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Structural and optical studies on antimony and zinc doped CuInS$_2$ thin films

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Abstract

The influence of Zn and Sb impurities on the structural, optical and electrical properties of CuInS$_2$ thin films on corning 7059 glass substrates was studied. Undoped and Zn or Sb doped CuInS$_2$ thin films were deposited by thermal evaporation method and annealed in vacuum at temperature of 450°C. Undoped thin films were grown from CuInS$_2$ powder using resistively heated tungsten boats. Zn species was evaporated from a thermal evaporator all together to the CuInS$_2$ powder and Sb species was mixed in the starting powders. The amount of the Zn or Sb source was determined to be in the range 0-4 wt% molecular weight compared with the CuInS$_2$ alloy source. The films were studied by means of X-ray diffraction (XRD), Optical reflection and transmission and resistance measurements. The films thicknesses were in the range 450 – 750 nm. All the Zn:CuInS$_2$ and Sb:CuInS$_2$ thin films have relatively high absorption coefficient between $10^4$ cm$^{-1}$ and $10^5$ cm$^{-1}$ in the visible and the near-IR spectral range. The bandgap energies are in the range of 1.472 – 1.589 eV for Zn:CuInS$_2$ samples and 1.396 – 1.510 eV for the Sb:CuInS$_2$ ones. The type of conductivity of these films was determined by the hot probe method. Furthermore, we found that Zn and Sb-doped CuInS$_2$ thin films exhibit P type conductivity and we predict these species can be considered as suitable candidates for use as acceptor dopants to fabricate CuInS$_2$-based solar cells.

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1. Introduction

"Ternary chalcopyrite CuInS$_2$ thin films exhibit many excellent physical and chemical properties such as high absorption coefficient of almost of $10^5$ cm$^{-1}$ in the visible spectral range [1], high tolerance to the presence of defects, an direct band gap closes to 1.5 eV, the optimum value for the photovoltaic conversion of solar energy" [2], possibility to avoid N or P-type conductivity [3] and high chemical stability. In contrast to other ternary semiconductor materials, CuInS$_2$ is nontoxic, low-cost and easy to fabricate by various thin film deposition techniques [4-6]. Because of these interesting properties, CuInS$_2$ is a material that can be used in various applications such as photovoltaic conversion devices and absorber in solar cells [7,8]. For controlling conduction

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type and obtained a 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 [9-11]. Additionally, the electrical properties of CuInS₂ thin films could be modified by thermal in a reducing atmosphere [12,13]. M. Zribi [9] proposed to investigate the effect of Na doping on the properties of CuInS₂ thin films and obtained more interesting results. T. Yamamoto [10] investigated the electronic structures of N-type doped CuInS₂ crystals using Zn and Cd species. Enzenhofer [11] 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 [14] 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 Zn-doped and Sb-doped CuInS₂ this films.

2. Experimental

2.1 Synthesis of CuInS₂ powders

Stoichiometric amounts of the element of 99.999% purity Cu, In, and S were used to prepare the initial ingot of CuInS₂. The mixture was sealed in vacuum in a quartz tube. In order to avoid explosions due to sulfur vapor 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 CuInS₂ phase was present in the ingot. Crushed powder of this ingot was used as raw material for the thermal evaporation.

2.2 Film preparation

CuInS₂/Zn and CuInS₂/Sb samples were prepared by co-evaporation of the CuInS₂ powder and the Zn or Sb 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. And Zn species were deposited simultaneously during the deposition of the CuInS₂ powder. For the CuInS₂/Sb samples, antimony was introduced in the starting powder, analogue to Cu, In and S elements. The mixture was sealed in vacuum in a quartz tube. Thermal evaporation sources were used which can be controlled either by the crucible temperature or by the source powder. The glass substrates were heated at temperature of 100°C. The amount of the Zn or Sb was determined to be 0 – 4 wt % molecular weight compared with the CuInS₂ alloy source. Film thickness was measured by interference fringes method [15]. Typical as-deposited films thicknesses were in the range of 450 – 750 nm after that all the films were annealed in vacuum at temperature of 450°C for 2 hours.

2.3 Characterization

The structure of the Zn-doped and Sb-doped CuInS₂ thin films was determined by means of X-ray diffraction (XRD) using a D8 advance diffractometer with CuKα radiation (λ = 1.5418 Å). The optical characteristics were determined at normal incidence in the wavelength range 300–1800 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

Figs 1 and 2 shows the results of our XRD measurements after annealing in vacuum at 450°C of undoped and Zn or Sb-doped CuInS₂ thin films. Vacuum-evaporated films are usually considered to be randomly oriented polycrystalline. It is found that the dopants concentration has great effects on the formation of polycrystalline CuInS₂. All diagrams present peak at 20 = 27.9° assigned to the (112) reflection of CuInS₂ phase. For the samples
doped with zinc, it is observed that the intensity of the (112) peak decreases obviously with increasing zinc concentration, which probably may be due to increase of the disorder component. Furthermore, the (112) intensity peak decreases when the Sb % molecular weight is equal or less that 3%, compared to undoped sample and become highly oriented for 4% antimony. We also note a few minor peaks with lower intensities identified as In$_6$S$_7$ and Cu phases for all samples doped with Zn and Sb dopants. The presence of the minor phases is in general attributed to a sun of internal origins obeying the thermodynamics of solid solutions, to defect chemistry and the thermal gradient which plays an important role as described elsewhere [16]. Indeed, the additional copper phase is mainly attributed to the higher mobility of Cu$^+$ and its migration toward the surface layers [17].

3.2 Optical and electrical properties

3.2.1 Optical transmission and reflection spectra

The effects of doping zinc and antimony on the optical reflection and transmission spectra in the wavelength range 300 – 1800 nm at normal incidence are studied. Figs 3 and 4 show the transmission spectra after annealing in vacuum of Zn-doped and Sb-doped CuInS$_2$ thin films with Zn or Sb content in the range 0 to 4 % molecular weight. 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.3 indicates that the transmission of samples doped with zinc for 1, 2 and 3 % molecular weight are higher that of the undoped 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. From fig 4, we note a decrease in the transmission values for the Sb-doped CuInS$_2$ films with increasing Sb % molecular weight compared to undoped ones. The reason of the decrease of the transmission is that the antimony is localized in the volume rather near the surface.

3.2.2 Absorption coefficient and optical band gap

To calculate the absorption coefficient $\alpha$ (hv), the following relation was used [18].

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

where d is the film thickness, R and T are the reflection and transmission coefficient, respectively. Figs 5 and 6 show the dependence of the absorption coefficient $\alpha$ versus the photon energy hv of the Zn-doped and Sb-doped CuInS$_2$ thin films with 0 to 4 % Zn or Sb molecular weight, respectively. It can be seen that all the films have relatively high absorption coefficients between $10^3$ cm$^{-1}$ and $10^5$ cm$^{-1}$ 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 4 % Zn molecular weight.
weight with sharp fall of the absorption at the band edge compared to that of the undoped or doped with other Zn content. From Fig. 6, it is clear that the absorption coefficient increases with increasing antimony % molecular weight. All the films have relatively high absorption coefficients, more than 5.10^4 cm^{-1} and remains constant along visible spectral range, which reached more than 10^5 cm^{-1} for the CuInS_2 samples doped with 4% Sb molecular weight.

Fig. 3. Transmission spectra of undoped and Zn-doped CuInS_2 thin films.

Fig. 4. Transmission spectra of undoped and Sb-doped CuInS_2 thin films.

Fig. 5. Absorption coefficients spectra of undoped and Zn-doped CuInS_2 thin film.

Fig. 6. Absorption coefficients spectra of undoped and Sb-doped CuInS_2 thin film.

Fig. 7. Relationship between (\alpha h \nu)^2 and photon energy for undoped and Zn-doped CuInS_2 thin film.

Fig. 8. Relationship between (\alpha h \nu)^2 and photon energy for undoped and Sb-doped CuInS_2 thin film.
The relation between the absorption coefficients $\alpha$ and the incident photon energy ($h\nu$) can be written for direct allowed band gap as\[^{[19]}\]:

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

where ‘$A$’ is constant and $E_g$ is the optical band gap. To determine optical transition, $(\alpha h\nu)^2$ versus $h\nu$ was plotted, and the corresponding band gaps were obtained from extrapolating the straight portion of the graph on the $h\nu$ axis at $(\alpha h\nu)^2 = 0$ (Figures 7 and 8). It is already well known that CuInS$_2$ is a direct gap semiconductor \[^{[1]}\], with the band extrema located at the centre of the Brillouin. The direct band gap energy is in the range 1.472-1.589 eV for Zn-doped CuInS$_2$ samples and in the range 1.396-1.510 eV for Sb-doped CuInS$_2$ samples.

3.2.3 Electrical properties

Besides the optical properties, the electrical properties are also an important aspect of the performance of Zn-doped or Sb-doped CuInS$_2$ thin films. Undoped CuInS$_2$ thin films presented higher electrical resistivity. The variations of the resistivity of CuInS$_2$ thin films on the Zn and Sb % molecular weight after annealing is shown in Fig.9. The resistivity decreases with an increase of Zn content in the range 0 – 3% molecular weight and the lowest electrical resistivity value is $8.10^{-1}$ Ω cm with high P-type conductivity. For the Sb-doped samples, all the films presented low electrical resistivity with clearly P-type conductivity for the samples doped wt 4 % Sb molecular weight. The resistivity values are in the range 1.32-0.22 Ω cm (figure9).

![Fig. 9. Variations of the resistivity of Zn and Sb-doped CuInS$_2$ thin films.](image)

4. Conclusion

The effects of zinc and antimony doping on the structural, optical and electrical properties of CuInS$_2$ thin films has been investigated. Undoped and Zn or Sb-doped CuInS$_2$ thin films were grown by thermal evaporation. The films are annealed in vacuum at temperature of 450°C for 2 hours. It was shown that Zn and Sb incorporation is possible and the control of dopants content is an important parameter to obtain doped CuInS$_2$ layers with high transmission. Moreover, up to 2 wt % Zn the transmission decrease which indicates that an increase in doping content deteriorates the transmission properties. In the other hand the transmission decrease with increasing Sb content. The absorption coefficients deduced from optical measurements are greater than $10^4$ cm$^{-1}$ in the range 1.4-2.6 eV for all the films. The direct band gap energy increased from 1.472 to 1.589 eV with increasing Zn % molecular weight and the Sb-doped samples have band gap energy of 1.396-1.510 eV. The Zn-doped and Sb-doped CuInS$_2$ thin films exhibit P-type conductivity. In particular, the electrical resistivity of the Zn-doped CuInS$_2$ thin films wt 3 %Zn reached $8.10^{-1}$ Ω cm and $22.10^{-2}$ Ω cm for the Sb-doped CuInS$_2$ thin films wt 4 %Sb. These resistivity measurements showed that films are semi-conducting in nature. After studying optical and electrical properties of Zn and Sb-doped CuInS$_2$ thin films, the films can be suitably employed in solar cells applications.
References