painted on top surface of the film keeping a distance of 5mm between the electrodes. Sheet resistance of as-prepared CuS (sample A) was 1.267 kΩ/□. After indium diffusion,
sheet resistance decreased to 119.5 $\Omega/\square$. Using hot probe technique, it was observed that both Cu$_x$S and CuInS$_2$ samples were p-type.

### 3.4.3.2 Hall measurement

Conductivity type, mobility and density of charge carriers of samples were investigated at room temperature using Hall measurement set up made by MMR Technologies Inc. having MP350 power supply to vary magnetic field and K50 temperature controller. These parameters were evaluated using Vander Pauw method by four-probe measurement technique [24].

Resistivity, mobility, and carrier concentration of Cu$_x$S and CuInS$_2$ films are given in table-3.2. Resistivity of Cu$_x$S is 19.5 $\Omega$- cm and this decreases as amount of In in the film increases. When 400Å of indium was introduced by thermal diffusion, mobility and carrier concentration became 5.10 cm$^2$/V-s and 4.77x10$^{20}$ cm$^{-3}$ respectively. On increasing the In layer thickness to 600 Å, slightly increased carrier mobility, with no significant change in carrier concentration, was observed (6.84x10$^{20}$ cm$^{-3}$ and 7.47 cm$^2$/V-s respectively). Mobility values obtained are greater than the values reported earlier for p-type CuInS$_2$ films, prepared using two source evaporation, (0.2 cm$^2$/V-s and 3.2 cm$^2$/V-s) [25], but is less than the mobility value reported for p-type crystals (15 cm$^2$/V-s) [26]. Type of carriers in all these films was found to be holes.

#### Table-3.2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity ($\rho$) $\Omega$- cm</th>
<th>Mobility ($\mu$) cm$^2$/V-s</th>
<th>Carrier density (cm$^{-3}$)</th>
<th>Hall coeff. cm$^3$/C</th>
<th>Type of carriers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_x$S</td>
<td>19.5</td>
<td>0.152</td>
<td>$2.11 \times 10^{18}$</td>
<td>2.96</td>
<td>holes</td>
</tr>
<tr>
<td>CuII(4)</td>
<td>$2.56 \times 10^{-3}$</td>
<td>5.10</td>
<td>$4.77 \times 10^{20}$</td>
<td>0.0137</td>
<td>holes</td>
</tr>
<tr>
<td>CuII(6)</td>
<td>$1.22 \times 10^{-3}$</td>
<td>7.47</td>
<td>$6.85 \times 10^{20}$</td>
<td>$9.11 \times 10^{-3}$</td>
<td>holes</td>
</tr>
</tbody>
</table>
3.3.4 Energy Dispersive X-ray analysis (EDAX)

Here the sample is irradiated by electron beam and emitted x-rays is directly measured using energy dispersive X-ray spectrometer, producing a spectrum of counts versus energy. As each x-ray photon enters the detector, it produces photoelectrons, whose total number is linearly proportional to the energy of the entering X-rays. Charge collected from detector is very small since only a few hundreds or thousands of electrons are produced by each X-ray photon. Hence it is amplified by a pre-amplifier whose output voltage is proportional to the X-ray energy [27].

In the present work, we used this technique to confirm presence of indium in the CuInS₂ samples. EDAX spectrum of CIII(2) and CIII(4) samples showed presence of Cu, In and S in the samples and is shown in Fig.3.5 and Fig.3.6 respectively. For CIII(4) sample, indium peak intensity is high, showing a higher concentration of indium in the film. Concentration of sulfur is also higher in this film than that for CIII(2) sample. There is one peak corresponding to Si, which is from the glass substrate used for the preparation of the films.

3.3.5 Scanning Electron Micrograph (SEM)

SEM is the most widely used instrument for obtaining microstructural and surface features of thin films. A finely focused electron beam is scattered over the surface of the specimen and secondary electrons emanating from the specimen are used for imaging the surface. Since secondary electrons come from the surface layer, picture obtained is a faithful reproduction of surface features. Secondary electron imaging can provide high-resolution imaging of fine surface morphology. Quantitative and qualitative chemical analysis information can also be obtained using Energy Dispersive X-ray spectrometer (EDS) with the SEM [28].
Fig. 3.5 EDAX spectrum of CIII(2)

Fig. 3.6 EDAX spectrum of CIII(4)
SEM was used to find out uniformity of CuInS$_2$ films prepared. Fig.3.7 gives the SEM micrograph of the same area of CIII(4) sample with two different magnifications. Films are uniform over a large area with defined grains and no pinholes or cracks are found. There are some agglomerated areas in this film, which may be due to segregated Cu$_{x}$S impurity phase. A similar feature was obtained for Cu-rich sprayed samples [29].

### 3.3.6 Electron Spectroscopy for Chemical analysis (ESCA)

ESCA is one of the major techniques for studying thin films. It provides information on the elemental composition of a sample as well as on the chemical state of the observed atoms.

In this technique, sample is irradiated using electromagnetic radiation of energy $h\nu$. Due to photoelectric effect, electrons are emitted with kinetic energy

$$E_{\text{kin}} = h\nu - E_B - \phi$$

where $E_B$ is binding energy of a particular electron shell and $\phi$ is the sample work function. Photoelectrons are energy-analyzed in the spectrometer and, since photon energy is known, one can determine characteristic binding energies of valence electrons coming from different elements present in the sample. Depending on the energy of incident radiation, this technique is called either “Ultra Violet Photoelectron Spectroscopy (UPS)” for lower photon energies ($\leq 50$eV) or “X-ray Photoelectron Spectroscopy (XPS)” for higher photon energies ($\geq 1$keV) [30].

Chemical composition of film was evaluated using XPS technique in the present work. XPS spectra of samples were recorded using an ULVAC-PHI unit (model: ESCA 5600 CIM) employing argon ion sputtering (Voltage = 3 kV, Raster size = 3x3 mm$^2$, pressure $10^{-8}$ mbar ) Al K$\alpha$ X-ray (1486.6eV) with a beam diameter of 0.8mm and power of 400W was used as the incident beam.
Fig. 3.7 SEM of CIII(4) sample at magnifications: (a) 10K; (b) 20K
XPS technique gives information about chemical state of elements present in surface layer only (of thickness few hundred angstroms). In order to know variation in stoichiometry as well as chemical state all along the thickness of the samples, we performed XPS depth profile of all these samples. Here the presence of the elements Cu, In, S, O, & Si was checked along the sample thickness. For this, measurements on sample surface was taken first and then the sample was etched slowly using Ar ion sputtering for 3 minutes to remove approximately 100Å thickness of the film. Again the sample was checked for these elements (this is called one cycle). This process was repeated till substrate surface was reached.

In this fashion, sample was etched for about 100 cycles and the depth wise presence of the elements plotted together for sample CIII(4) is shown in Fig.3.8. Binding energies of the elements are represented along the X-axis. The spectra were calibrated against shifts due to machine errors, using the C 1s line (of the hydrocarbon contamination in the films) as the standard. (Binding energy of C 1s is 284.5 eV). After 40 cycles, peaks corresponding to O, and Si could be seen, which indicates the beginning of the glass substrate (SiO₂). So the film is present up to this, after which the glass substrate starts. Hence from this cycle, only peaks corresponding to O and Si were obtained.

From (Fig.3.8), it is obvious that indium diffused uniformly throughout the depth of the sample and is present up to the glass substrate. At the surface, there is one peak at binding energy value 531.7 eV corresponding to O, which is due to surface contamination. Its atomic concentration decreases along depth of the sample as evident from Fig.3.9b. It can also be seen that all these elements have diffused slightly into the glass substrate, probably during the annealing of the films at 300°C for 2 hours. Binding energy values obtained are 952.5 eV & 932.5 eV for Cu 2p₃/₂
& Cu 2p\textsubscript{1/2}; 452.5 eV & 444.6 eV for In 3d\textsubscript{5/2} & In 3d\textsubscript{3/2}; and 162 eV for S 2p, which are in agreement with reported values of CuInS\textsubscript{2} \cite{23,31,32}. Similar binding energy values were obtained for Cu levels in CuInS\textsubscript{2} \cite{33} and they also noticed no significant shift in binding energy for Cu levels from metallic state.

Fig.3.9 shows depth profile of atomic concentrations of Cu, In & S for samples C\textsc{iii}(2), C\textsc{iii}(4) & C\textsc{iii}(6). For sample C\textsc{iii}(2), Cu and In are not uniformly present throughout the depth of the sample (Fig.3.9a). Concentration of In is maximum at surface and gradually decreases to very small value (7.5%) near the substrate. After applying Ar ion sputtering for 10 minutes, it was found that Cu/In ratio in the film is equal to 1 (28.4% each). At the same time in the depth, the ratio increases to 5.58. Although S was uniformly present throughout the depth of the sample, its atomic percentage was only around 10%. So it becomes clear that indium layer of thickness 200Å is not sufficient to produce films of uniform composition.

Fig.3.9b shows depth profile of atomic concentration of sample C\textsc{iii}(4). From the figure, it is clear that Cu, In and S are present almost uniformly from the surface to the substrate. Cu/In ratio in the film is 1.29 Here also sample exhibits a deficiency of sulfur. Atomic concentration of sulfur is almost half the value expected for stoichiometric CuInS\textsubscript{2}. This may be probably due to the preferred sputtering of group VI elements such as sulfur and selenium. Also sensitivity factors of Cu and S are very different. Similar problem was observed in the case of Cu\textsubscript{2-x}Se films prepared in our lab. In that case, for applying correction, Cu/Se ratio was measured with a standard sample of CuSe powder and the correction factor was found to be 2 \cite{4,5}.

Percentage atomic concentration of sample C\textsc{iii}(6) is shown in Fig.3.9c. Here again the concentration of Cu & In is not uniform throughout depth of the
sample. Cu/In in that film is 1.5 after etching for 20 minutes. Percentage of sulfur is lower than that of CIII(4).

In the case of sample CIII(4), there is slight decrease in atomic concentration of S at the surface and in the bulk. This may be due to the fact that S has a high vapor pressure and hence during deposition process, mainly at the stage of indium diffusion, some S may escape from the surface of the film.

From Fig.3.9a, b&c, it is evident that all above samples contain a good percentage of oxygen. This is due to the fact that after coating indium, all samples were annealed at 300°C for 2 hours in rotary vacuum. To reduce the oxygen content in the films, for later preparations, all the samples were annealed in high vacuum ($\sim 10^{-5}$ torr). XPS spectra of such samples showed nearly zero percentage concentration of oxygen throughout the depth of the sample (Fig3.16b).
**Fig. 3.9a**, At. conc. % vs sputter time graph of sample CIII(2)

**Fig. 3.9b**, At. conc. % vs sputter time graph of sample CIII(4)
Fig. 3.9c, At.% vs sputter time graph of sample CIII(6)
3.5 Sulfurization of CuInS$_2$ films

From the results of above analyses, one can understand that it is possible to prepare CuInS$_2$ thin films by evaporating indium over chemical bath deposited Cu$_x$S films and subsequently annealing the films. The best result was obtained for sample prepared by diffusing 400Å indium [sample CIII(4)]. The XRD spectrum matched well with standard data. XPS depth profile of the sample showed presence of Cu, In and S throughout the depth. However, atomic concentration of S was less than that of stoichiometric CuInS$_2$. In order to increase the S content in the films, samples were annealed in sulfur vapor in an open tube at different temperatures for different durations. Again these films were characterized using the above techniques. Following section deals with the annealing of CIII(4) sample and the characterization.

3.6 Experimental Details

Sulfur-annealing chamber had two horizontal tubular sections; the upper one was “sample chamber” and the lower one was “sulfur-powder-chamber”. Resistive heating could be given to both sections separately. Sample chamber could be heated to 300°C and sulfur chamber to 200°C. Two thermocouples were used to measure temperature of these two chambers separately.

Sulfur chamber was maintained at a temperature of about 150°C to obtain a sulfur flux during the process. Temperature of samples was varied as 100°C, 130°C, 160°C, 200°C, 250°C & 300°C keeping the annealing time constant at 1 hour. Deposition of sulfur in cold regions at the end of the chamber indicated existence of sulfur flux. When sample was annealed at temperatures below 200°C, a thin layer of S gets deposited on film surface.
When annealed at temperatures greater than 200 °C, there is a clear reduction in thickness of the film. Hence after several trials, temperature of the sample source was fixed at 200 °C and the films were annealed for different time periods. These films were again characterized.

3.7 Results and Discussions

3.7.1 XRD

XRD spectrum of samples annealed at 200 °C in sulfur atmosphere for ½ hour, 1 hour, 1½ hours and 2 hours (named as S½, S1, S1½ and S2 respectively) are illustrated in Fig.3.10. After annealing for ½ hour, peak corresponding to (112) plane became sharper, showing an improvement in the crystallinity of the films. However, on increasing the annealing time, intensity of the peak decreased.

Grain size of these films was found to increase with sulfur annealing time. For the S1 & S2 samples, grain size values were 65 nm & 118 nm respectively.
In order to clarify effect of S annealing on resistivity and mobility of CuInS$_2$ films, Hall effect measurement was carried out. Table-3.3 shows results of samples annealed for different time. Resistivity increased for samples annealed for a time up to 1 hour. After that, resistivity again decreased. Variation of mobility and carrier
Concentration with annealing time is represented in Fig. 3.11. It is evident that annealing in sulfur vapor decreases mobility and carrier density.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity (( \rho )) Ω cm</th>
<th>Mobility (( \mu )) cm²/Vs</th>
<th>Carrier density (cm⁻³)</th>
<th>Hall coeff. cm³/C</th>
<th>Type of carriers</th>
</tr>
</thead>
<tbody>
<tr>
<td>C111(4)</td>
<td>2.56×10⁻³</td>
<td>5.10</td>
<td>4.77×10²⁰</td>
<td>0.0137</td>
<td>holes</td>
</tr>
<tr>
<td>S1/2</td>
<td>6.52×10⁻³</td>
<td>2.95</td>
<td>3.25×10²⁰</td>
<td>1.92×10⁻²</td>
<td>holes</td>
</tr>
<tr>
<td>S1</td>
<td>0.2067</td>
<td>3.22</td>
<td>9.37×10¹⁸</td>
<td>0.6659</td>
<td>holes</td>
</tr>
<tr>
<td>S11/2</td>
<td>6.52×10⁻³</td>
<td>2.59</td>
<td>3.25×10²⁰</td>
<td>0.0192</td>
<td>holes</td>
</tr>
<tr>
<td>S2</td>
<td>1.12×10⁻²</td>
<td>1.93</td>
<td>2.89×10²⁰</td>
<td>2.16×10⁻²</td>
<td>holes</td>
</tr>
</tbody>
</table>
3.7.3 Optical Properties

Fig. 3.12 shows transmission graph of Cu$_2$S film. As prepared CuInS$_2$ (CIII(4)) and films annealed in sulfur atmosphere. As prepared CuInS$_2$ sample (CIII(4)) has transmission around 12%. On annealing, transmission increases slightly for all samples except the one annealed for 1½ hours. For the sample annealed for 2 hours, transmission corresponds closely to the transmission of Cu$_2$S films. This may be due to formation of Cu$_2$S impurity phases in the sample. There is also a decrease in atomic concentration of indium in the sample as indicated by XPS analysis (section 3.7.5).
Absorption spectra of these samples are illustrated in Fig.3.13 and variation in optical band gap with annealing time is represented in Fig.3.14. There is an increase in band gap with increase in annealing time. This may be due to the increase in grain size of the films with annealing time, as revealed by XRD analysis.
Figure 3.13 Absorption spectrum of annealed samples.

Figure 3.14 Variation in the optical band gap with annealing time.
3.7.4 Photosensitivity measurements

Photoelectrical properties of these samples were investigated by measuring photosensitivity (S) defined as,

\[ S = \frac{(R_D - R_L)}{R_D} \times 100 \]  \hspace{1cm} (3.9)

where \( R_D \) is dark resistance of the film, \( R_L \) is the resistance of the film under illumination. Photosensitivity is measured for different samples annealed in sulfur atmosphere for different periods. These samples were irradiated with white light of intensity 40mW/cm\(^2\). An I-R filter was used to remove heat content in the radiation. Variation of S with annealing time is represented in Fig.3.15. Photosensitivity is high for the samples annealed in sulfur atmosphere for 30 to 60 minutes.

![Graph showing photosensitivity vs. annealing time](image)

**Fig.3.15. Photo response of films annealed for different time**

3.7.5 XPS analysis

Accurate and quantitative analysis of atomic percentage in this compound is difficult to obtain using XPS because binding energies and sensitivity factors of
Cu2p and S2p are very different. ($S2p = 162$ eV, $s = 0.44$ and $Cu2p_{3/2} = 932.6$ eV, $s = 5.3$) [23]. However, a qualitative analysis of CuInS$_2$ samples annealed in sulfur atmosphere for 1 hour and 2 hours was analysed using XPS. Atomic percentage (at %) vs. sputter time graph of these samples is depicted in Fig. 3.16. Table 3.4 gives approximate at % of Cu, In and S in these films. Also ratio of atomic concentration of Cu to In and the ratio of the total (Cu+In) in the film to the S content in the film is shown in the table. From this, it follows that when samples are annealed for 1 hour, there is an improvement in sulfur content in the film. (increases from 21% to 33%) (Fig.3.16a). On increasing annealing time to 2 hours, there is no significant increase in S content compared to the one annealed for 1 hour (Fig.3.16b). On the other hand, there is decrease in atomic concentration of In. Regarding oxygen, from Fig3.16 it is very clear that at % in the film is nearly 0% for 1 hour annealed sample. But, at % of oxygen is 3% for the sample annealed for 2 hours.
Fig. 3.16a, At. conc. % vs sputter time graph of sample CIII(4), annealed for 1 hour

Fig. 3.16b, At. conc. % vs sputter time graph of sample CIII(4), annealed for 2 hours
Table-3.4
Atomic percentage from XPS analysis

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Cu%</th>
<th>In%</th>
<th>S%</th>
<th>Cu/In in the film</th>
<th>(Cu+In)/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI\text{II}(4)</td>
<td>37</td>
<td>27</td>
<td>21</td>
<td>1.37</td>
<td>3.04</td>
</tr>
<tr>
<td>CI\text{II}(4)S1</td>
<td>40</td>
<td>27</td>
<td>33</td>
<td>1.48</td>
<td>2.03</td>
</tr>
<tr>
<td>CI\text{II}(4)S2</td>
<td>41</td>
<td>23</td>
<td>33</td>
<td>1.78</td>
<td>1.93</td>
</tr>
<tr>
<td>Standard CuInS\text{2} powder[23]</td>
<td>12</td>
<td>36</td>
<td>52</td>
<td>0.33</td>
<td>0.923</td>
</tr>
</tbody>
</table>

The BE values of these samples are given in Table-3.5. There are no appreciable change in the BE values due to S annealing.

Table-3.5
Binding Energy values of samples (in eV) annealed in sulfur atmosphere.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu 2p_{3/2}</th>
<th>Cu 2p_{1/2}</th>
<th>In 3d_{5/2}</th>
<th>In 3d_{3/2}</th>
<th>S 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI\text{II}(4) as prepared</td>
<td>952.5</td>
<td>932.6</td>
<td>452.5</td>
<td>445</td>
<td>162</td>
</tr>
<tr>
<td>S1</td>
<td>951.8</td>
<td>932.5</td>
<td>452.5</td>
<td>445</td>
<td>162</td>
</tr>
<tr>
<td>S2</td>
<td>952.5</td>
<td>932.5</td>
<td>452.5</td>
<td>445</td>
<td>162</td>
</tr>
</tbody>
</table>

3.8 Conclusion

We prepared CuInS\text{2} thin films using a new and low cost technique. The films obtained were characterized using different techniques. Even though XRD
peaks were clearly indicating the formation of CuInS$_2$ compound, XPS analysis indicated that the films are deficient in sulfur. In order to increase sulfur content, films were annealed in sulfur atmosphere for different times. There is an increase in atomic concentration of sulfur due to annealing up to one hour. But this could not be increased above 33%. There is reduction in the at % of In with increase in the annealing time and about 3% of Oxygen is present in samples annealed for two hours.

**Part-II CuInS$_2$ thin films from CBD CdS films**

With an aim of fabrication of CuInS$_2$/CdS solar cells, we tried another new procedure for the preparation of CuInS$_2$ thin films. In the earlier part of this chapter, we saw that it is possible to prepare CuInS$_2$ thin films by thermally diffusing indium into the Cu$_x$S layer. If we can convert top layer of a sufficiently thick CdS into Cu$_x$S, and then convert it into CuInS$_2$, CuInS$_2$/CdS solar cells can be fabricated in an easy way. Metallurgical junction will be formed within the CdS film thereby avoiding atmospheric contamination of the interface. With this intention, we tried to prepare CuInS$_2$ films using CBD CdS films.

**3.9 Experimental Details**

Preparation of CuInS$_2$ is a three-stage process, the first stage is preparation of CdS using chemical bath deposition; second is preparation of Cu$_x$S from CdS and the third stage is preparation of CuInS$_2$ by evaporating indium on Cu$_x$S and subsequently annealing the samples.
i) Preparation of CdS thin films

Among various deposition techniques used for preparation of CdS films, chemical deposition is rather simple and inexpensive. It yields stable, uniform, adherent and hard films with good reproducibility. These films are found to be near-stoichiometric [34].

For the present case, CdS thin films are prepared on glass substrate as well as on SnO$_2$ coated glass plates using CBD. Details of this technique are mentioned in section 3.2.1. Basic principle involved is the chemical reaction between cadmium chloride and thiourea in aqueous solution. Chemical deposition of CdS films requires slow release of Cd$^{2+}$ ions in aqueous medium. This is achieved by forming a complex with triethanolamine (TEA). Cd$^{2+}$ ions released from the Cd(TEA)$_2$ complex and S$^{2-}$ ions from thiourea condense on the substrate. Thus film formation is an ion-by-ion condensation process. pH of the solution is controlled by adding ammonia solution.

Chemical equation representing the above reaction is,

$$\text{CdCl}_2 + 2\text{TEA} \rightarrow 2\text{Cl}^- + \text{Cd(TEA)}_2$$

$$\text{Cd(TEA)}_2 + \text{CS(NH}_2)_2 + \text{H}_2\text{O} \rightarrow \text{CdS + TEA + O = C (NH}_2)_2$$

For preparing the bath, 10ml cadmium chloride (1M) was mixed with 4ml of TEA. A thick white precipitate was formed. To this, 25% ammonia solution was added slowly, till the precipitate just dissolved completely. Then 10 ml of thiourea was added. pH of the solution is around 10.5. Well-cleaned substrates were dipped in this solution and beaker containing the solution was kept in hot air oven with temperature stabilized at 80$^0$C. No stirring was given. The arrangement was kept undisturbed for 75 minutes for deposition. Single-dipped and double-dipped films were prepared for the present study.
ii) Preparation of Cu$_x$S thin films

Cu$_x$S thin films were prepared by converting CBD CdS films using the well-known Clevite process, which is widely used for Cu$_x$S formation in high efficiency Cu$_x$S/CdS solar cells [13]. Clevite process for polycrystalline cell fabrication was developed during 1970's and the most notable feature of this process is fabrication of the Cu$_x$S layer in CdS substrates by ion exchange. In addition, ion exchange process affects only the cations so that sulfur content of CdS remains intact [35].

In the present case, CdS samples were dipped in 0.5M CuCl$_2$ solution (50 ml) for different periods, (<1 minute) until yellow colour of CdS film turns black. When CdS is dipped in the CuCl$_2$ solution, Cd ions are replaced by Cu ions and thus Cu$_x$S is formed. Reaction can be represented by the following equation

$$\text{CdS} + x\text{CuCl}_2 \rightarrow \text{Cu}_x\text{S} + \text{CdCl}_2$$

To terminate the reaction, and to remove unreacted CuCl$_2$, sample was rinsed in distilled water kept at room temperature. Excess water was removed and the sample was dried in hot air.

As the time of dipping was increased in order to convert the CdS film completely to Cu$_x$S, cracks are developed in the film. Also, the Cu$_x$S film gets detached from the substrate. To reduce time of dipping, temperature of the CuCl$_2$ solution was increased to 95°C. Then the time of dipping was optimized as 3 seconds for the complete conversion of the double dipped CdS film to Cu$_x$S.

iii) Evaporation of In on Cu$_x$S

Pure indium (99.999%) was deposited on Cu$_x$S samples prepared as mentioned above. Thickness of the indium layer was varied as 100Å, 400Å, and 600Å. Then these films were annealed at 300°C in vacuum (10^{-5} torr) for two hours. Evaporated indium completely diffused into Cu$_x$S film to form CuInS$_2$. 


3.11 Results and Discussions

3.11.1 XRD Analysis

Before conversion into a Cu_xS layer, CdS samples were investigated using X-ray diffraction studies. Fig 3.17 represents the XRD pattern of CdS and the Cu_xS film formed by converting the CdS film. Table-3.6 Shows the angular position θ, corresponding inter planar distances and (h k l) values of these films. Diffraction pattern of the as-prepared CdS film exhibits peaks corresponding to cubic CdS phase. When CdS is converted to Cu_xS, comparison of observed X-ray diffraction spectra with standard JCPDS data revealed that the Cu_xS film consists of many phases. Most of the lines were identified as those of chalcocite. Hence it was quite impossible to give an estimation of composition (ie, value of x) of these films. Similar problem was faced by Rezig et al. who reported structural and optical properties of topotaxially-grown Cu_2S [17]. They also observed that Cu-rich chalcocite phase transforms into minor phases, when let under air-ambient atmosphere. This transformation is enhanced in the case of thin layers and it is argued that copper migration to the surface is the origin of this formation.

When 100Å indium is evaporated onto the Cu_xS film, there is slight variation in XRD pattern and it shows presence of CuInS_2 phase in the sample. When In layer thickness is increased to 400 Å, CuInS_2 peak appears in the XRD pattern, which shows formation of chalcopyrite CuInS_2 phase with preferred orientation along the (112) plane. In addition to peaks corresponding to CuInS_2, some Cu_xS peaks are also present. But on increasing In layer thickness to 600 Å, all Cu_xS peaks disappear and CuInS_2 peaks become prominent as shown in Fig 3.18. The d values are listed in Table 3.7.
Table 3.6 – XRD analysis of CdS and Cu\textsubscript{x}S

<table>
<thead>
<tr>
<th>Sample</th>
<th>(2\theta)</th>
<th>(d) Å</th>
<th>(h k l)</th>
<th>Phase identified</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Observed</td>
<td>Standard</td>
<td></td>
</tr>
<tr>
<td>CdS</td>
<td>26.65</td>
<td>3.342</td>
<td>3.360</td>
<td>(111) CdS (c)</td>
</tr>
<tr>
<td></td>
<td>43.75</td>
<td>2.067</td>
<td>2.058</td>
<td>(220) CdS (c)</td>
</tr>
<tr>
<td></td>
<td>27.95</td>
<td>3.189</td>
<td>3.16</td>
<td>(101) CdS (H)</td>
</tr>
<tr>
<td></td>
<td>29.35</td>
<td>3.040</td>
<td>3.04</td>
<td>(102) CuS</td>
</tr>
<tr>
<td>Cu\textsubscript{x}S</td>
<td>31.0</td>
<td>2.882</td>
<td>2.89</td>
<td>(200) CuS\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td>32.5</td>
<td>2.752</td>
<td>2.74</td>
<td>(103) Cu\textsubscript{1.96}S</td>
</tr>
<tr>
<td></td>
<td>46.25</td>
<td>1.961</td>
<td>1.98</td>
<td>(060) Cu\textsubscript{2}S</td>
</tr>
</tbody>
</table>

Fig. 3.17. XRD pattern of CdS and Cu\textsubscript{x}S films
Fig. 3.18  XRD of CuInS$_2$ sample
Table 3.7

X-ray analysis data of CuInS₂

<table>
<thead>
<tr>
<th>d(Å)</th>
<th>(hkl)</th>
<th>Phase</th>
<th>d(Å)</th>
<th>(hkl)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.32</td>
<td>(111)</td>
<td>CuS₂</td>
<td>3.21</td>
<td>(112)</td>
<td>CuInS₂</td>
</tr>
<tr>
<td>3.21</td>
<td>(112)</td>
<td>CuInS₂</td>
<td>2.97</td>
<td>(103)</td>
<td>CuInS₂</td>
</tr>
<tr>
<td>3.03</td>
<td>(103)</td>
<td>CuInS₂</td>
<td>2.77</td>
<td>(004)</td>
<td>CuInS₂</td>
</tr>
<tr>
<td>2.78</td>
<td>(200),(004)</td>
<td>CuInS₂</td>
<td>1.97</td>
<td>(204)</td>
<td>CuInS₂</td>
</tr>
<tr>
<td>2.06</td>
<td>(220)</td>
<td>CuS₂</td>
<td>1.67</td>
<td>(312),(116)</td>
<td>CuInS₂</td>
</tr>
<tr>
<td>1.97</td>
<td>(220)</td>
<td>CuInS₂</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.11.2 XPS Analysis

XPS analysis of the CuInS₂ films was carried out by investigating Cu, In, S and C spectra, using MgKα line (1253.6 eV) for excitation. (Fig.3.19). Analysis was repeated by removing layers of the film by Ar ion sputtering for 1 minute, 2 minutes and 3 minutes. Binding energy values were corrected with reference to C 1s peak at 284.5 eV. Peaks corresponding to Cu, In & S are clearly visible at binding energies 933.01 eV & 953.4 eV for Cu 2p₃/₂ & Cu 2p₁/₂, 444.75 eV & 452.42 eV for In 3d₅/₂ & In 2d₃/₂, and 161.12 eV for S 2p respectively. These values are in agreement with the binding energy values of different elements in CuInS₂; which confirms formation of CuInS₂ phase.
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Fig. 3.19 XPS of CuInS₂ sample
3.12 Trial for the fabrication of CuInS$_2$/CdS solar cell

In the above section, we saw that it is possible to prepare CuInS$_2$ thin films by the thermal diffusion of indium into Cu$_x$S films, prepared from CBD CdS films. As mentioned earlier, CuInS$_2$/CdS heterojunction can be fabricated in a quite simple way if the top layer of a sufficiently thick CdS film can be converted into CuInS$_2$. This process has the advantage that it will avoid atmospheric contamination at the interface.

We tried to fabricate CuInS$_2$/CdS cell using the above-mentioned method. SnO$_2$ coated glass plates were used as the substrate and it will serve as the back electrode of the cell. Over this, CdS films of thickness 1.5μm (triple-dipped) were deposited using CBD. These films were then dipped in CuCl$_2$ solution kept at a temperature of about 90°C for 3 seconds so that top layer is converted to Cu$_x$S. Then 600Å indium is evaporated over this film and is annealed at 300°C for 2 hours. Indium uniformly diffused into the film to form CuInS$_2$ layer at the top and hence CuInS$_2$/CdS structure was fabricated. Silver was used as the top electrode. The I-V characteristic of the cell was measured at an intensity of 40mW/cm$^2$ (Fig.3.20). This junction gave a voltage of 480mV; but there was no significant current.

Low value of the photocurrent points toward the limitations of the preparation process. In this method, there is a chance of shorting during the dipping process for the preparation of Cu$_x$S film due to rapid diffusion of highly mobile copper ions through the imperfections in the CdS layer. Also, there may be an inhomogeneous pattern of growth of Cu$_x$S layer due to the sudden interruption of reaction as soon as the desired thickness is reached. In addition, this process lacks control of stoichiometry.
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3.13 CONCLUSION

CuInS$_2$ thin films were prepared using CBD CdS film and were characterized. Junction was fabricated by converting the top layer of CdS to CuInS$_2$. Although open circuit voltage of this junction was quite measurable, current was very feeble.
References


