

STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF ANNEALED Sb-DOPED CuInS₂ THIN FILMS GROWN BY THERMAL EVAPORATION METHOD

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Structural optical and electrical properties of undoped and Sb-doped CuInS₂ thin films grown by single source thermal evaporation method on corning 7059 glass substrates heated at 100°C were studied. Sb species was mixed in the starting powders. The amount of the Sb source was determined to be in the range 0-4 Wt % molecular weight compared with the CuInS₂ alloy source. The films were annealed in vacuum at temperature of 200°C and in air atmosphere at temperature of 400°C for 2h. The effect of these annealing atmospheres on the properties of the films was studied by means of X-ray diffraction (XRD), optical reflection and transmission and resistance measurement. All the CuInS₂/Sb films have relatively high absorption coefficient between 2.10^4cm^{-1} and 10^5cm^{-1} in the visible and the near-IR spectral range. We found that Sb-doped CuInS₂ thin films exhibit p-type conductivity and air annealing exhibit n-type conductivity.

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1. Introduction

Ternary chalcopyrite CuInS₂ thin films exhibit many excellent physical and chemical properties such as high absorption coefficient of almost 10^5cm^{-1} in the visible spectral range [1], high tolerance to the presence of defects [2], an direct band gap closes to 1.5 eV, the optimum value for the photovoltaic conversion of solar energy [3], possibility to avoid n and p-type conductivity [4] and high chemical stability. In contrast to other ternary semiconductor materials, CuInS₂ is nontoxic, low-cost and easy to fabricate by various thin film deposition techniques [5-7]. For controlling a conduction type and obtaining low resistivity, several impurities doped CuInS₂ bulks have been studied. In several studies, it was shown that the structural, optical and electrical properties of CuInS₂ thin films could be obviously improved by optimized deposition conditions and doping [8-10]. Additionally, the electrical properties of CuInS₂ thin films could be modified by thermal in a reducing atmosphere [11,12]. Akaki et al [13] studied the structural, electrical and optical properties of Bi-CuInS₂ thin films grown by vacuum evaporation method. Zribi et al [8] investigated the effect of Na doping on the properties of CuInS₂ thin films and obtained more interesting results. The incorporation of iron during the crystal growth of CuInS₂ by chemical vapor transport was studied [14,15] and the results of electrical and photoluminescence measurements of P-doped and Zn-doped CuInS₂ crystals were reported [16]. T. Yamamoto et al [9] investigated the electronic structures of n-type doped CuInS₂ crystals using Zn and Cd species and showed that p-type doping using the group V elements such as N, P and As increases the Madelung energy, which gives rise to instability of ionic charge distribution in p-type doped CuInS₂ crystals [17]. Enzenhofer et al [10] showed that the open circuit voltage of solar cells based on CuInS₂ can be enhanced via controlled doping of small amounts of Zinc. In our previous paper [18] the incorporation of the doping element Sn in CuInS₂ was succeeded by annealing the Sn-doped films in vacuum. In this paper, we report on structural, optical and electrical properties of the Sb-doped CuInS₂ thin films after annealing in vacuum and in air atmosphere.

2. Experimental

2.1. Synthesis of targets and films

Amount of the elements of 99.999% purity Cu, In, S and Sb, five different powders of CuInS_2/Sb (0,1,2,3 and 4 Wt % molecular weight) were prepared. X-rays diffraction of powders analysis showed that in all cases the principal phase present in the ingots is the CuInS_2 . Crushed powder of every ingot was used as raw material for the thermal evaporation. The Sb-doped CuInS_2 thin films were deposited on corning 7059 glass substrates heated at 100 °C by single source thermal evaporation method in vacuum at 10^{-6} torr. After what the films were annealed in vacuum at temperature of 200°C and in air atmosphere at temperature of 400°C for 2 h.

2.2. Characterization techniques

The structure of the CuInS_2/Sb samples was investigated using D8 Advance diffractometer. The optical characteristics were determined at normal incidence in the wavelength range 300 to 1800 nm using a Shimadzu UV/Vis-spectrophotometer. The resistance was measured using a digital universal meter and the type of conductivity of these films was determined by the hot probe method. Film thicknesses were measured by interference fringes method [19] and were in the range of 450-750 nm.

3. Results and discussion

3.1. Structure of targets and films

Figure 1 shows the X-ray diffraction patterns of undoped and Sb-doped CuInS_2 thin films after annealing in vacuum at 200°C. It can be seen that samples presented a sharp peak at $2\theta = 27.9^\circ$ assigned to the (112) reflection of CuInS_2 phase for the samples doped 0, 1,2 and 3 % Sb molecular weight and become highly oriented when the Sb content is 4 % molecular weight. We note also some additional diffraction peaks at 26.49° and 43.4° , which can be associated to binary compounds In_6S_7 and Cu crystal. **Figure 2** shows the X-ray diffraction patterns of the films after annealing in air atmosphere at temperature of 400°C for 2 h. All the annealed films are oriented (112) plane and there is an improvement in the growth of the films after annealing in air for all the samples containing antimony. On the other hand, few minor peaks with lower intensities, associated to copper Cu, CuO and In_6S_7 phases, can be observed from the patterns.

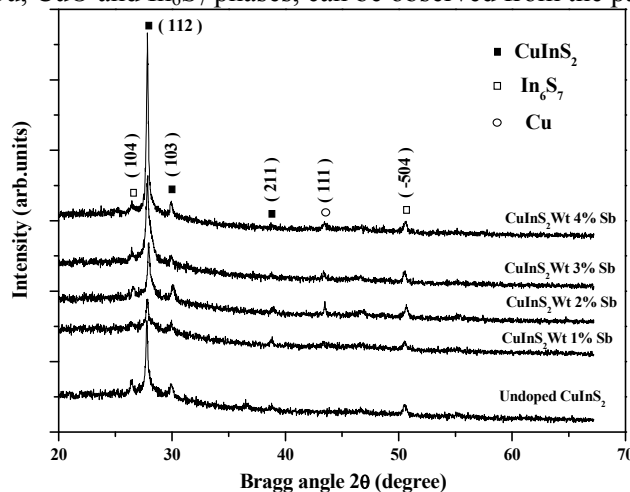


Fig. 1 X-ray diffraction patterns after annealing in vacuum.

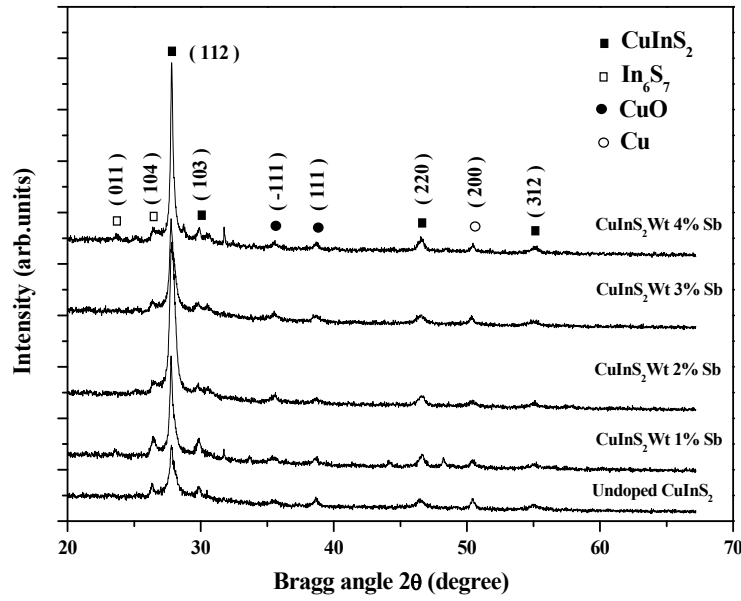


Fig.2. X-ray diffraction patterns after annealing in air atmosphere.

In the other hand the grain size along the (112) peak can be evaluated by using the Debye Scherer relation:

$$L = \frac{0.9\lambda}{\cos \theta_0 \Delta(2\theta)} \quad (1)$$

Where λ is the wavelength of the X-ray radiation used, $\Delta(2\theta)$ the half intensity width of the peak and θ_0 the Bragg angle. The grain sizes are in the range 20 – 50 nm for all the samples undoped and Sb-doped.

3.2. Optical properties

To calculate the absorption coefficient $\alpha(h\nu)$, the following relation was used [20].

$$\alpha = \frac{1}{d} \ln \left[\frac{(1-R)^2}{T} \right] \quad (2)$$

Where d is the film thickness, R and T are the reflection and transmission coefficient, respectively. **Figure 3** shows the dependence of the absorption coefficients α versus the photon energy $h\nu$ of the Sb-doped CuInS₂ thin films after annealing in vacuum. The films have relatively high absorption coefficients between $2 \cdot 10^4 \text{ cm}^{-1}$ and 10^5 cm^{-1} in the visible.

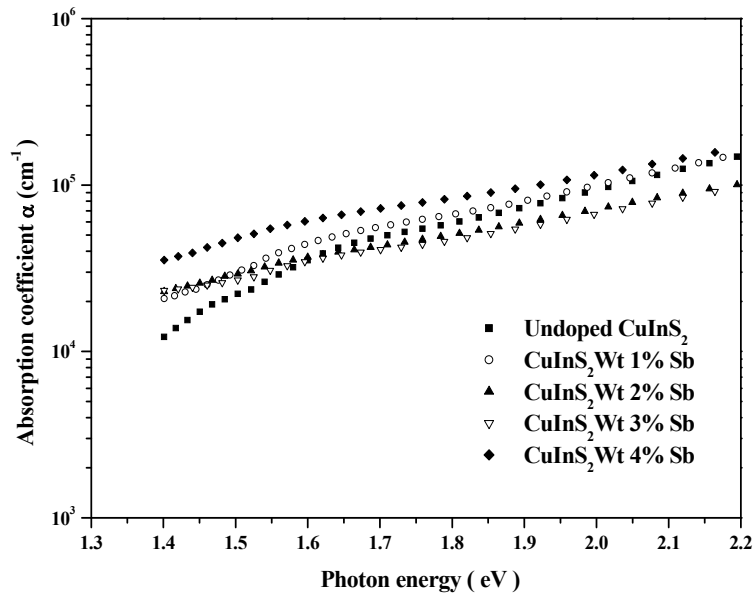


Fig. 3 Absorption coefficients spectra after annealing in air vacuum.

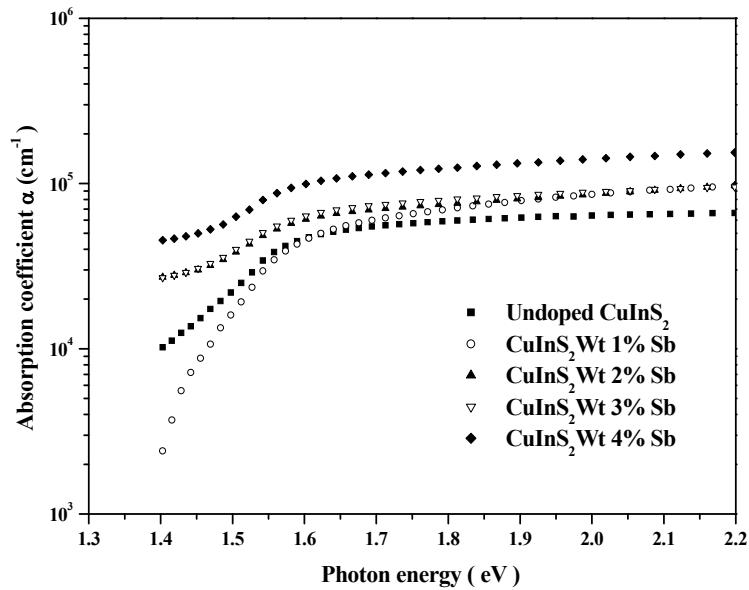


Fig. 4 Absorption coefficients spectra after annealing in air atmosphere.

Fig. 4 shows the absorption coefficients versus the photon energy for the Sb-doped CuInS_2 thin films after annealing in air atmosphere. It is clear that the absorption coefficient increases with increasing Antimony % molecular weight. All the films have relatively high absorption coefficients more than $5 \cdot 10^4 \text{ cm}^{-1}$ and remain constant along visible spectral range, which reached 10^5 cm^{-1} for the CuInS_2 samples doped 4 Wt % Sb molecular weight. In the other hand, the relation between the absorption coefficients α and the incident photon energy ($h\nu$) can be written for direct allowed band gap as:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (3)$$

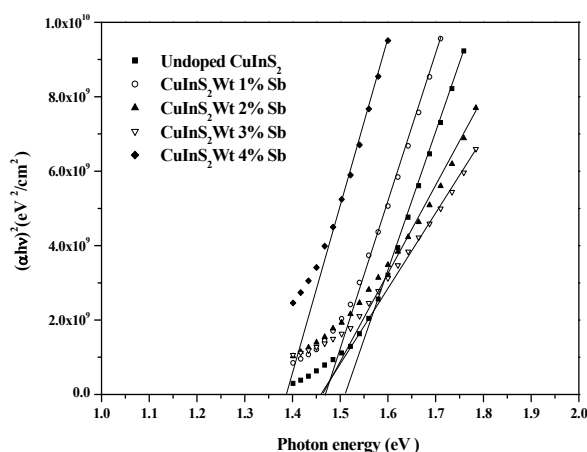


Fig. 5 Relationship between $(\alpha hv)^2$ and photon energy after annealing in vacuum.

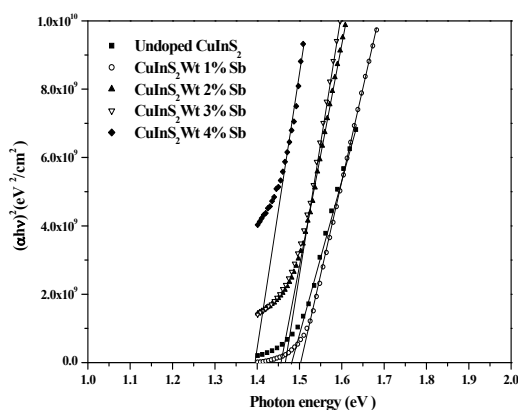


Fig. 6 Relationship between $(\alpha hv)^2$ and photon energy after annealing in vacuum.

Where 'A' is constant and E_g is the optical band gap. To determine optical transition, $(\alpha hv)^2$ versus hv was plotted, and the corresponding band gaps were obtained from extrapolating the straight portion of the graph on the hv axis at $(\alpha hv)^2 = 0$ (Figures 5 and 6). It is now well established that CuInS_2 is a direct gap semiconductor [21], with the band extrema located at the centre of the Brillouin. The direct band gap energy (Figure 7) decreases from 1.51 to 1.39 eV with increasing Sb content (0 to 4% molecular weight) for samples annealed in vacuum and in air atmosphere.

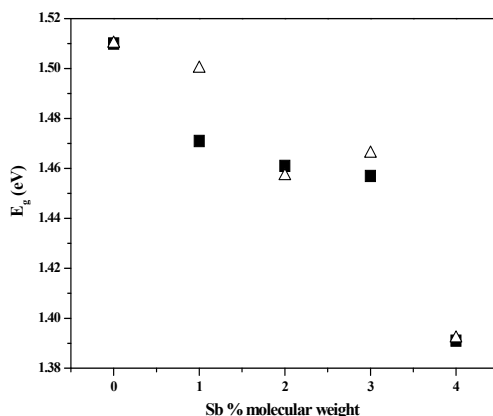


Fig. 7 Relationship between the optical bands gaps of CuInS_2/Sb with different Sb % molecular weight (Square) After annealing in vacuum and (Triangle) After annealing in air.

3.2. Electrical properties

Besides the optical properties, the electrical properties are also an important aspect of the performance of Sb-doped CuInS_2 thin films. After annealing in vacuum (**figure 8.a**), all the films presented moderate lower electrical resistivity with p-type conductivity for the samples doped wt 4% Sb molecular weight. The resistivity decreases from $5.51 \cdot 10^2 \text{ } \Omega\cdot\text{cm}$ to $1.6 \cdot 10^2 \text{ } \Omega\cdot\text{cm}$ with increasing Sb content. After annealing in air atmosphere, the resistivity values decreases from 1.32 to $0.22 \text{ } \Omega\cdot\text{cm}$ (**Figure 8.b**). All the undoped films and doped with 1,2,3 and 4 wt % Sb molecular weight exhibit high N-type conductivity. We note also an evolution from the P-type conductivity to the N-type conductivity for the CuInS_2 sample doped with 4% Sb molecular weight .After annealing, all samples indicate low resistivity. One of the reasons is that probably the concentrations of donor and/or acceptor impurities in all CuInS_2 samples may not change by Sb-doping. Indeed in our previous works [18] we show that the undoped CuInS_2 films were converted to irreversible n-type conductivity after annealing in air atmosphere with low resistivity if the annealing temperature is higher 200°C . The XRD results indicate the same secondary phase (CuO) in both cases and no antimony oxide were detected. Perhaps the n-type Sb doped CuInS_2 thin films are more stables than the n-type CuInS_2 . However this proposition needs more studies to confirm it.

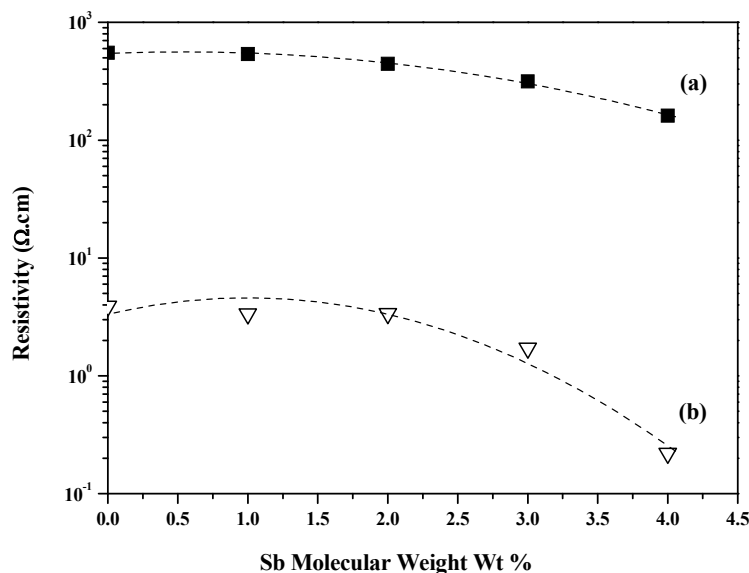


Fig. 8 Resistivity versus Sb % molecular weight of undoped and Sb-doped CuInS_2 thin films (a) After annealing in vacuum and (b) After annealing in air atmosphere.

4. Conclusions

The effects of antimony incorporation on the structural, optical and electrical properties of CuInS_2 thin films were studied. Sb species was mixed in the starting powders for different Sb % molecular weight. undoped and Sb doped CuInS_2 thin films grown by single source thermal evaporation method on corning 7059 glass substrates heated at 100°C were deposited and subsequently annealed in vacuum at temperature of 200°C and in air atmosphere at temperature of 400°C for 2h. The absorption coefficients deduced from optical measurements are greater than $2 \cdot 10^4 \text{ cm}^{-1}$ in the range 1.4-2.2 eV and remains constant along the visible spectral range with a value of 10^5 cm^{-1} for the CuInS_2 doped wt 4% Sb molecular weight after annealing in air atmosphere. The Sb-doped samples after annealing have bandgap energy of 1.39-1.51 eV. The resistivity of the films decreases from $5.51 \cdot 10^2$ to $1.61 \cdot 10^2 \text{ } \Omega\cdot\text{cm}$ as the Sb % increases from 0 to 4

wt % molecular weight after annealing in vacuum and from 3.9 to 0.22 Ω .cm after annealing in air atmosphere. As-deposited CuInS₂ samples doped wt 4% Sb molecular weight are p-type conductivity and an evolution to high n-type conductivity for all the samples after annealing in air at critical temperature of 200°C for undoped samples and 100°C for doped ones.

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