Structural, optical and electrical properties of P-type conductivity Zn-doped $CuInS_2$ thin films

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Structural and optical properties of Zn-doped $CuInS_2$ thin films grown by double source thermal evaporation method were studied. Evaporated thin films were grown from $CuInS_2$ powder by vacuum evaporation using resistively heated tungsten boats. The element Zn was evaporated from a thermal evaporation source. The amount of the Zn source was determined to be 0-4 % molecular weight compared with $CuInS_2$ source. The effects of Zn on films properties were investigated using X-ray diffraction (XRD) and optical transmission and reflection spectra. The films were annealed in vacuum at 260°C for 2 hours. The Zn-doped samples have bandgap energy of 1.467-1.585 eV. We found that the Zn-doped $CuInS_2$ thin films exhibit P-type conductivity and we predict that Zn species can be considered as suitable candidates for use as doped acceptors to fabricate $CuInS_2$-based solar cells.

Keywords: $CuInS_2$, Structural properties, Optical properties, Electrical properties.

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1. Introduction

Because of their high absorption coefficient of sun light and their high tolerance to the presence of defects (grain boundaries, vacancies, interstitials…), ternary chalcopyrite, CI(S,Se) are becoming among the leading candidates for high efficiency and low-cost terrestrial photovoltaic devices. Indeed, polycrystalline CI(S,Se) based solar cells have achieved efficiencies of about 19% on a laboratory scale [1-3] and around 14% for module [4]. $CuInS_2$ a photoabsorbing semiconductor with a direct band gap closes to 1.5 eV [5] has recently been introduced into industrial production [6]. It exhibits a high light absorbing coefficient in the visible spectral range and stability. Different methods to prepare non-doped $CuInS_2$ are currently under investigation, such as metal organic decomposition (MOD) [7], evaporation from a $CuInS_2$ powder source [8], aerosol-assisted chemical vapour deposition (AACVD) [9], co-evaporation [10], molecular beam deposition [11], spray [12], chemical bath deposition [13], ion layer gas reaction [14] (ILGAR) and electro-deposition [15]. For controlling a conduction type and obtaining a low resistivity, several impurities doped $CuInS_2$ bulks have been studied. The process can be of interest for application in $CuInS_2$-based cell design [16]. Sb doping of $CuInS_2$ was investigated [17] using vacuum evaporation method. A single phase Sb-doped $CuInS_2$ can be prepared by annealing above 400°C in Ar or N_2. Furthermore, the Sb-doped $CuInS_2$ films became close to stoichiometry in comparison with non-doped $CuInS_2$ thin films. The effect of Na doping on the properties of $CuInS_2$ thin films has been investigated [18]. Samples were prepared by the co-evaporation of $CuInS_2$ and Na on corning 7059 glass substrates. An evolution from the N-type conductivity to wards the P-conductivity is observed. The optical band gap of the thin Na-$CuInS_2$ films decrease linearly with increasing the Na

concentration. The incorporation of the doping element Sn in $CuInS_2$ was succeeded [19] by annealing the Sn-doped films in vacuum. After annealing the Sn-doped $CuInS_2$ exhibit N-type conductivity. In our previous paper [20], single source thermal evaporation technique was carried out for $CuInS_2$ films on the glass substrate, and the films were subsequently annealed in air atmosphere from 100 to 350°C. From X-ray diffraction (XRD) spectra, the polycrystalline $CuInS_2$ thin films begin to grow by annealing at 260°C to obtain an irreversible N-type conductivity with moderate resistances and the presence of In_2O_3 secondary phase. It has been shown that the open circuit voltage of solar cells based on $CuInS_2$ can be enhanced via controlled doping of small amounts of Zinc [21]. In this paper, we report on structural, morphological and optical properties of the Zn-doped $CuInS_2$ thin films grown by double source thermal evaporation method.

2. Experimental procedures

2.1. Synthesis of $CuInS_2$

Stoichiometric amounts of the elements of 99.999% purity Cu, In, and S were used to prepare the initial ingot of $CuInS_2$. The mixture was sealed in vacuum in a quartz tube. In order to avoid explosions due to sulphur vapour pressure, the quartz tube was heated slowly (20°C/h). A complete homogenization could be obtained by keeping the melt at 1000°C thermal expansion of the melt on solidification was avoided. X-rays of powder analysis showed that only homogenous $CuInS_2$ phase was present in the ingot. Crushed powder of this ingot was used as raw material for the thermal evaporation.

2.2. Film preparation

$CuInS_2$/Zn thin films were prepared by co-evaporation of the $CuInS_2$ powder and the Zn element in a high vacuum system with a base pressure of 10^{-6} torr. Zn of 4N purity was evaporated from thermal evaporator. An open ceramic crucible was used. Zn was deposited simultaneously during the deposition of the $CuInS_2$ powder. Thermal evaporation sources were used which can be controlled either by the crucible temperature or by the source powder. The glass substrates were no heated during the evaporation process. The amount of the Zn source was determined to be 0-4 % molecular weight compared with the $CuInS_2$ alloy source. Film thickness was measured by interference fringes method [22]. Typical as-deposited films thicknesses were in the range of 580-770 nm after that the films were annealed in vacuum at the temperature of 260°C for 2 hours.

2.3. Characterization

The structure of the Zn doped thin films was determined by means of X-ray diffraction (XRD) using a D8 Advance diffractometer with CuK_α radiation (λ= 1.5418 Å). The optical characteristics were determined at normal incidence in the wavelength range 300 to 1800 nm using a Shimadzu UV/VIS-spectrophotometer. The film's thicknesses were calculated from the positions of the interference maxima and minima of reflectance spectra using a standard method. The type of conductivity of these films was determined by the hot probe method.

3. Results and discussion

3.1 Structural properties

Fig. 1 shows the results of our XRD measurements after annealing of non-doped and Zn doped $CuInS_2$ thin films. Vacuum-evaporated films are usually considered to be randomly oriented polycrystalline. It is found that the zinc concentration has great effects on the formation of polycrystalline $CuInS_2$. All diagrams present peak at $2\theta = 27.9°$ assigned to the (112) reflection of $CuInS_2$ phase. And there is an improvement in

the growth of the films after annealing for all the samples containing Zn. It is also observed that the intensity of the (112) peak decreases obviously

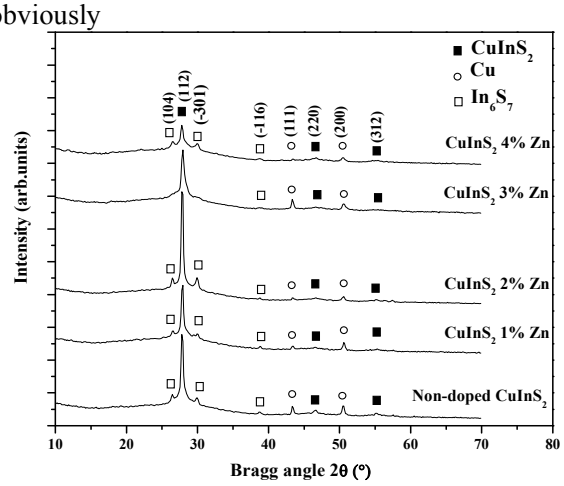


Figure 1 X-ray diffraction patterns of non-doped and Zn doped $CuInS_2$ thin films with different Zn % molecular weight after annealing.

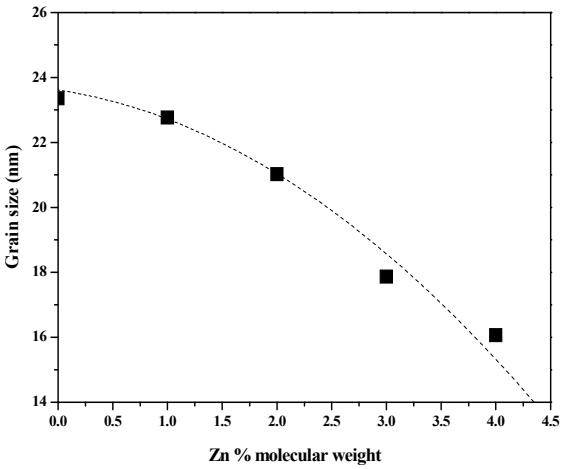


Figure 2. Variation of the grain size of non-doped and Zn doped $CuInS_2$ thin films with different Zn % molecular weight after annealing.

with increasing zinc concentrations, which probably may be due to increase of the disorder component. However, we can note a few minor peaks with lower intensities identified as In_6S_7 and Cu phases. The presence of the minor phases is in general attributed to a sum of internal origins obeying the thermodynamics of solid solutions, to defect chemistry and the thermal gradient which plays an important role as described elsewhere [23]. Indeed, the additional copper phase is mainly attributed to the higher mobility of Cu^+ and its migration toward the surface layers [24]. The grain size along the (112) peak can be evaluated by using the Debye Scherrer relation:

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

where λ is the wavelength of the X-ray radiation used, Δ(2θ) the half intensity width of the peak and θ_0 the Bragg angle. Fig. 2 shows the variation of grain size of non-doped and Zn doped $CuInS_2$ thin films with

different Zn % molecular weight after annealing. As we can see from figure 2 the grain size is decreasing from 23 to 16 nm with increasing the Zn % molecular weight.

3.2. Optical and electrical properties

3.2.1. Optical transmission and reflection spectra

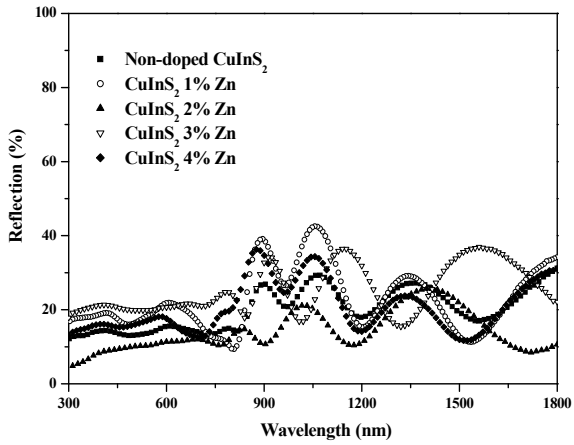
The effects of doping zinc on the optical reflection and transmission spectra in the wavelength range 300-1800 nm at normal incidence, before and after annealing in vacuum of non-doped and Zn doped $CuInS_2$ thin films are studied. Figures 3 and 4 show reflection and transmission spectra after annealing. All the transmission spectra show interference pattern with moderate sharp fall of transmittance at the band edge, which is an indication of good crystallinity. Fig. 4 indicates that the transmission of 1, 2 and 3 Zn % molecular weight doped $CuInS_2$ films are higher that of the non-doped and the doped films with 4 Zn % molecular weight. This indicates that an increase in Zn doping content from a critical Zn % molecular weight value has great effect on the transmission properties. This value corresponds in this work to 2% Zn content value. We note also an improvement in sharp fall of the transmission at the band edge after annealing in particular for 2 and 3 Zn % molecular weight. This is an indication of good crystallinity which confirms the XRD results.

3.2.2. Absorption coefficient and optical band gaps

The absorption coefficient (α) has been determined as a function of wavelength from measured reflectance R and transmittance T using the following equation [25, 26].

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

where d is the film thickness. Fig. 5 shows the absorption coefficient versus the photon energy for the non-doped and doped $CuInS_2$ thin films with 0 to 4 Zn % molecular weight after annealing in vacuum at 260°C for 2 hours. It can be seen that all the films have relatively high absorption coefficients between 10^4 cm^{-1} and 10^5 cm^{-1}



Fiure. 3. Reflection spectra of non-doped and Zn-doped $CuInS_2$ thin films with different Zn % molecular weight after annealing.

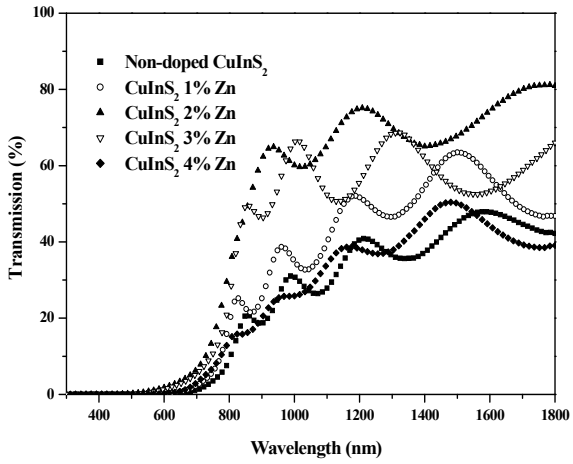


Figure 4. Transmission spectra of non-doped and Zn-doped $CuInS_2$ thin films with different Zn % molecular weight after annealing.

in the visible and the near-IR spectral range. Fig. 5 clearly shows an improvement in the optical performance of $CuInS_2$ films doped with 3 Zn % molecular weight with sharp fall of the absorption at the band edge compared to that of the non-doped or doped with other Zn content. This result is very important because we know that the spectral dependence of absorption coefficient affects the solar conversion efficiency **[27]**. In the high absorption region close to the beginning of band-to- band optical transmission (absorption coefficients $\alpha > 10^4$ cm^{-1}) the absorption is characterized by the following relation [28, 29].

$$\alpha h\nu = A\left(h\nu - E_{opt}\right)^m \tag{3}$$

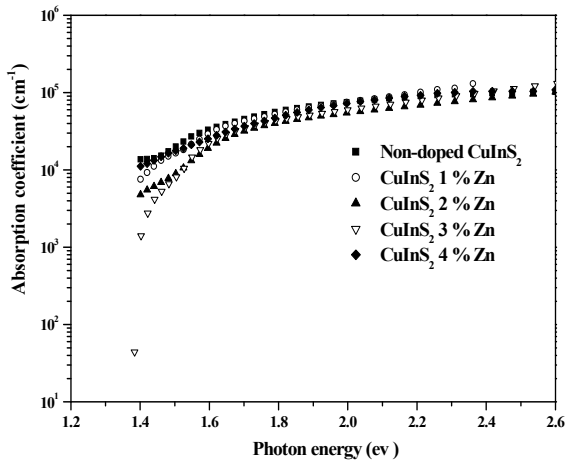


Figure 5. Absorption coefficients spectra of non-doped and Zn-doped $CuInS_2$ thin film with different Zn % molecular weight after annealing.

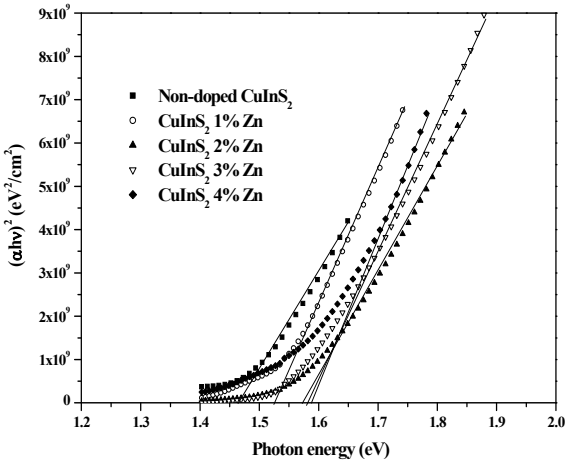


Figure 6. Relationship between $(\alpha h\nu)^2$ and photon energy for non-doped and Zn-doped $CuInS_2$ thin film with different Zn % molecular weight after annealing.

where A is a constant, E_{opt} is the optical gap and m is an integer number which characterizes the transition process. Different authors [29-31] have suggested different values of m for different glasses. The usual method for determining the values of E_{opt} involves plotting a graph of $(\alpha h\nu)^{\frac{1}{m}}$ vs $h\nu$. An appropriate value of m is used to linearize the graph, the value of E_{opt} is given by the intercept on the hν axis and the constant A can be determined from the slope. The best fit was found to be m = ½ which indicates that direct photon transition is involved (Fig. 6). It is now well established that $CuInS_2$ is a direct gap semiconductor [32-34], with the band extrema located at the centre of the Brillouin. The absorption coefficient α is related to the energy gap E_{opt} according the equation [35].

$$(\alpha h\nu)^2 = A\left(h\nu - E_{opt}\right) \tag{4}$$

The direct band gap energy (Fig. 7) increased after annealing from 1.467 to 1.585 eV with increasing Zn content. We attribute this difference to the presence of an amorphous component and possibly the structural defects, since it cannot be excluded that the polycrystallinity of the films influences the optical absorption behaviour and thus also the gap energy derived from the spectra. Also the amount of disorder in the material probably plays an important role in the optical band gap, since the XRD analysis indicated that for the higher Zn % molecular weight a deterioration of the structural properties was observed which give rise to defect states and thus induce smearing of absorption edge.

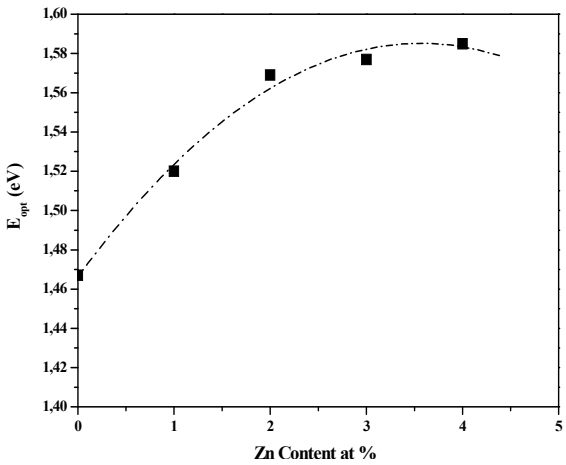


Fig. 7. Relationship between the optical bands gaps of $CuInS_2$/Zn with different Zn % molecularweight after annealing.

3.2.3. Electrical properties

Besides the optical properties, the electrical properties are also an important aspect of the performance of Zn doped $CuInS_2$ thin films. The effects of Zinc doping on the electrical resistivity of $CuInS_2$ thin films were investigated. As-deposited samples and annealed non-doped $CuInS_2$ thin films presented higher electrical resistivity. The variations of the resistivity of $CuInS_2$ thin films on the Zn % molecular weight after annealing in vacuum at 260°C is shown in Fig.8. The resistivity decreases with an increase of Zn content in the range of 0-3 Zn % molecular weight. It can be seen from Fig.8 that the lowest electrical resistivity value of doped 3 Zn % molecular weight is $8.10^{-1}\Omega$ cm with high P-type conductivity. After what the resistivity increases which can be explain probably by the increase of the amorphous component.

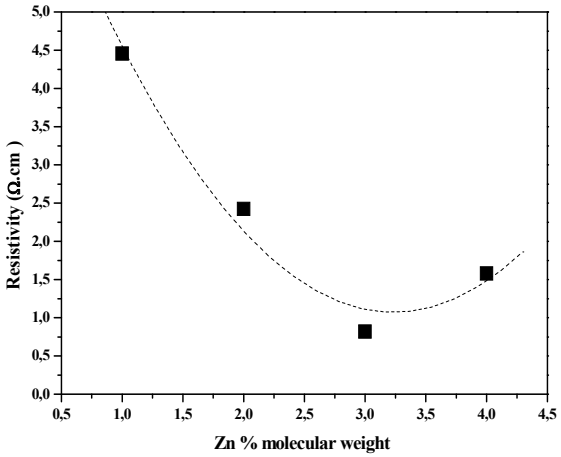


Fig. 8. Variations of the resistivity of Zn-doped $CuInS_2$ thin films with different Zn % molecular weight after annealing.

4. Conclusions

The effect of Zn doping on the structural and optical properties of $CuInS_2$ thin films has been investigated. Non-doped and Zn-doped $CuInS_2$ thin films were grown by double source thermal evaporation. The films are annealed in vacuum for 2h at 260°C. It was shown that Zn incorporation is possible and the control of Zn content is an important parameter to obtain Zn-doped $CuInS_2$ layers with high transmission. Moreover, up to 2 at % Zn the transmission decrease which indicates that an increase in doping content deteriorates the transmission properties. The absorption coefficients deduced from optical measurements are greater than $10^4 cm^{-1}$ in the range 1.4-2.6 eV after annealing. The direct band gap energy increased after annealing from 1.467 to 1.585 eV with increasing Zn % molecular weight. We attributed the higher values compared to that corresponding to the evaporated $CuInS_2$ thin films to the structural defects. The Zn-doped $CuInS_2$ thin films exhibit P-type conductivity. In particular, the electrical resistivity of the Zn-doped $CuInS_2$ thin films with 3 Zn % molecular weight reached $8.10^{-1}\Omega$.Cm.

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