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OPTICAL PROPERTIES OF $CuInS_2$ THIN FILMS PREPARED BY SPRAY PYROLYSIS

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Abstract. *Polycrystalline $CuInS_2$ (CIS) absorber films for solar cells were prepared by spray pyrolysis of aqueuos solution of copper chloride, indium chloride and thiourea onto heated glass substrates. By optimizing the spray parameters, such as reducing/increasing the temperature of the substrate and molar ratio of Cu/In in the spraying solution, the optical characteristics of films, which are well matched to the solar spectrum, were identified. In all cases, those CIS thin films were of p-type conductivity. Transmission measurements were performed to examine the optical properties of the films; the absorption coefficient and the optical band gap of the films were calculated by transmission spectra. The absorption spectra of the films showed that this compound is a direct band gap one and its gap varied between 1.30 - 1.78eV. Those thin films were analyzed by X-ray diffraction in order to understand the effect of layers structure on their optical properties.*

I. INTRODUCTION

The $CuInS_2$ (CIS) compound belongs to the family of direct band gap I-III-IV_2 chalcopyrite semiconductor. This compound exhibits a large fundamental absorption coefficient ($\alpha \sim 10^5 cm^{-1}$) and a band gap ($E_g \approx 1.55eV$) optimally close to the peak of the spectral distribution of solar energy [1-5]. No high toxic component is included in this compound semiconductor. The highest reported efficiency of CIS based solar cells is close to 12% [2,3,6-8]. However, at the present time, the main fundamental physical parameters important for practical application of this material and among them, the band gap, are known only approximately. This is primarily caused by the fact that the growth of high-quality CIS chalcopyrite polycrystalline and films encounters technological problems.

There are various methods for the preparation of CIS thin films such as chemical vapour transport [4,9], chemical bath deposition [2,3], solvothermal route [10], wet chemical process [6], sol-gel spin-coating [8], spray pyrolysis [1,5,7,11], etc. Among these methods, spray pyrolysis, used in the present study, does not require vacuum. It is also an inexpensive technique, which has proved its convenience to deposited optically smooth, uniform and homogeneous films over a large area [1,7]. Using this method, the solution is sprayed directly onto the substrate. A stream of gas is used for atomization of the solution through the nozzle. The problem encountered presently in sprayed films due to non-uniform droplet sizes formed at the outlet of the spray nozzle with contribute to the poor grain size and hence lower transparency [13,14].

In this study, we present the optical properties of spray CIS films and their dependence on the preparation conditions as growth temperature and molar ratio of Cu/In in spraying solution.

II. EXPERIMENTAL PROCEDURES

In the present study, hydrated copper chloride $CuCl_2.2H_2O$ (Merck), indium chloride $InCl_3$ (Aldrich) and thiourea $CS(NH_2)_2$ (Merck) were used as initial chemicals. Deionised water was used for solution. Copper to indium molar ratio (R) in the solution was varied in the range of Cu/In = 0.85 - 1.25, while S/Cu ratio was always kept constant (~3.6) for all the cases. The nozzle to substrate distance was about 40 cm. The solution was sprayed onto heated glass substrates at the temperature (T_{sub}) of 320 - 410°C ± 1°C and nitrogen was used as carrier gas [11].

The band gap was determined from optical transmittance spectra in the UV region of 200 - 900 nm as measured with a Carry 100 Spectrophotometer. X-ray diffraction (XRD) patterns were recorded with a PANalytical Diffractometer using the Cu-Kα radiation. The thickness of the films was measured using an Alpha-Step IQ profilometer and its conductivity type was determined by a hot point probe.

III. RESULTS AND DISCUSSION

Structural properties

The effect of the substrate temperature and Cu/In molar ratio in the initial solutions on the crystallinity of CIS thin films was analyzed by the XRD spectra.

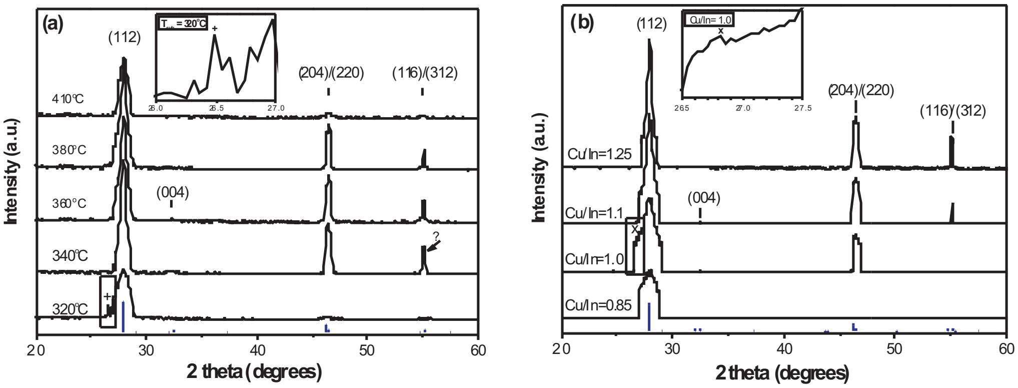

Fig. 1. XRD patterns of CIS thin films (a) deposited at different substrate temperatures (T_{sub} = 320 - 410°C) (b) deposited with various Cu/In in the solution (Cu/In = 0.85 - 1.25))

Fig. 1a shows XRD patterns of CIS films deposited at $T_{sub} = 320$ - 410˚C by using the solution of Cu/In = 1.1 and S/Cu = 3.6. In our research in [11], we reported that the substrate temperature strongly affects on the growth of the CIS films. We identified the extra reflection peaks closed to the (112) peak (marked by '+' in Fig. 1a) indicating poor crystallinity of the films at $T_{sub} = 320$˚C. This additional diffraction could belong to residues of the thermal decomposition products of metal chloride thioure complexes formed in the spraying solution. On the other hand, at $T_{sub} = 340$ - 380˚C, the preferred orientation along (112) direction together with (004), (204/220) and (116/312) directions were formed. These results indicate that the structural phase is of tetragonal chalcopyrite (ASTM card - No 00-027-0159). At $T_{sub} = 340$˚C, a weak peak was also detected (marked by "?" in Fig. 1a), which was ambiguous to us. The film grown at $T_{sub} = 410$˚C showed a low crystallinity. This could be explained by the absence of the spitting of (204/220) and (116/312) peaks. Consequently, the crystallinity CIS films with tetragonal structure can be grown at the substrate temperature range of $T_{sub} = 340$ - 380˚C.

Therefore, we could investigate the XRD spectra of deposited CIS films with different Cu/In ratio at $T_{sub} = 360$˚C (see Fig. 1b). In case of the Cu/In ≤ 1 (indium excess), we observed the appearance of additional diffraction peaks at $2\theta = 26.7^o$ in XRD spectra (marked by 'x' in Fig. 1b). According to Lopez et. al. [5], this additional phase may be related to the phase of In_2S_3 (ASTM card - No 00-033-0623). As a result, it is indicated that in case of indium excess the crystalllinity of the films was poor. This phenomenon might be attributed to the intrinsic defects of indium in copper sites (In_{Cu}) and indium interstitials (In_i) as reported in [5]. In case of the Cu/In ≥ 1.1 (copper excess), we found the significant diffraction peaks corresponding to the tetragonal structure as discussed above. Besides, the (112) peak increased and became sharper with increasing Cu/In in the solution. The improvement of crystallinity of CIS films with increase of the Cu/In ratios from 0.85 to 1.25 can be explained by copper ions mobility. This result means that copper excess in the solution strongly effects on the formation tetragonal structure.

Optical properties

Transmission and reflection spectra

Optical transmission for thin films was measured in the range 300 - 900 nm and was shown in Fig. 2.

Fig. 2a presents optical transmittance spectra of the sprayed CIS film at various substrate temperatures. It is seen that the lowest transmission was obtained in the film grown at $T_{sub} = 320$˚C. The further increase in growth temperature increased the transmittance of sprayed films. A possible cause for this feature might be the changes in the structure of the film as discussed in the previous section. Another reason for the increase in transmission could be attributed to the reduction of films thickness with increasing the growth temperature.

Fig. 2b shows the optical transmittance spectra of the films at different Cu/In ratio in the range of 0.85 - 1.25. It was evident that the increase of Cu/In ratio led to the decrease of the optical transparency of the films in the visible region because copper excess in the solution may create impurity phases and increase grain size effects in material that related with the decrease of transmission.

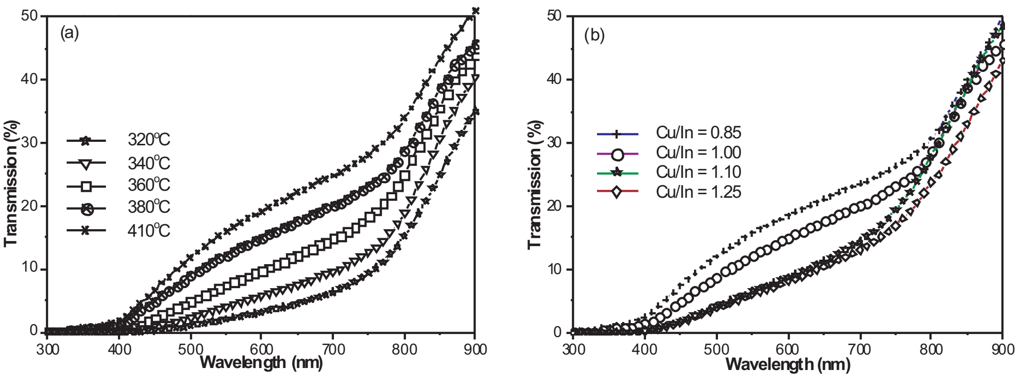

Fig. 2. (a) Optical transmittance spectra of the films at different substrate temperatures; (b) Optical transmittance spectra of the films at various Cu/In ratios.

Absorption coefficient

The absorption coefficient α of the films was calculated based on the following relation [12]:

$$T = \frac{(1-R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)} \tag{1}$$

where R and T are the spectral reflectance and transmittance, d is the film thickness.

At greater optical density (αd ¿ 1), the interference effects due to internal reflections as well as reflectance at normal incidence are negligible and the previous equation can be approximated:

$$T \sim \exp(-\alpha d)$$

Optical absorption coefficient is given by the formula:

$$\alpha = \frac{\ln(1/T)}{d} \tag{2}$$

where d is the film thickness and T the measured transmittance. We calculated the absorption coefficient for $\mathrm{CuInS_2}$ thin films having the average thickness values between 231- 592 nm.

Fig. 3 (a, b) shows the absorption coefficient of CIS thin films with different substrate temperatures and Cu/In ratios. In the range of visible light, the order of their absorption coefficient reached $10^{-5}\mathrm{cm}^{-1}$ and decreased with the increase of wavelength. This value is close to reported values [4,7,9,10]. The trend is α increased not only with increment of substrate temperature but also with increment of Cu/In molar ratio. Besides, the soft variation of the absorption coefficient at the absorption threshold suggests that there was a contribution of transitions from states within the band gap to light absorption.

Determination of the gap energy

In our case, for an direct band gap material the absorption coefficient (α) can be related to the incident energy ($h\nu$) by the following equation [1-7,9,10]:

$$\alpha h\nu = C(h\nu - E_g)^{1/2} \tag{3}$$

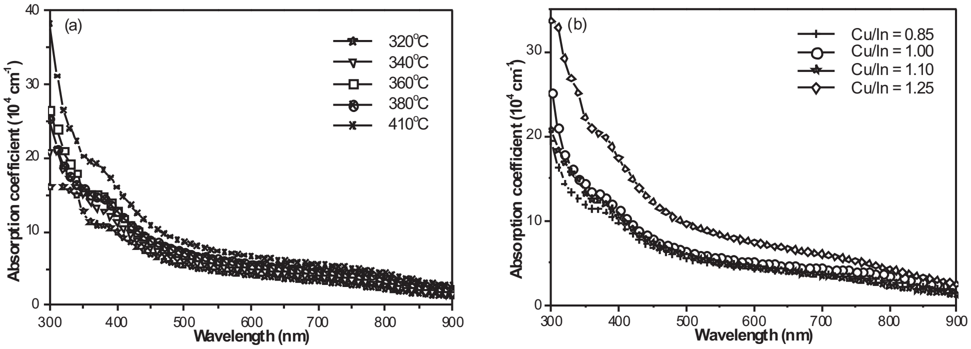

Fig. 3. (a) Absorption coefficient as a function of photon energy, for thin films prepared at (a) different substrate temperatures and (b) at various Cu/In ratios in the solution.

where C is a constant, E_g is the optical band gap and h is the Planck constant. For a direct band gap semiconductor, the $(\alpha h\nu)^2$ versus $h\nu$ characteristic is predicted to be a straight line with a photon energy axis intercept giving the value of the band gap.

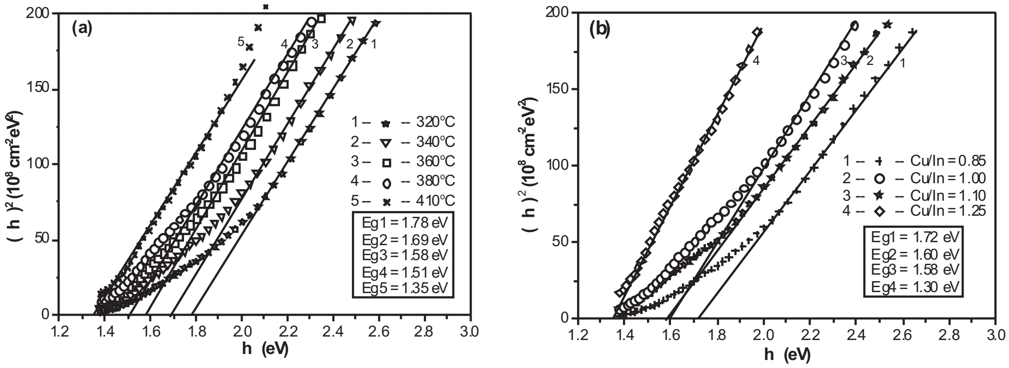

Fig. 4. (a) a plot of $(\alpha h\nu)^2$ vs $h\nu$ for $CuInS_2$ films at (a) different substrate temperatures (b) various Cu/In ratios in the solution

Fig. 4(a) presents the plot of $(\alpha h\nu)^2$ vesus $h\nu$, which was used for the calculation of the band gap for films deposited at different substrate temperatures. It was observed that the band gap of CIS thin films increased from 1.35 to 1.78 eV as the temperature of the substrate decreased. The increase of optical band gap of those thin films may be attributed to the presence of unsaturated defect such as the secondary phase (mark by "+" in Fig. 1) and the unknown phase (mark by "?" in Fig. 1), which increased the density of localized states in the band gap.

On the other hand, the band gaps of sprayed CIS films with various Cu/In molar ratios are illustrated in Fig. 4(b). It can be seen that the band gaps decreased from 1.72 to 1.30 eV when the Cu/In molar ratio increased. Carrier degeneracy in CIS due to continuous distribution of defect states was reported as a possible reason for this decrease in band gap. The change in Cu/In ratio led to the deviations from stoichiometry in CIS resulting in some defects in crystalline lattice, such as copper and indium vacancies (V_{Cu}, V_{In}), substitution copper in indium sites (Cu_{In}) and the defect pairs. Such defects and defect pairs which had particularly low formation energies in grain boundaries could produce gap-states near the band edge [5]. It can be concluded that the decrease in optical band gap with increasing in ratio of Cu/In is attributed to variation of stoichiometric in material.

In addition, the type of conductivity in the film was checked using hot probe method. The results indicated that all deposited CIS thin films has p-type conductivity.

IV. CONCLUSIONS

The thin films of $CuInS_2$with tetragonal chalcopyrite structure were prepared by varying of Cu/In ratio in spray solution at growth temperatures of $T_{sub} = 340$ - 380°C. All the films were of p-type conductivity. The optical studies revealed that these films showed the absorption coefficient of about 10^5cm^{-1} and the band gap energy varied from 1.30 to 1.78eV, which were in accordance with the requirement optical absorbers in solar cells. It was observed that the band gap decreased with the increase of the substrate temperature or with the increase of Cu/In molar ratio. Obtained results confirmed that by using this technological process can fabricate suitable thin films material for solar cells.

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