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Illumination-induced changes on the optical functions and valence band splitting parameters of flash evaporated $CuInTe_2$ films

I.T. Zedan [a,*], E.M. El-Menyawy [b]

[a] Basic Science Department, High Institute of Engineering and Technology, El-Arish, North Sinai, Egypt
[b] Solid State Electronics Laboratory, Solid State Physics Department, Physical research Division, National Research Centre, 33 El-Bohouth St., Dokki, Giza 12622, Egypt

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ABSTRACT

Chalcopyrite $CuInTe_2$ thin films have been deposited by flash evaporation technique on optically flat quartz substrates. The influence of light illumination on the structural and optical properties of $CuInTe_2$ thin films has been reported. The structural properties of the films are investigated by energy dispersive X-ray, grazing incident in-plane X-ray diffraction and transmission electron microscope. The transmittance and reflectance spectra of the films are measured at normal incidence of light, from which, the refractive and absorption indices of the films are determined. The optical absorption process of as-deposited and illuminated $CuInTe_2$ films is found to be characterized by three direct transitions. The triplet transitions are explained in terms of the valence band splitting under the influence of the tetragonal crystalline field and spin-orbit interaction. Below the lowest optical band gap, the absorption coefficient exhibits exponential behavior, in which Urbach's energy of as-deposited and illuminated films is determined as 0.45 and 0.41 eV, respectively. Single oscillator and Drude models are employed to determine the optical dispersion parameters for as-deposited and illuminated films.

1. Introduction

Chalcopyrite semiconductors in the configuration type of Cu–III–VI_2 have been extensively studied due to their potential applications in a variety of electro-optical devices [1,2], potential optoelectronic applications as solar energy converters, nonlinear optical devices, light emitting diodes, and detectors. Among these materials, $CuInTe_2$ possess unique characteristics such as direct optical transitions, high absorption coefficient in the visible light region of solar spectrum, large non-linear susceptibility in the infrared region and high vapour pressure of Te [3]. $CuInTe_2$ has isothermal bulk modulus lower than that of $CuInS_2$ and $CuInSe_2$ but has larger thermal expansion coefficient [4]. $CuInTe_2$ shows great promise for thin film solar cell applications because it can be can be made both p and n-types [5].

Chalcopyrite thin films have been prepared by different methods such as solvo- or hydrothermal routes [6], spray pyrolysis [7], electrochemical deposition [8], sol–gel methods [9], flash evaporation technique [10], pulsed laser deposition [11] and thermal evaporation technique [12]. The main conclusion drown by these studies is that the changes in the physical properties of the films are induced by the stoichiometric deviations and it would be interesting to know the range of compositions that can appear in single phase. Better understanding of such properties would be useful for the fabrication of materials with optimized parameters for devices fabrication. Effects such as heat treatment and pressure have been performed and studied for $CuInTe_2$ [12,13]. Boustani et al. [12] pointed out that $CuInTe_2$ films with a single phase can be obtained by the heat treatment temperatures higher than 300 °C. Choi and Yu [13] showed that the optical band gap increases with increasing pressure. The fabrication and the study of the physical properties of $CuInTe_2$ thin films have been reported by many authors .Meanwhile, to the best of our knowledge there are not published reports on the effect of light illumination on the optical properties of $CuInTe_2$ films which gave us the motivation of this study. Exposure of inorganic and even organic films to light was found to affect the optical properties of the films [14,15]. Cu–III–VI_2 is regarded as to be the ternary analogue of the II–VI binary materials. They crystallize in the structure called the chalcopyrite constructed by doubling the unit cell of II–VI binary's (zinc blende) in vertical direction which can cause a splitting in the valence band due to spin-orbit and crystal-field effects.

In this work, the influence of light illumination on the optical functions and valence band splitting parameters of flash evaporated $CuInTe_2$ films is investigated.

* Corresponding author. Tel.: +20 1117304860; Fax: +26 83328372.
E-mail address: islamzedan@hotmail.com (I.T. Zedan).

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2. Experimental techniques

Copper, Indium, and Tellurium (with purity of 99.999 wt%) were used for obtaining the $CuInTe_2$. The synthesis of $CuInTe_2$ compound was carried out using quartz ampoule, evacuated at 10^{-5} Torr, in oscillatory furnace. The temperature of the oscillatory furnace was raised, with a rate 50 °C/h, up to 700 °C and the ampoule was kept at this temperature for 2 h, then up to 1100 °C for 3 h. Then, the melt was cooled to room temperature through two days.

Thin films of $CuInTe_2$ were grown by flash evaporation technique by using high vacuum coating unit (Edwards, E 306 A). The pressure of the working chamber was pumped down to 2×10^{-6} Torr. The films were deposited onto pre-cleaned quartz substrates. To study the effect of illumination, tungsten lamp of 200 Watt was used. The films were exposed to light for one hour.

The composition of the films was investigated by energy dispersive X-ray analysis (EDX) using JSM 6400 JEOL model SEM attached with NORAN, EDX detector. X-ray diffraction characterization of the powder was carried out using filtered CuK_α radiation (Philips PW 1700) operated at 40 kV and 25 mA. X'Pert Pro PANalytical was used to investigate the structure of $CuInTe_2$ films in terms of grazing incident in-plane X-ray diffraction technique. JEOL JEM-1230 transmission electron microscope (TEM) is used to determine the morphology of particles and electron diffraction of the films.

The transmittance and reflectance of films deposited onto quartz substrate were measured at room temperature using unpolarized light at normal incidence in the wavelength range (400–2500 nm) using a dual beam spectrophotometer ((JASCO model V-570 UV–vis–NIR. The absolute values of total measured transmittance (T_m) and reflectance (R_m) were calculated by [16]:

$$T = T_m \left(1 - R_q\right) \quad (1)$$

and

$$R = R_m R_{Al} \left[(1 - R_q)^2 + 1\right] - T^2 R_q \quad (2)$$

where R_q and R_{Al} are the reflectance of reference quartz substrate and that of the reference aluminium mirror, respectively. The refractive and absorption indices of the films are determined from the absolute values of the measured transmittance and reflectance spectra by using Murmann's equations for absorbing films deposited on non absorbing substrates. The method used for obtaining optical constants is given elsewhere [17].

3. Results and discussion

3.1. Structural characteristics

X-ray diffraction studies were carried out in order to identify the crystallinity and the phase of $CuInTe_2$. Fig. 1 demonstrates the typical X-ray diffraction patterns of the $CuInTe_2$ in powder form. The sharp diffraction peaks in the powder pattern indicate polycrystalline nature. All the main diffraction peaks coincide with their standard bulk crystal structure patterns for $CuInTe_2$ (JCPDS 82-0450) with tetragonal structure. The indexing illustrates that the $CuInTe_2$ chalcopyrite material is prepared in single phase. The main diffraction peaks observed at 24.68°, 40.86° and 48.33° corresponds to the (1 1 2), (2 0 4)/(2 2 0), (1 1 6)/(3 1 2) reflection directions of the as-synthesized powder. The lattice parameters for $CuInTe_2$ under investigation is determined as $\boldsymbol{a}$ = 5.398 and $\boldsymbol{c}$ = 10.529 Å.

Fig. 2 illustrates the EDX of $CuInTe_2$ films deposited on glass substrate. The atomic percentages of copper, indium, and tellurium are obtained as 26.76, 22.77 and 50.48%, respectively. It can be seen that the obtained $CuInTe_2$ films are cupper rich. The percentage of Te is also relatively higher than the stoichiometric value.

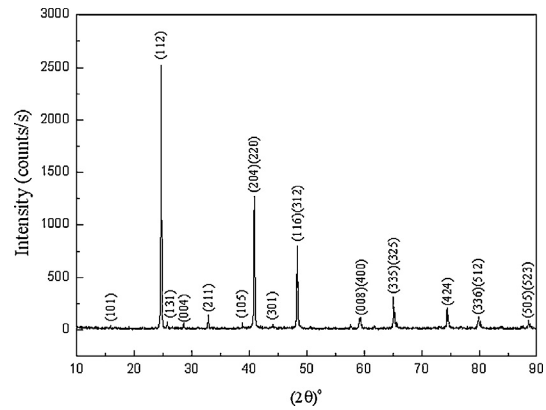

Fig. 1. X-ray diffraction pattern of $CuInTe_2$ powder.

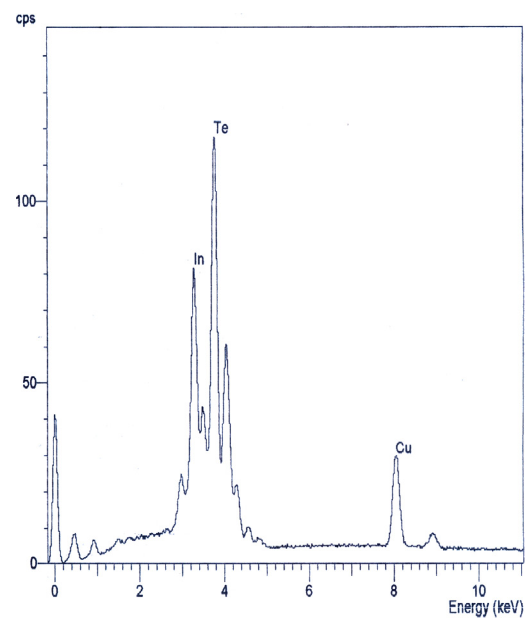

Fig. 2. EDAX spectra of $CuInTe_2$ thin films.

Fig. 3 shows the grazing incident in-plane X-ray (GIIXR) diffraction spectra of as-deposited and illuminated $CuInTe_2$ films. The spectra of both films show a broad hump in the diffraction angle range (15–38°). The hump is ascended with low intensity peaks. These results suggest that the films are partially crystalline and

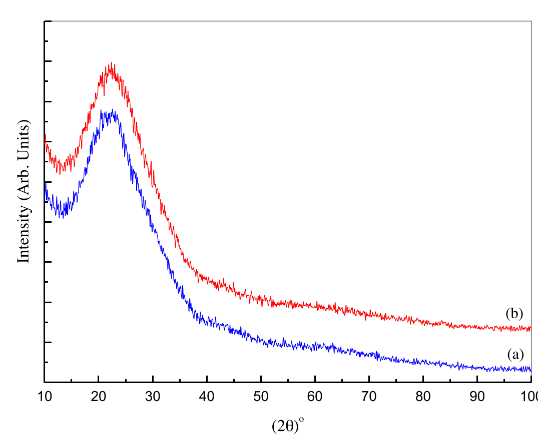

Fig. 3. GIIXR diffraction of $CuInTe_2$ films: (a) as-deposited and (b) illuminated.