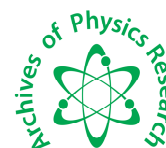




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Influence of antimony (Sb) concentration and temperature on the properties of Sprayed Sb-doped CuInS₂ thin films for solar cell applications

C. Mahendran^a and N. Suriyanarayanan^{b,*}

^aDepartment of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore, Tamil Nadu, India

^bDepartment of Physics, Government College of Technology, Coimbatore, Tamil Nadu, India

ABSTRACT

Copper Indium Disulphide (CuInS₂) is an absorber material for solar cells and Photovoltaic applications. By suitably doping the material with the suitable dopants such as Bi, Zn, Na, P, Cd, Sn, N, and As its structural, optical, Photoluminescence properties and electrical conductivities could be controlled and modified. It is observed that the film growth temperature, the ion ratio (Cu / In =1.25) and Sb- doping affects the structural, optical and photoluminescence properties of CuInS₂ thin films grown in the temperature range of 300–400^o C. The XRD patterns confirm that the Sb-doping suppresses the growth of polycrystalline CuInS₂ (0.02M Sb-doping) along (112) preferred plane. From the crystallographic parameter measurements, it is found that the 0.01M Sb-doped CuInS₂ thin films show better crystalline quality than 0.02M doped samples. Improved optical transmittance properties are observed in 0.02M Sb- doped samples in the wave length range 350-1100nm. The optical absorption coefficient (α (hv)) for the Sb- doped samples (0.02 M) is found to be in the order of 10⁵ cm⁻¹. The optical band gap (E_g) energies for 0.02M Sb-doped CuInS₂ thin films increase with increase of temperatures from 300–400^oC. SEM patterns reveal that, large size crystals of (1 μ m) flower like structure are formed on the surface for 0.02M doped samples. Well defined sharp blue and green band emissions are observed in PL spectra and defects related PL spectra are discussed.

Keywords: Optical properties; Structural properties; Photoluminescence; Spray pyrolysis.

INTRODUCTION

The direct conversion of sunlight into electricity using photo voltaic properties of suitable material is an elegant energy conversion process. The major key issue in this area of research is low cost manufacturing processes. Thin film solar cells have many advantages including low-

cost processing, light weight and flexibility in comparison to the conventional silicon-based solar cells. CuInS₂ thin film is one of the most promising ternary chalcopyrite materials for the solar cell absorber [1, 2]. It exhibits many excellent physical and chemical properties such as high absorption coefficient almost 10⁵ cm⁻¹ in the visible spectral range [3], high tolerance to defects [4], high chemical stability, a direct band gap of 1.5 eV, which is the optimum value for the photovoltaic conversion of solar energy [5] and possibility to avoid n and p-type conductivities [6]. But it can be made both n-type and p-type, enabling the fabrication of both homo junction and hetero-junction structures by suitably doping CuInS₂ bulk or thin films. CuInS₂ thin films have high absorptive layers and belong to semiconducting ternary compounds of I-III-VI₂ with chalcopyrite structure. CuInS₂ contains non-toxic compounds, low cost and easy to fabricate by various thin film deposition techniques [7,8,9]. For controlling conduction type and obtaining a low resistivity, several impurities doped CuInS₂ bulk or thin films have been studied. The incorporation of iron during the crystal growth of CuInS₂ by chemical transport is studied [10] and the results of electrical and photoluminescence measurements of phosphor doped and zinc doped CuInS₂ crystals are reported [11]. The structural, optical and electrical properties of Bi-CuInS₂ are studied by Akai et al and the effect of Na doping on CuInS₂ are investigated by Zribi et al. The electronic structures of n-type doped CuInS₂ crystals using Zn and Cd species are studied. The work on p-type doping using V group elements such as N, P and As increase the Madelung energy [12] which results into instabilities of ionic charge distribution in p-type doped CuInS₂ crystals [13]. The present study reveals the variation of structural, optical and photoluminescence properties of Sb-doped (0.02M) CuInS₂ thin films (Cu/In=1.25) grown in the temperature range 300 - 400°C on heated glass substrates by spray pyrolysis method. It is an attractive, low cost method and the application of that enables the deposition of the films of larger area with good uniformity [14-18].

MATERIALS AND METHODS

Sb-doped CuInS₂ thin films are deposited by spray pyrolysis on to glass substrates from aqueous solutions of CuCl₂, InCl₃,SC(NH₂)₂ and SbCl₃ using compressed air as the carrier gas. At first, aqueous solutions (0.1M) of the salts are prepared, then they are mixed with appropriate portions in order to have copper to indium molar ratio (Cu/In = 1.25) and sulphur/copper ratio (S/Cu) 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 doped with antimony tri-chloride (SbCl₃) of 0.02M. 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 (2.5X2.5cm²) heated at different temperatures from 300 - 400°C.

The X-ray diffraction (XRD) patterns of sprayed films are recorded using the XPERT-PRO Goni scan diffractometer with CuK α radiation. The phases are identified using JCPDS data files. The optical transmittance spectra are recorded in the wavelength range 350-1100 nm using double beam Beckman Ratio Recording spectrophotometer. The surface morphologies of the films are investigated using a Jeol, JSM-6390, JM-Spot size 35. The compositional analysis is carried out using energy dispersive X-ray spectroscopy (EDAX). Photoluminescence (PL) spectra of the films are recorded using a Cary Eclipse instrument in fluorescence emission scan mode with excitation wavelength of 400,702 and 806 nm.

RESULTS AND DISCUSSION

3.1 Structural analysis of (0.02 M) Sb-doped CuInS₂ films

Fig. 1 shows the XRD patterns of antimony doped (0.02 M) polycrystalline CuInS₂ thin films grown in the temperature range 300-400°C. Better crystalline quality of Sb-doped polycrystalline CuInS₂ thin films are obtained in the case of 0.01 M doped CuInS₂ thin films than 0.02 M Sb-doped samples [19]. Further addition of Sb (0.02 M) destroys the crystal structure. Characteristic peaks corresponding to (103), (200), (211), (220), (312) and (224) plans of Sb-doped(0.02M) CuInS₂ thin films without preferential orientation along (112) plane with chalcopyrite structure are recorded at 300°C PDF (27-159).. The growth of CuInS₂ is suppressed by Sb-doping (Fig. 1).

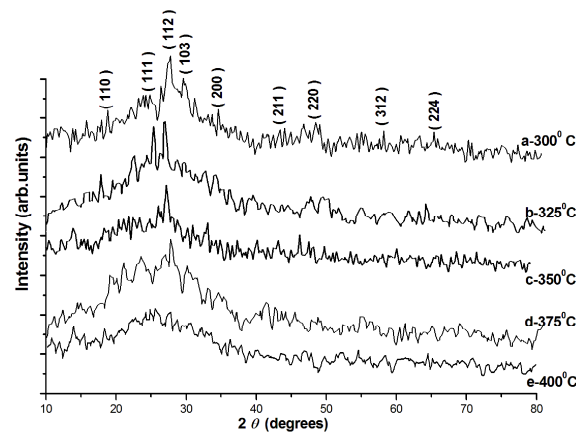


Fig.1. XRD of sprayed Sb-doped (0.02 M) CuInS₂ films Prepared at different substrate temperatures

Broadening of peaks appears in the case of 0.02 M doping (Fig. 1) due the formation of nano sized grains inside the film. The XRD patterns of the Sb-doped CuInS₂ thin films show additional peaks of secondary phases such as CuIn₃S₅ along (111) and (110) plans. With the increases of substrate temperatures from 325 - 375°C, all the height of peaks is gradually suppressed. Further increase in temperature to 400°C and beyond, the film becomes amorphous. Considering the possible formation mechanism of Sb-doped CuInS₂ thin films during spray pyrolysis additional peaks such as Sb₂S₃, Cu₂S, Cu and In₆S₇ or Sb alloys are formed [20]. Further, the secondary phases of CuIn₅S₈ PDF (24-361), CuIn₁₁S₁₇ PDF (34-79), Cu₇S₄ PDF (24-58, 33-489) and In₂S₃ PDF (25-390, 32-456) could be responsible for additional reflections [21].The presence of few minor phases in general attributed to a sum of internal origins obeying thermodynamics of solid solutions, to defect chemistry and the thermal gradient which plays an important role as described elsewhere [22].

The lattice constants a and c are calculated using the following equation [22]

$$\frac{1}{d^2_{(hkl)}} = \left[\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right] \text{-----} \quad (1)$$

The 0.01 M Sb-doped CuInS₂ lattice constants ($a = b = 5.526 \text{ \AA}$ and $c = 11.120 \text{ \AA}$) are very close to the standard values ($a = b = 5.523 \text{ \AA}$ and $c = 11.141 \text{ \AA}$) JCPDS (27-159) [19]. But greater variations are noticed in the case of 0.02 M Sb-doped CuInS₂ thin films ($a = b = 5.541 \text{ \AA}$ and $c = 11.17 \text{ \AA}$). This variation is due to the development of large amount of intrinsic stress in the 0.02M Sb-doped CuInS₂ samples. Further 0.01 M doped samples SEM analysis reveals that, large size crystals of 200nm -1 μm are formed on the surface, which prevents the surface defects and intrinsic defects. Hence, better crystalline quality of polycrystals is obtained in the case of 0.01 M Sb-doped CuInS₂ thin films than 0.02 M doped samples [19]. The Sb-doped CuInS₂ thin films are composed of compactly packed nano-sized crystals of average grain size 15-90 nm are formed by 0.01 M doping [19] and 15-70 nm are obtained in the case of 0.02 M doping. The undoped films have shown 25-125 nm [23]. The above grain sizes are calculated by Debye-scherrer relation.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad \text{-----} \quad (2)$$

Where, D is the grain size in nm, λ is the wavelength $\text{CuK}\alpha = 1.5404 \text{ \AA}$, β is the full-width at half-maximum of the peak in radian and θ is the Bragg angle. The undoped CuInS₂ thin films show (112) orientation chalcopyrite structure with other secondary peaks [23].

3.2 EDAX Analysis

EDAX analysis confirms the presence of Cu, In, S and Sb in the doped films Fig.2. It is observed that there is a slight decrease in the concentrations of In, S, Cu and Sb from the films as the temperature of the substrate is increased from 300-400°C for 0.02 M Sb-doped samples. But 0.02 M Sb-doped sample at 350°C shows an increase of Indium by 8.5% of mass when compared to 0.01M Sb-doped samples at 350°C [19].

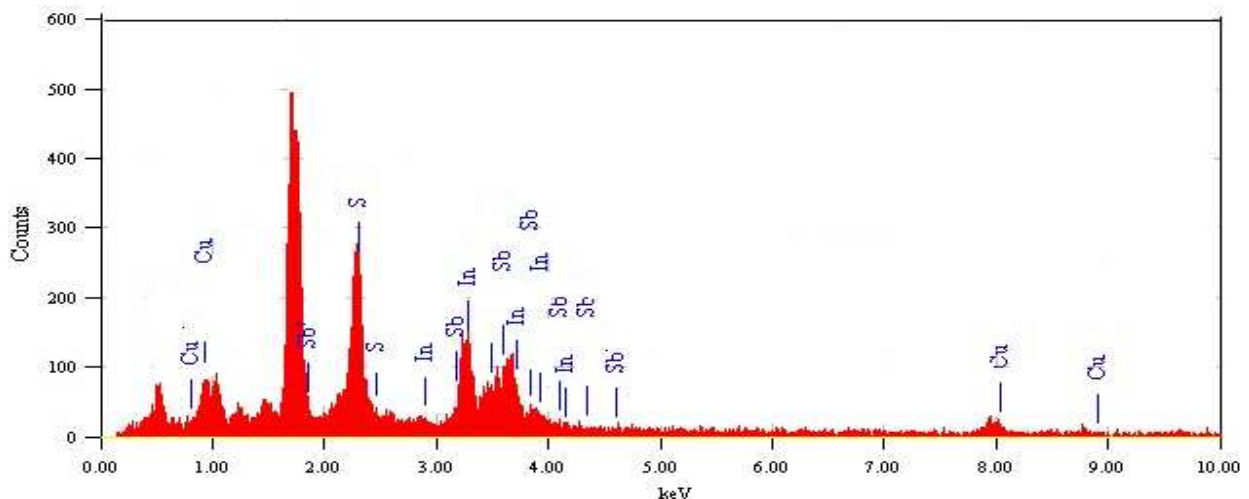


Fig.2. EDAX spectrum of sprayed Sb-doped (0.02 M) CuInS₂ film Prepared at 350°C .

The antimony incorporation can occur in different ways, namely occupying the indium site and / or occupying the sulfur site and / or Cu site. It is found that both 0.01 [19] and 0.02 M Sb-doped samples show n-type conductivity above 300°C similar to the undoped one [24]. Since there are

so many intrinsic donors such as In interstitials and / or S vacancy or Cu vacancy defects. Further, the concentrations of donor and / or acceptor impurities in all CuInS₂ samples may not change by Sb-doping, and that the introduced Sb acceptor with low amount (0.02 M) cannot compensate all the donors sufficiently. It is also found that [6] n-type CuInS₂ crystals obtained by Sb-doping above 300°C. Hence n-type Sb-doped CuInS₂ thin films are obtained in this process.

3.3 Optical properties

The optical transmittance and absorption spectra of the 0.02 M doped CuInS₂ thin films in the wavelength range 350-1100 nm are presented in Fig. 3 and 4.

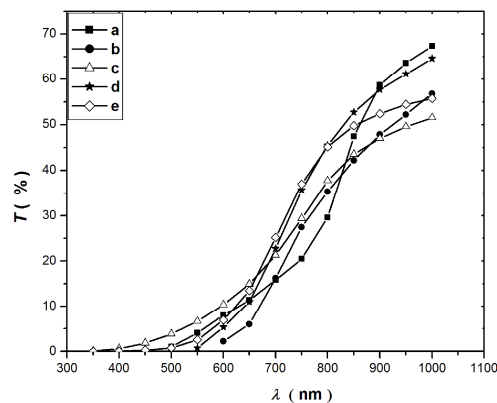


Fig.3. The transmittance spectra of Sb-doped (0.02 M) CuInS₂ films sprayed at different substrate temperatures:(a) 300°C (b) 325°C (c) 350°C (d) 375°C (e) 400°C.

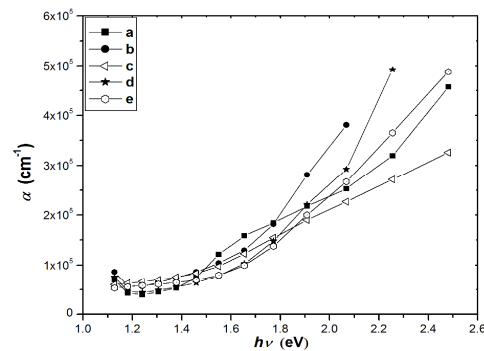


Fig.4. The absorption spectra of Sb-doped (0.02 M) CuInS₂ films sprayed at different substrate temperatures: (a) 300°C (b) 325°C (c) 350°C (d) 375°C (e) 400°C.

Fig .3 is the transmission spectra (350-1100 nm) exhibited by 0.02 M Sb- doped CuInS₂ thin films grown in the temperature range 300-400°C. In all the films there is an intrinsic interband absorption (350-600 nm) in the visible region by Sb-doped CuInS₂ thin films whereas absorption occurs only at 300 °C for 0.01M doped samples.[19]. About 60-70% of transmission is shown by all the films grown in the temperature range 300-400°C. Improved optical transmission property is observed in the case of 0.02 M doped CuInS₂ thin films in the range of 350-1100 nm than 0.01 M doped films [19] and films prepared by vacuum evaporation methods [24-25].

Since, in the 0.02 M Sb-doped CuInS₂ films, there may be a possibility of more number of Sb atoms are localized throughout the volume and near the surface than 0.01M doped samples. [25]. The decrease in the thickness of the film from 832 - 662 nm between the temperature range 300-400°C (Table 1) may also be the reason for better transmittance than 0.01 M Sb-doped CuInS₂ thin films. The undoped CuInS₂ thin films show 70% light transmission in all the temperatures and no absorption is exhibited by the films [23].

To calculate the absorption coefficient α (hv), the following relation is used.

$$\alpha = \frac{2.303}{t} [\log 1/T] \quad \text{-----} \quad (3)$$

t is thickness of the film and T is the transmittance. Fig.4 shows the dependence of the absorption coefficient α versus the photon energy hv of the 0.02 M Sb-doped CuInS₂ thin films grown in the temperature range 300-400°C. The films have relatively high absorption coefficient in the range of 10⁵ to 5.10⁵ cm⁻¹ for 0.02 M Sb-doped samples in the visible range (Fig 4). Higher value of absorption coefficient is obtained for 0.01 M doped sample (8.10⁵cm⁻¹) when the substrate temperature is at 300°C in the visible range [19]. The absorption coefficient is in the order of 10⁵ cm⁻¹ in the visible range for 0.02 M Sb-doped CuInS₂ thin films which is the suitable value to be used as an efficient solar energy absorber for solar cells and photovoltaic applications.

For the Direct band gap semiconductors α (hv) can be related to the equation

$$(\alpha hv)^2 = A(hv - E_g) \quad \text{-----} \quad (4)$$

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

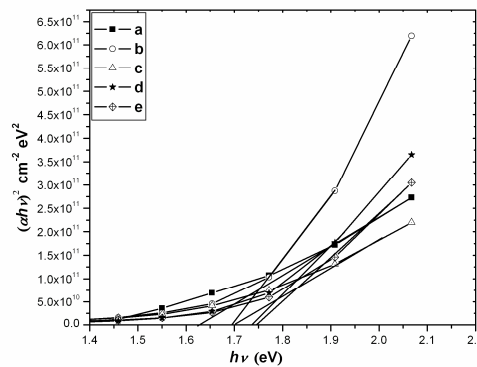


Fig.5. Variation of optical band gap energy values (E_g) of Sprayed Sb-doped (0.02 M) CuInS₂ films prepared at different substrate temperatures 300 - 400°C.

A plot of $(\alpha hv)^2$ versus hv for the Sb-doped (0.02 M) CuInS₂ films deposited at various temperatures is presented in Fig.5. The 0.01 M Sb-doped CuInS₂ thin films show an increase in

band gap energies (E_g) from 1.35-1.40 eV as the temperature of the substrate increases from 300-400°C [19]. But the band gap energies obtained are comparatively smaller than undoped CuInS₂ thin films (Table 1). The Slight increase in band gap energy (E_g) values for the 0.01 M Sb-doped samples should be related to increase in the crystalline state of the film. The value obtained is in good agreement with the expected value and well agree with the values obtained by other researchers [25,26]. The increase in E_g values with increase of substrate temperatures is due to the reduction of the density of band tail states, (i e) reduced localized disordered regions [27]. Further, large sized crystals (1 μ m) are formed on the surface of the 0.01 M Sb-doped films. They prevent intrinsic defects and surface defects [19]. Hence, the 0.01 M Sb-doped CuInS₂ thin films show better crystalline quality than 0.02M doped samples. In the case of 0.02 M Sb- doped samples (Fig 5) the band gap energies (E_g) increase from 1.63-1.75 eV (Table 1). These values are comparatively very larger than undoped and 0.01 M doped samples [23,19]. Even though large size crystals are observed on the surfaces of 0.02 M Sb-doped samples Fig.6 (a-e) certain portions of surface of the films are always exposed to defects indicating that the formed crystals are not close enough as formed in the case of 0.01 M Sb-doped samples (Fig.6a-e). Hence there is a large opportunity for the incorporation of intrinsic and surface defects. They may increase the localized disordered regions and destroy the crystal structure by increasing E_g values. Though most of the chlorine from the precursor and doping solutions are evaporated, a very small amount may contaminate the films. The presence of chlorine in the form of chlorine anions may react with Sb- doped CuInS₂ thin films to form covalent bonds and also occupies some sulfur vacancies [28].

Table1. Variation of band gap energies (E_g) and thickness of the film with temperature

S. No	Temperature (°C)	CuInS ₂ undoped		CuInS ₂ /0.01 M Sb-doped		CuInS ₂ /0.02 M Sb-doped	
		E_g (eV)	Thickness (nm)	E_g (eV)	Thickness (nm)	E_g (eV)	Thickness (nm)
1	300	1.66	694	1.35	752	1.63	832
2	325	1.63	672	1.36	691	1.69	804
3	350	1.62	652	1.37	662	1.70	718
4	375	1.60	621	1.38	659	1.74	683
5	400	1.58	609	1.40	626	1.75	662

From the Table 1 it is observed that, in the case of 0.02 M Sb-doped films the E_g (1.63-1.75 eV) values increase as the temperature is increased form 300-400°C. Due to increase in temperature there may be a slight reduction in density of band tail states (ie) very small reduction in disordered regions [27]. But this reduction is comparatively large when compared to 0.01 M doped samples (Table 1). The thickness of the film decreases with increase in temperatures for undoped, 0.01M and 0.02M Sb-doped CuInS₂ samples.

3.4 Surface morphologies

Fig. 6(a)-(e) shows the SEM photographs of 0.02 M Sb-doped CuInS₂ thin films grown in the temperature range 300-400°C. SEM structure shows dense and rough surface with small size crystals ranging from 200nm-400 nm are formed when the substrate temperature is at 300°C (Fig.6a). These crystals grow in size with increase of temperatures. About 200nm - 1 μ m large size crystals are grown on the surface at 325 °C (Fig.6b). Fig.6c shows the agglomerated areas of indium rich films formed at 350 °C [29]. The agglomerated islands are not only on the surface

and they are grown through the film. These agglomerated areas show polycrystalline structure with rough surface and the crystals sizes are about 300-400nm are formed on this surface. When the substrate temperature is at 375°C the surface morphology (Fig. 6d) entirely changes and flower like Sb- doped CuInS₂ crystals of large size (1µm) are formed. These large size crystals are composed of small number bundle of rod like structures grown from the crystals. This feature is due to the fact that, the copper containing liquid phase forms and concentrates on the surface and it leads to the three dimensional growth of crystals on the surface [29]. Further increase of substrate temperature to 400°C and beyond the films becomes amorphous (Fig.6e).

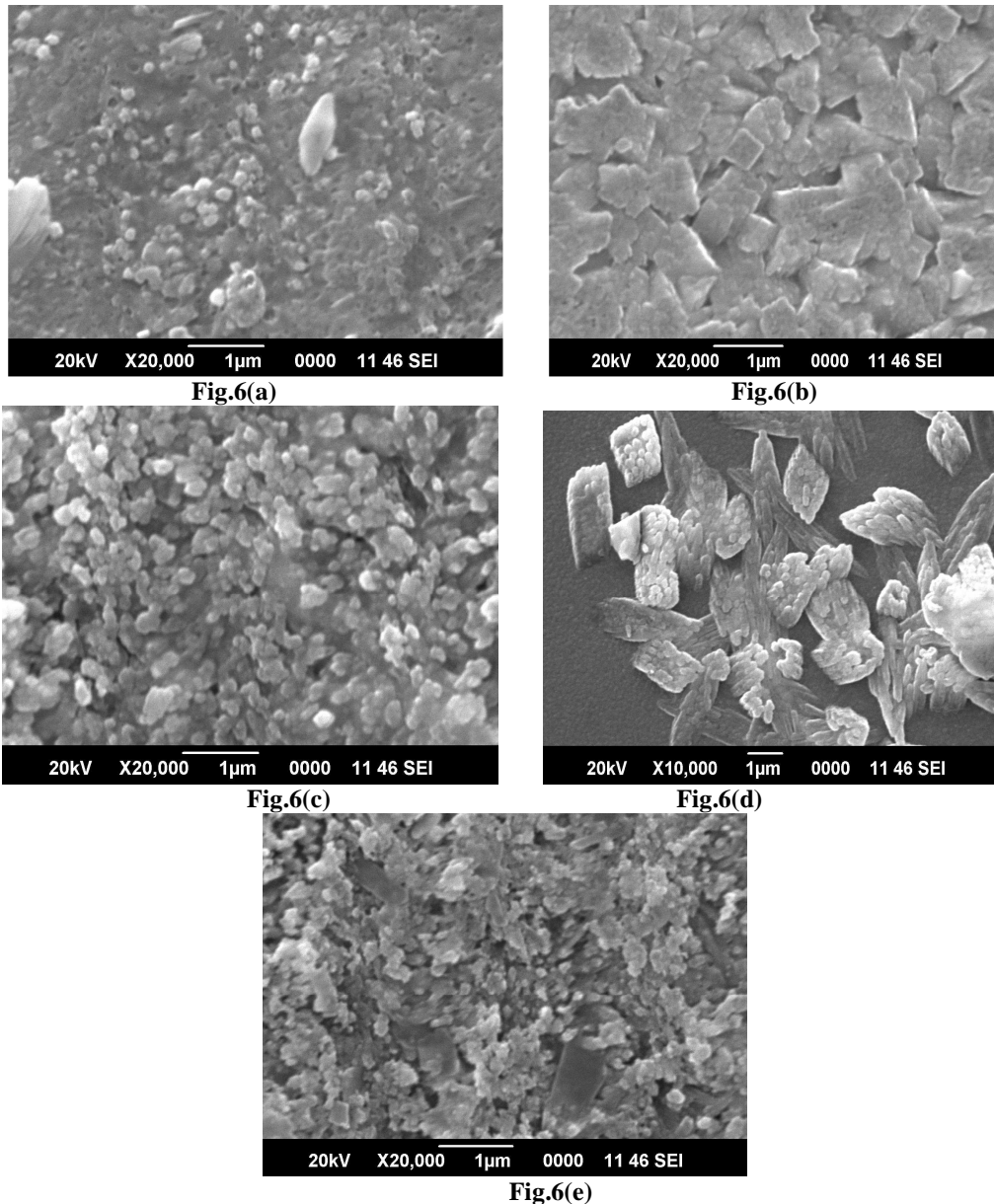


Fig 6. SEM micrographs of sprayed Sb-doped (0.02 M) CuInS₂ films prepared at different substrate temperatures: (a) 300°C (b) 325°C (c) 350°C (d) 375°C (e) 400°C

But in the case of 0.01 M Sb-doped CuInS_2 , vertical rod like structure of three dimensional Sb-doped CuInS_2 crystals are seen on the surface [19].

3.5 Photoluminescence

Fig.7(a)-(c) shows the emission spectra of Sb-doped thin films grown in the temperature range 300-400°C. Photoluminescence spectra have been recorded at room temperature with excitation wave lengths of 400, 720 and 806 nm for 0.02 M Sb-doped samples.

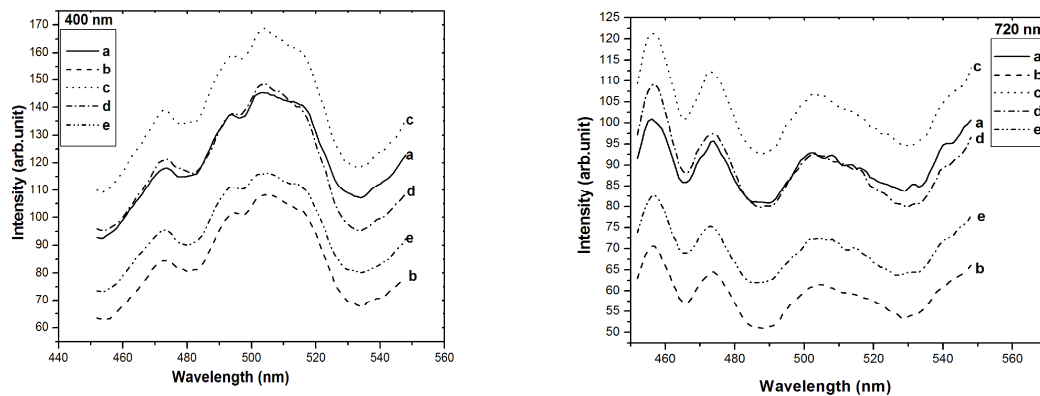


Fig.7a.,7b Photoluminescence spectra of sprayed Sb-doped(0.02 M) CuInS_2 excited by 400 nm and 720nm at various substrate temperatures (a) 300°C (b) 325°C (c) 350°C (d) 375°C (e) 400°C.

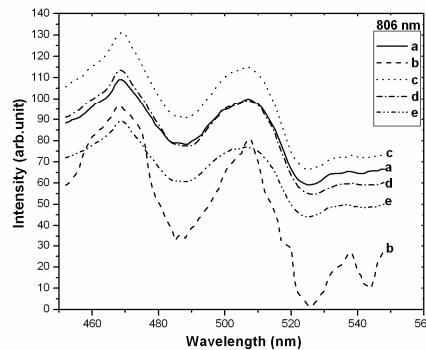


Fig.7c. Photoluminescence spectra of sprayed Sb-doped (0.02 M) CuInS_2 films excited by the 806 nm at various substrate temperatures: (a) 300°C (b) 325°C (c) 350°C (d) 375°C (e) 400°C.

About four deep emission peaks are observed in the wavelength range 470-540 nm (Blue and Green band emissions) when the sample is excited by 400 nm (Fig. 7a) for 0.02 M doped samples. This feature corresponds to Donor Acceptor Pair transition between (DAP), a sulfur vacancy and an In vacancy or Cu on an In site [30-33]. The increase and decrease in the emissions of intensities in the temperature range 300-400°C are due to transition from various defects and intrinsic energy levels. Similar trend with low intensities of emissions are noticed in 0.01 M samples [19]. Three well defined (Blue and Green band emissions) peaks are shown by the 0.02 M doped samples grown in the temperature range 300-400°C and the peaks are found to shift towards the shorter wavelength region as the samples are excited by 720 nm (Fig. 7b). The

emission intensities of 0.01 M doped and undoped samples are found to be low compared to 0.02 M doped samples [23, 19]. Further, increase in excitation wavelength to 806 nm depicts two sharp and well defined blue and green band emissions (Fig. 7c).

When compared to 0.01 M doped samples the 0.02 M doped samples show deep emissions in all the cases of excitation [19]. This feature is due to the recombination of deep donors and deep accepters [23]. In the PL spectra the peaks are found to broaden with increase of substrate temperature and the inhomogeneous broadening of peaks can be attributed to high concentration of defects. The broadening of peaks is typical for the non-equilibrium process of film growth and is caused by non-stoichiometry and metastable order and disorder on cation sub lattice [34]. Further, the broadening of peak is due to the fact that the large crystals are found to produce more defects than small crystals. These defects may act as non-radiative recombination centre which quench the radiative band edge recombination [35]. All emissions are associated with defects emerging during the growth of crystallites and are related to deformation of crystals due to dislocations and large vacancies [36]. Better and well defined PL spectra (Blue and Green band emission) are obtained by 0.01 and 0.02 M Sb-doped samples than undoped one [23, 19]

CONCLUSION

Antimony doped (0.02 M) CuInS₂ thin films are deposited on glass substrates in the temperature range 300-400°C. The XRD patterns confirm that the growth of polycrystalline Sb-doped CuInS₂ thin films. The growth is suppressed by Sb-doping (0.02 M) along (112) preferential plane. It is observed that the 0.01 M Sb-doped CuInS₂ thin films show better crystalline quality than 0.02 M doped CuInS₂ thin films. N-type Sb-doped CuInS₂ thin films are obtained in this process. Better optical transmittance property is observed for 0.02 M Sb-doped CuInS₂ thin films than 0.01 M doped thin films. It shows an absorption band in the visible region (material is opaque) in all the films grown in the temperature range 300-400°C. About 70% of light transmission is observed in all the films in the wave length range 600-1100 nm (material is transparent). The absorption coefficient (α (hv)) for both Sb-doped samples (0.02 M) is found to be in the order of 10^5 cm^{-1} . The Band gap energies (E_g) for 0.02 M Sb-doped CuInS₂ thin films increase with increase of temperatures from 300-400°C. SEM patterns show flower like large size crystals are (1 μm) formed on the surface. At 400°C and beyond the Sb-doped CuInS₂ thin films become amorphous. Well defined deep blue and green band emissions are exhibited by 0.02 M Sb-doped CuInS₂ thin films than 0.01 M doped and undoped samples. Defects related PL emissions are discussed.

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