CHAPTER 8

POLYOL ASSISTED SYNTHESIS OF CuInS$_2$ THIN FILMS
AND CHARACTERISATION

8.1 INTRODUCTION

Synthesis of nano or micro materials with specific structure and morphology has grown considerable attention in field of material science in recent years (Qi et al 2000, Gudiksen et al 2001, Heath et al 1993, Iijima et al 1991 and Keis et al 1999). The study on these materials confirms that the controls of properties of these materials and the manners in which they organize greatly affect the products optical and electronic properties (Li et al 1999, Huang et al 2001, Peng et al 2000 and Lu et al 2002). Hence the analysis of formation, nucleation and growth mechanism will helps to understand and control there processes at the atomic level through chemistry employed.

CuInS$_2$ is a direct band gap of 1.5eV, ternary compound material with chalcopyrite structure. It can also be used in photo chemical applications because of its band gap matches will the solar spectrum (Thiel et al 1982). The most successful synthetic method developed for producing colloidal semiconducting nano crystal involve the use of co-ordinating solvents or surface ligands showing long hydrocarbon chains to inhibit particle growth.

Although much effort have been devoted to remove the growth inhibiting reagents including several ligand exchange stages by mild chemical
treatment, complete removal of coordinating solvent or surface ligands has proven to be difficult. A need therefore exists for the fabrication of free-surfactant, ternary or quaternary chalcogenide nanocrystals redispersible in low boiling point solvent required for the subsequent film forming stage. Indeed, the size and surface charge control is extremely difficult as long as conventional reactions are employed such as the reaction between metallic cations (Cu$^+$, Zn$^{2+}$) and various sources of S$^{2-}$ such as thiourea, thioacetamide. Hence, this chapter proposed a fabrication of CuInS$_2$ thin films in ethylene glycol solvent.

This ternary (CuInS$_2$) chalcogenide dispersed nanoparticles involving high-temperature polycondensation of tailored oxy-hydroxy-thiourea-$M^{n+}$ ($M^{n+}$ = metallic cation) complex precursors.

8.2 MATERIALS AND METHODS

Ethylene glycol assisted CuInS$_2$ thin films are deposited by spray pyrolysis on to glass substrates from aqueous solutions of CuCl$_2$, InCl$_3$, SC(NH$_2$)$_2$ and C$_2$H$_4$(OH)$_2$ using compressed air as the carrier gas. At first, aqueous solutions (10ml) of the salts are prepared, and then they are mixed with appropriate portions in order to have copper to indium molar ratio (Cu/In = 1.25) and (Cu+In)/S fixed to 1 in the solution. The copper (II) chloride and indium (III) chloride are mixed and then thiourea solution is added. The resulting solution is added with C$_2$H$_4$(OH)$_2$ of (10ml). The solutions are prepared by dissolving in de-ionized water. Then the solution is sprayed using spray rates of 2ml/min in air on to glass substrates (2.5×2.5 cm$^2$) heated at different temperatures from 300,350 and 400°C.

The X-ray diffraction (XRD) patterns of sprayed films are recorded using the XPERT-PRO Gonio scan diffractometer with CuK$_{α}$ radiation. The phases are identified using JCPDS data files. The optical transmittance
spectra are recorded in the wavelength range of 300–1100 nm using double beam Beckman Ratio Recording spectrophotometer. The compositional analysis is carried out using energy dispersive X-ray spectroscopy (EDAX).

8.3 RESULTS AND DISCUSSION

8.3.1 Structural Analysis

Figure 8.1 Shows the XRD patterns of CuInS$_2$ thin films deposited in the temperature range 300-400°C prepared by the polyol process. The characteristic peaks corresponding to CuInS$_2$ along (200), (204), (220), (312), (224) and (400) with highly preferred orientation along (112) plane are formed and matched well with the standard JCPDS (75-016). The results indicate that the reduced Cu-In composites react with sulphur ions from thiourea result into mixed phases of In$_2$S$_2$ and CuS.

Well crystallised CuInS$_2$ is obtained by mass transporation or diffusion between the CuS and In$_2$S$_3$ particles that are formed in the solution at higher temperatures (300-400°C) (Lee et al 2009). As the temperature increases, (350 and 400°C) multi-crystalline phases of In$_2$S$_3$, CuS and CuInS$_2$ and other unknown crystalline phases are much reduced in this process, compared to the films formed without ethylene glycol. Hence, this process enhances the quality and purity of CuInS$_2$ thin films.

The CuInS$_2$ thin films obtained from this polyol process are consistial of compactly packed nano-sizes crystals of grain size in the range of 16-72 nm. Calculated from the Debye-Scherrer relation equation 5.2. In the case of undoped samples the average grain size is found to be in the range of 26-125 nm.
8.3.2 Energy Dispersive X-ray Analysis

The Cu, In, S presence is confirmed from the EDAX measurements. (Cu-12.88 at %), (In-35.32 at %) and (S-51.8 at %). No other impurities are detected indicating that film obtained from this process is pure than other processes.

8.3.3 Optical Properties

The optical transmittance spectra of CuInS$_2$ thin films in the wavelength range 300-1100nm are shown in Figure 8.2. About 90% transmission occurs in all the films deposited in the temperature range of 300-
400°C in the UV-visible and IR regions. Improved optical transmittance property is observed in the UV-visible and IR regions than the films obtained by vacuum and thermal evaporation processes (Ben Rabeh et al 2007). The decrease in film thickness (Table 8.1) and increase in temperature have no effect on the transmission properties of the films.

![Diagram showing transmittance spectra](image)

**Figure 8.2** The transmittance spectra of Ethylene glycol assisted CuInS$_2$ film sprayed at different substrate temperatures:
(a) 300°C (b) 350°C (c) 400°C

It is observed that the films have relatively high absorption coefficient in the range $8 \times 10^4$-$2.5 \times 10^4$ cm$^{-1}$ in the UV-visible spectral range. The $\alpha$ value is found to be in the under of $10^4$ cm$^{-1}$. Hence, CuInS$_2$ films prepared in this process can be used as an efficient absorber for solar cells and photovoltaic application in the UV-visible region. But in the IR region $\alpha$ value is found to be very low and 90% light transmission is noticed (Figure 8.2). Hence, CuInS$_2$ thin films prepared by this process in the temperature range can also be used as an IR transmitter.
Figure 8.3  Variation of optical band gap energy values ($E_g$) of sprayed of Ethylene glycol assisted CuInS$_2$ films prepared at different substrate temperatures: (a) 300ºC (b) 350ºC (c) 400ºC

The film prepared without ethylene glycol show $\alpha$ value in the order of $10^5$-$10^6$ cm$^{-1}$, which is found to be quite higher and the spectral dependence of $\alpha$ at such higher values may drastically affect the solar conversion efficiency of solar cells.

Table 8.1 Variation of optical band gap energies ($E_g$) and thickness of Polyol assisted CuInS$_2$ film with temperatures.

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>Ethylene glycol assisted CuInS$_2$</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$E_g$ (eV)</td>
</tr>
<tr>
<td>300</td>
<td>1.61</td>
</tr>
<tr>
<td>350</td>
<td>1.59</td>
</tr>
<tr>
<td>400</td>
<td>1.5</td>
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</tbody>
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For direct band gap semiconductors $\alpha$ is related by the equation 4.2. A plot of $hv$ against $(\alpha hv)^2$ is presented in the Figure 8.3. It is observed that $E_g$ slightly decreases from 1.61-1.5eV as the substrate temperature increases (Table 8.1). It is attributed to the decreases in crystalline defects at the elevated temperatures due to the addition of ethylene glycol. The crystalline state increases even at high temperatures, hence even at 400ºC CuInS$_2$ thin films assisted with ethylene glycol can be used as an efficient solar absorber ($E_g = 1.5$eV). For the films without ethylene glycol $E_g$ value decreases (1.66-1.58eV) and this reduction is due to the presence of unsaturated defects and localised disorder region which increase the density of localised states in the band gap.

### 8.3.4 Transmission Electron Micrograph Analysis

The TEM (Figure 8.4) photographs of CuInS$_2$ thin films prepared by polyol process in the temperature range 300-400ºC. Polyol assisted CuInS$_2$ thin films confirms the presence of nano sized grains of 48-71nm, present inside the film.

![Figure 8.4 TEM Photograph of Ethylene glycol assisted CuInS$_2$ films prepared at 350ºC](image)
8.4 CONCLUSION

The (112) oriented ethylene glycol assisted CuInS₂ thin films are deposited in the temperature range 300-400°C. The addition of ethylene glycol enhances the growth and crystallinity of CuInS₂ thin films. EDAX analysis confirms the presence of Cu, In, S in the films and no other impurity is detected. About 90% of light transmission occurs in the UV-visible and IR regions. The absorption coefficient $\alpha$ is found to be in the order of $10^4$ cm⁻¹. Hence CuInS₂ thin films prepared in this processes can be used as an efficient solar absorber in the UV-visible region and an efficient IR transmitters in the IR regions. TEM image confirms the presence of nano-sized grains inside the films.