# Structural and optical properties of polyol assisted nano-crystalline $CuInS_2$ thin films

C. MAHENDRAN[a*], N. SURIYANARAYANAN[b]

[a]*Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore 641 020, Tamil Nadu, India*
[b]*Department of Physics, Government College of Technology, Coimbatore 641 013, Tamil Nadu, India*

Polyol assisted Copper indium disulphide ($CuInS_2$) is an absorber material for solar cell and photovoltaic applications. In this work, ethylene glycol (10ml) assisted $CuInS_2$ thin films are grown in the temperature range 300, 350 and 400ºC on heated glass substrates. It is observed that the film growth temperature, the ion ratio (Cu/In = 1.25). The XRD patterns confirm that the polyol assisted $CuInS_2$ polycrystalline thin films along (112) preferred plane and in other characteristic planes. Better crystalline qualities are obtained than undoped one. The EDAX results confirm the presence of Cu, In, and S. About 90% of light transmission occurs in the wavelength range 350-1100 nm. The band gap energy increases as the temperature increases from 300-400ºC (1.50-1.61eV). The absorption coefficient α is found to be in the order of $10^4$ cm$^{-1}$.

## 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 [1-5]. 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 [6-9]. 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 [10]. Various deposition methods are available for $CuInS_2$ thin films, among them spray pyrolysis is a cost effective method, that enables the $CuInS_2$ thin films deposition with easer area and good uniformity. In this paper, we present the structural, optical properties of polyol assisted synthesis of $CuInS_2$ thin film using spray pyrolysis.

## 2. Experimental

Ethylene glycol-doped $CuInS_2$ thin films are deposited by spray pyrolysis on to glass substrates from aqueous solutions of $CuCl_2$, $InCl_3$, $SC(NH_2)_2$ and $C_2H_4(OH)_2$ 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 $C_2H_4(OH)_2$ 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 400ºC. The X-ray diffraction (XRD) patterns of sprayed films are recorded using the XPERT-PRO Gonio scan diffractometer with CuKα 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).

## 3. Result and discussions

### 3.1 structural analysis

Fig. 1 Shows the XRD patterns of $CuInS_2$ thin films deposited in the temperature range 300-400ºC 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 resutial in to mixed phases of $In_2S_2$ and CuS.
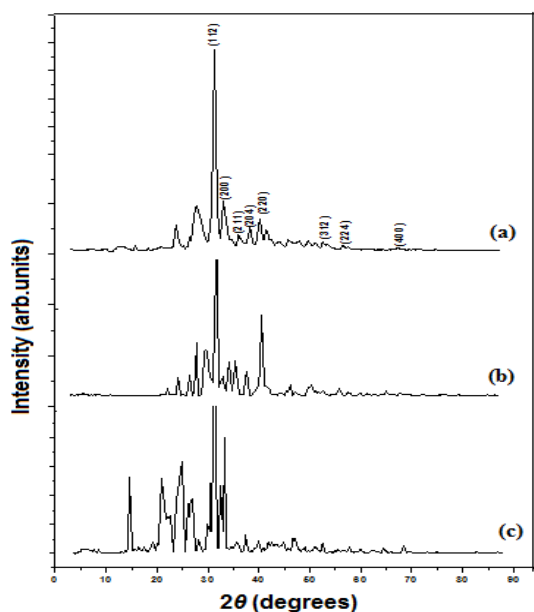
Fig. 1. XRD of sprayed Ethylene glycol assisted CuInS₂
film  sprayed  at different  substrate  temperatures:
(a) 300ºC   (b) 350 ºC   (c) 400 ºC.

Well crystallised CuInS₂ is obtained by mass transporation or diffusion between the CuS and In₂S₃ particles that are formed in the solution at higher temperatures (300-400ºC) [11]. As the temperature increases, (350 and 400ºC) multi-crystalline phases of In₂S₃, CuS and CuInS₂ and other unknown crystalline phases appear in this phases are much reduced in this process, compared to the films formed without ethylene glycol [12].  Hence, this process enhances the quality and purity of CuInS₂ thin films. The CuInS₂ 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

$$D = \frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

$D$ is the grain size in nm, $\lambda$ is the wavelength of CuKα = 1.5404 Å, $\beta$ is the full-width at half-maximum of the peak in radian and $\theta$ is the Bragg angle.  In the case of undoped samples the average grain size is found to be in the range of 26-125nm [12].

### 3.2 EDAX analysis

Fig. 2 Shows the EDAX measurements of CuInS₂ thin films deposited in the temperature range at 350ºC. EDAX analysis confirms the presence of Cu, In, and S. (Cu-12.88 at %), (In-35.32 at %) and (S-51.8 at %).  No other impurities are defected indicating that film obtained from this process is pure than other processes [12].
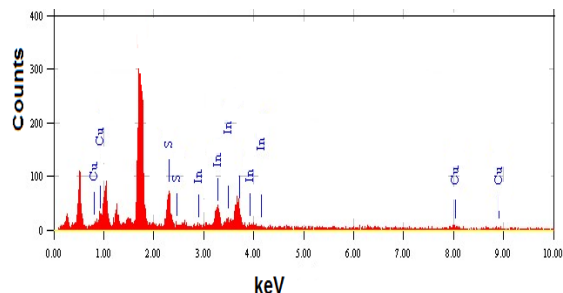


Fig. 2. EDAX spectra of sprayed Ethylene glycol assisted
CuInS₂ film prepared at 350°C.

### 3.3 Optical properties

The optical transmittance spectra of CuInS₂ thin films in the wavelength range 300-1100 nm are shown in Fig. 3. About 90% transmission occurs in all the films deposited in the temperature range of 300-400ºC in the UV-visible and IR regions.
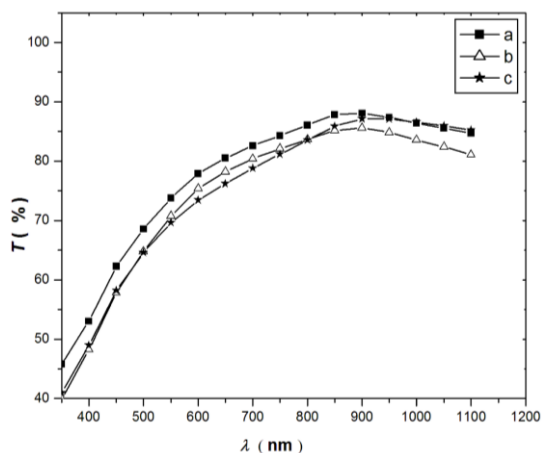


Fig. 3. The transmittance spectra of Ethylene glycol assisted CuInS₂ film sprayed at different substrate temperatures: (a) 300ºC   (b) 350ºC   (c) 400ºC.

Improved optical transmittance property is observed in the UV-visible and IR regions than the films obtained by vacuum and thermal evaporation processes [13].  The decrease in film thickness (Table 1) and increase in temperature have no effect on the transmission properties of the films [12].

Table 1. Variation of optical band gap energies ($E_g$) and thickness of the film with temperature.

| Temperature (°C) | Ethylene glycol assisted CuInS₂ | |
| --- | --- | --- |
| | $E_g$(eV) | Thickness(nm) |
| 300 | 1.61 | 625 |
| 350 | 1.59 | 620 |
| 400 | 1.5 | 616 |

It is observed that the films have relatively high absorption coefficient in the range $8\times10^4$-$2.5\times10^4$ cm$^{-1}$ in the UV-visible spectral range (Fig. 4).
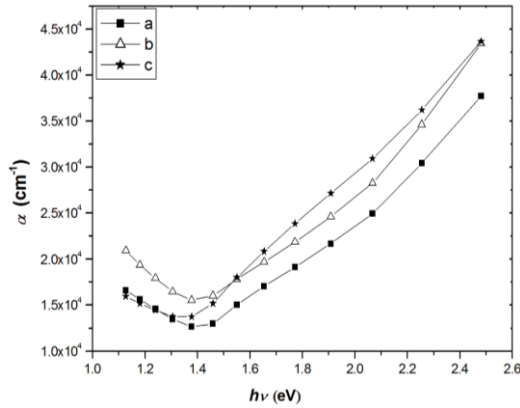


*Fig. 4. The absorption spectra of Ethylene glycol assisted CuInS$_2$ films prayed at different substrate temperatures: (a) 300°C  (b) 350°C  (c) 400°C.*

The α 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 α value is found to be very low and 90% light transmission is noticed (Fig. 3). Hence, CuInS$_2$ thin films prepared by this process in the temperature range can also be used as an IR transmitter. The film prepared without ethylene glycol show α value in the order of $10^5$-$10^6$cm$^{-1}$, which is found to be quite higher and the spectral dependence of α at such higher values may drastically affect the solar conversion efficiency of solar cells [12].  For direct band gap semiconductors α is related by the equation

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad (2)$$

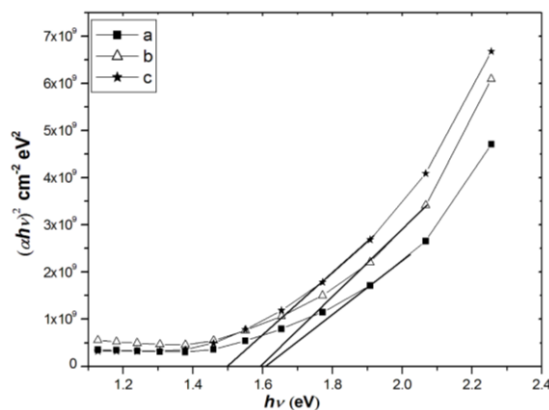$A$ is a constant, $E_g$ is the band gap energy and hν the photon energy.



*Fig. 5. Variation of optical band gap energy(E$_g$) of sprayed of Ethylene glycol assisted CuInS$_2$ films prepared at :(a) 300°C  (b) 350°C  (c) 400°C.*

A plot of hν against $(\alpha h\nu)^2$ is presented in the figure 5. It is observed that E$_g$ slightly decreases from 1.61-1.50 eV as the substrate temperature increases (Table 1).  This is attributed to the development of other crystalline phases and secondary phases during the growth of films (or) the development of very small defects and disorders inside the film. 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 [12].

### 3.4 TEM analysis

The TEM photographs (fig. 6) of CuInS$_2$ thin films prepared by polyol process in the temperature range 300-400 °C.
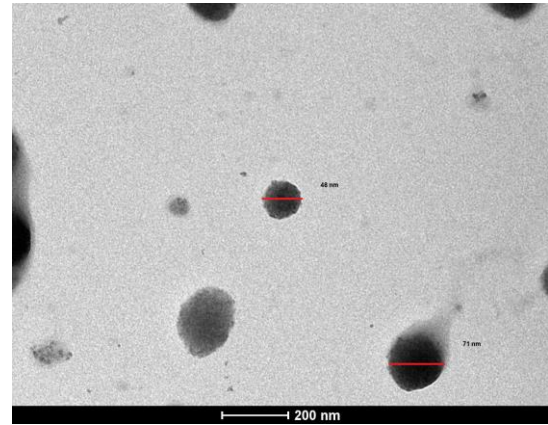


*Fig. 6. TEM Photograph of Ethylene glycol assisted CuInS$_2$ films prepared at 350°C.*

Polyol assisted CuInS$_2$ thin films confirms the presence of nano sized grains of 48-71nm. Present inside the film.

### 4. Conclusions

The (112) oriented ethylene glycol assisted CuInS$_2$ thin films are deposited in the temperature range 300-400°C. The addition of ethylene glycol enhances the growth and crystallinity of CuInS$_2$ thin films.  EDAX analysis confirms the presence of Cu, In, S in the films and no other impurity is defected.  About 90% of light transmission occurs in the UV-visible and IR regions. The absorption coefficient α is found to be in the order of $10^4$cm$^{-1}$. Hence CuInS$_2$ 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. The Zn-doped CuInS$_2$ thin films are composed of compactly packed nano-sized crystals of grain size in the range of 3–5nm [14]. TEM image confirms the presence of nano-sized grains inside the films.

## References

[1] L. Qi, H. C. Olfen, M. Antonietti, Chem. Mater. **12**, 2392 (2000).

[2] M.S. Gudiksen, J. Wang, C.M. Lieber, J. Phys. Chem. B **103**, 4062 (2001).

[3] J. Heath, F.K. LeGoues, Chem. Phys. Lett. **208**, 263 (1993).

[4] S. Iijima, Nature **354**, 56 (1991).

[5] K. Keis, L. Vayssieres, S.–E. Lindquist, A. Hagfeldt, Nanostruct. Mater. **12**, 487 (1999).

[6] M. Li, H. Schnablegger, S. Mann, Nature **402**, 393 (1999).

[7] M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, Science **292**, 1897 (2001).

[8] X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavankch, A. P. Alivisatos, Nature **404**, 59 (2000).

[9] Q. Lu, F. Gao, D. Zhao, Chem. Phys. Lett. **360**, 355 (2002).

[10] F. A. Thiel, J. Electrochem. Soc. **129**, 1570 (1982).

[11] Lee et al, J. Nano sci. Nano technol. **11**, 1 (2011).

[12] C. Mahendran, N. Suriyanarayanan, Physica B **405**, 2009 (2010).

[13] M. Ben Rabeh, M. Kanzari, B. Rezig. Thin Solid Films **515**, 5943 (2007).

[14] C. Mahendran, N. Suriyanarayanan, Mat. Sci. Semi. Proce. **15**, 522 (2012).

_____
*Corresponding author: vcmahe@yahoo.com