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PREPARATION AND CHARACTERIZATION OF SPRAYED $AgInSe_2$ THIN FILMS

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Silver Indium Diselenide ($AgInSe_2$) thin films were prepared by spray pyrolysis technique. Structural, Electrical and optical properties of $AgInSe_2$ thin films deposited at different deposition temperatures were studied. The deposition temperature is varied in the range 200°C to 300°C. All prepared films are polycrystalline thin films where the crystallite size increases with increasing the deposition temperature. The conductivity temperature data for the prepared films was analyzed according to the thermoionic emission over grain boundary potential model. The calculated value of activation energy for our films was varied from 597 meV to 451 meV depending on the deposition temperature. The bandgap (E_g) has been obtained from the optical transmission spectra. By increasing the deposition temperature, the optical band gap varied from 1.15 to 1.02 eV. To our best knowledge, we report here the first synthesis of $AgInSe_2$ thin films by spray pyrolysis technique.

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1. Introduction

The family of the ternary semiconducting compounds (I III VI_2) has been widely investigated because of their potential applications to photovoltaic solar cells, light emitting diodes, and nonlinear optical devices [1–5]. These compounds have photovoltaic potential for solar cells since their optical bandgap lies between 0.8 and 2.0 eV and they can be grown either n or p type. $AgInSe_2$ is a ternary analogue of CdSe which has been used for a number of electronic devices [6, 7]. Silver indium diselenide $AgInSe_2$ is one in this family and has a nearly ideal chalcopyrite structure. $AgInSe_2$ is a semiconductor with energy gap of 1.19 eV [8]. Extensive studies on the electrical and optical properties of bulk crystalline $AgInSe_2$ have been carried out [9–11]. For thin film deposition, different methods such as coevaporation [12], sputtering [13], spray pyrolisis [14], selenization [15], flash evaporation [16] and thermal evaporation [17] have been used for deposition of I–III–VI_2 compounds. No published work use sprays pyrolysis technique before to prepare $AgInSe_2$. Spray pyrolysis (SP) is an attractive method because large-area films with good uniformity can be grown at low cost [18,19]. In this paper, $AgInSe_2$ thin films were prepared by spray pyrolysis technique, for first time, at different deposition temperature. In this work, the variation in structural, electrical and optical properties of sprayed $AgInSe_2$ films with the deposition temperature is presented.

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2. Experimental details

An aqueous solution of $AgNO_3$, $InCl_3$ and $SeC(NH_2)_2$ was used to deposit $AgInSe_2$ thin films. At first, aqueous solutions (0.2 M) of these salts were prepared. Then they were mixed with appropriate portions in order to have copper to indium molar ratio of 1 ([Ag]/[In] = 1), and selenium to indium molar ratio of 4 ([Se]/[In] = 4). The solution was sprayed onto the preheated glass substrates at temperatures ranging from 200°C to 300°C. The compressed air was used as atomization gas. The distance between the nozzle and substrate, pressure of the carrier gas, spray time and spray rate were optimized to obtain good quality $AgInSe_2$ thin films.

The substrates were ultrasonically cleaned in acetone, methanol and distilled water. The obtained films thickness was measured using Stylus method. Structural analysis was done using X-ray diffraction (XRD) with the Philips X'pert X-ray diffractometer employing CuKα line (k =1.5405 Å). The chemical composition of the prepared films was studied by the energy dispersive spectroscopy (EDS). The optical properties of the prepared films were measured by Jasco V750 UV–VIS–NIR spectrophotometer. The Sheet resistance of the prepared films was measured at room temperature using four probe method where the measurement of electrical conductivity as a function of temperature was carried out using Keithley electrometer model 6517A.

3. Results and discussion

3.1. Structural and compositional properties

Deposition temperature is the main parameter which allows controlling the composition of the $AgInSe_2$ films in the SP technique. Fig. 1 shows the X-ray diffraction patterns for representative films deposited at different deposition temperatures. It can be noticed that all prepared films are polycrystalline materials. Film grown at the lowest deposition temperature had bad crystalline quality with very small crystallite size, also its pattern show presence of In_2Se_3 peak beside the main peaks of $AgInSe_2$. It can be attributed to incomplete reaction to fabricate $AgInSe_2$ compound due to the limited heat energy at this low deposition temperature. However by increasing the deposition temperature, the crystalline quality and the grain size enhanced where the sharpness and the numbers of the peaks, related to $AgInS_2$, increase with the absence of the other impurities or phases.

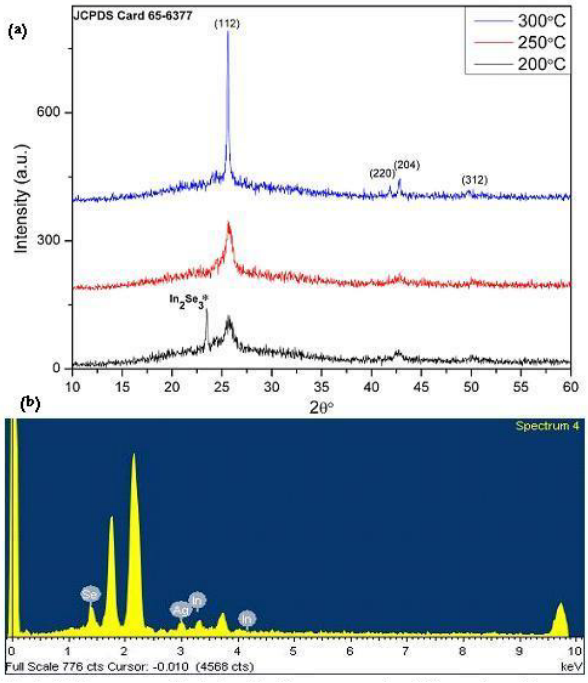

Fig. 1. XRD patterns of $AgInSe_2$ thin films prepared at different deposition temperature and EDS pattern of sample prepared at 200 ^oC.

Table 1 shows the chemical composition results for films prepared at different deposition temperatures using constant molar ratio of: Ag:In:Se in the starting solutions. According to these values, it is noticed that the Se percentage in the prepared film decrease by increasing the deposition temperature. Also it observed that, by increasing the deposition temperature, the film become to be nearly stoichiometric composition comparing to the film prepared at lower deposition temperature.

Table 1. EDS data of sprayed $AgInSe_2$ films prepared at different deposition

Deposition Temperature (°C)	Atomic percentage of different elements (at %)		
	Ag	In	Se
200	17.70	14.23	68.07
250	18.81	23.94	57.26
300	23.17	21.15	55.67

3.2. Optical properties

The optical transmittance of the sprayed $AgInSe_2$ films is presented in Fig. 2. There is significant change in optical transmittance of $AgInSe_2$ films as the deposition temperature increased from 200°C to 300°C. The decrease in film thickness with increase in temperature from 200°C to 300°C has noticeable effect on optical transmittance of sprayed $AgInSe_2$ thin films. The band gap energy (E_g) and absorption coefficient (α) for the sprayed $AgInSe_2$ films are determined from the optical transmission data. The absorption coefficient (α) can be calculated by [20]:

$$\alpha = (2.303/t)[\log(1/T)]$$

Where t is the thickness of the film and T is the transmittance.

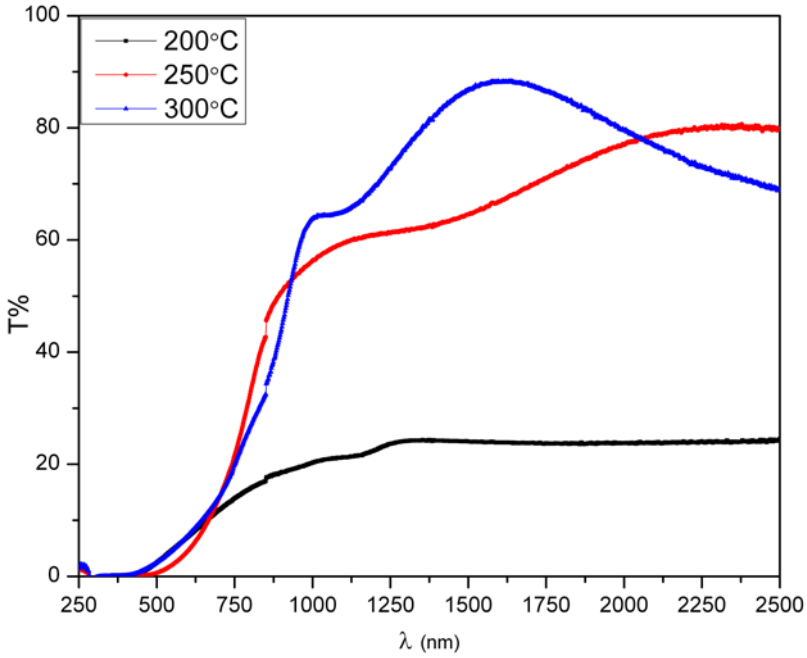

Fig. 2. Transmittance spectra of $AgInSe_2$ thin films prepared at different deposition temperatures.

The optical band gap (E_g) for direct optical transitions was calculated and given by the well known expression, [12, 13]

$$\alpha = \frac{A(h\nu - E_g)^{\frac{1}{2}}}{h\nu}$$

Where A is a constant, and E_g is the optical band gap. The band-gap value can be obtained from the best linear approximation in the $(\alpha h\upsilon)^2$ vs. $(h\upsilon)$ plot and extrapolating its linear portion to zero absorption coefficient.

As easily understood from Fig.3, the optical band gap exhibits deposition temperature dependence. It shifts towards lower energy side with increasing the deposition temperature from 200°C to 300°C. The decrease in direct band gap energy with increase in deposition temperature is confirmed, which attributed to the decreasing in the film thickness and crystallinity enhancement with increasing the deposition temperature. Note that most of chalcopyrite semiconductors, exhibit a gradual decrease of E_g with increasing the deposition temperature. [21,22]

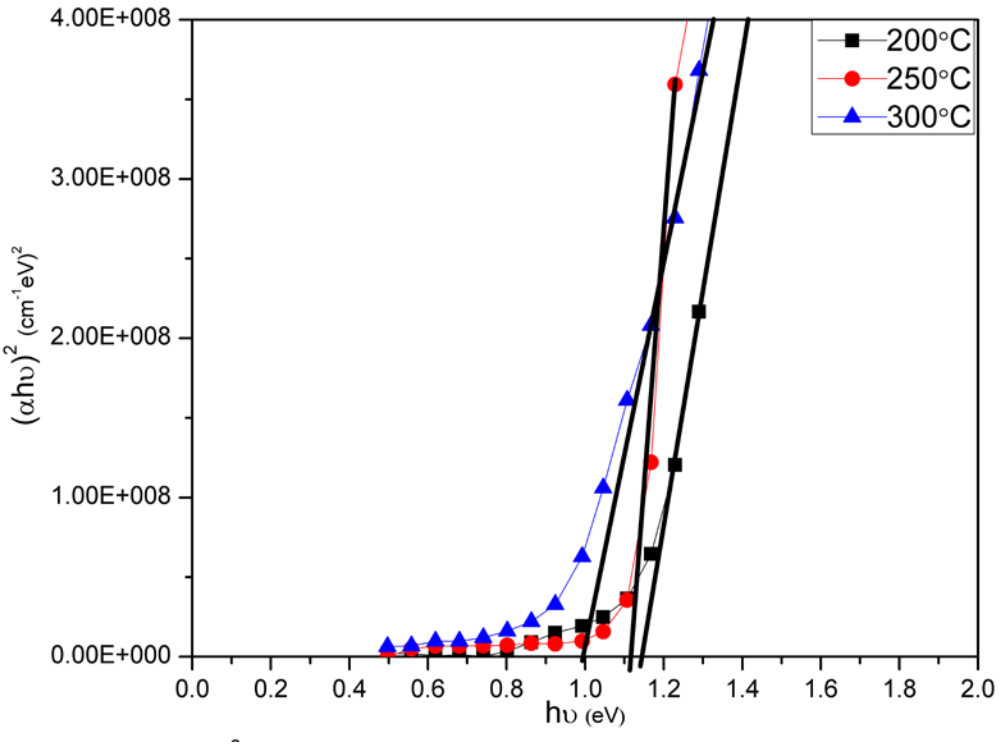

Fig. 3. $(\alpha h\nu)^2$ versus$(h\nu)$plot of sprayed $AgInSe_2$ thin films prepared at different deposition temperatures.

3.3. Electrical properties

The experimental data of conductivity σ as a function temperature T for sprayed $AgInSe_2$ prepared at different deposition temperatures is plotted in Fig. 4. This figure shows that the conductivity increased by increasing the deposition temperature. This result is in line with XRD data where the crystallinity and grain size improved with increasing the deposition temperature.

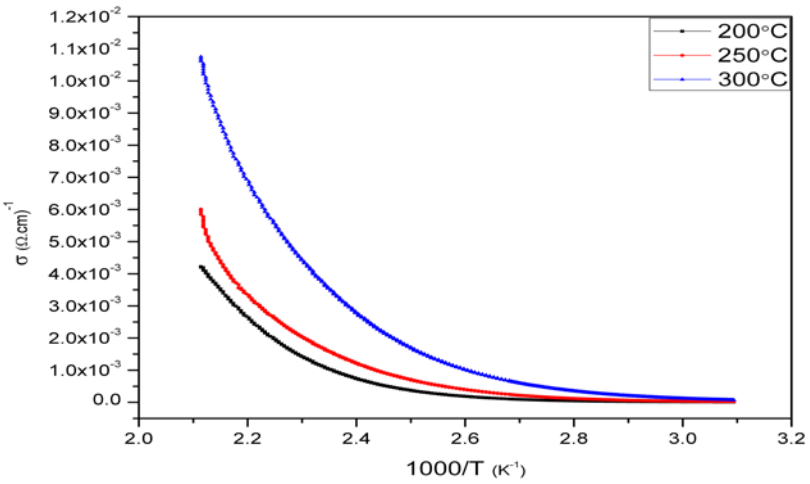

Fig. 4. Electrical conductivity versus (1000/T) plot of $AgInSe_2$ thin films deposited at different deposition temperature.

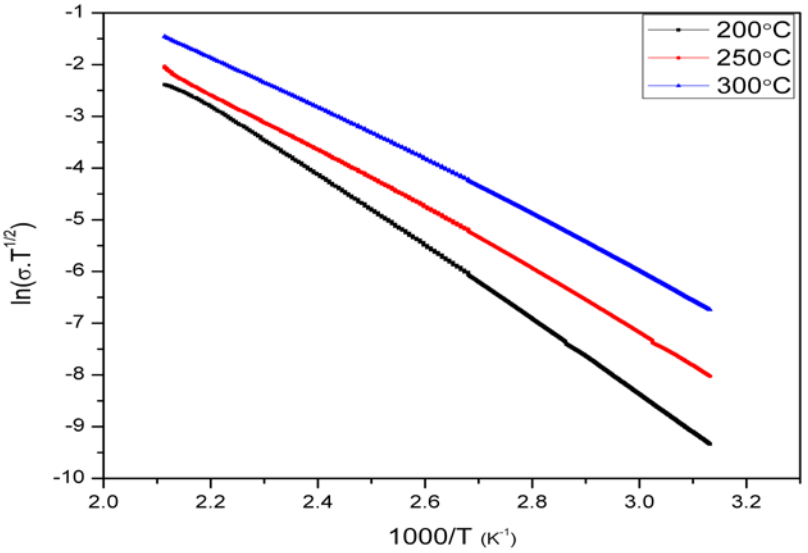

Fig. 5. $In(\sigma.T^{1/2})$ versus (1000/T) plot of $AgInSe_2$ thin filmsdeposited at different depositon temperature.

As discussed previously in the section of XRD results that all the prepared films are polycrystalline, where the polycrystalline thin films are composed of crystallites (grains) surrounded by grain boundaries (sometimes called internal surfaces) [23]. The conduction mechanism for the polycrystalline thin films is significantly influenced by these built-in grain boundary potentials. Therefore, the conductivity–temperature data for the our polycrystalline films were analyzed according to thermionic emission over the grain boundary potential model proposed by Seto [24] where the conductivity is given by

$$\sigma\sqrt{T} = \sigma_0 \exp\left(\frac{-E_a}{kT}\right)$$

Where σ_o is the pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant and T is the absolute temperature.

Fig. 5. shows the plots of $\ln(\sigma T^{1/2})$ vs. 1000/T based on the experimental data of fig. 4. The linear behavior of the $\ln(\sigma T^{1/2})$ vs. 1000/T curves confirms that the conductivity of sprayed $AgInSe_2$ films in this temperature range is mainly governed by the grain boundary limited

conduction which is the dominant conduction mechanism in polycrystalline films. As a result of detailed analysis of the temperature dependent conductivity data, it is noticed that the activation energy is a function of the deposition temperature where the crystallinity of the film enhanced with increasing the deposition temperature.

4. Conclusions

$AgInSe_2$ thin films have been deposited by spray pyrolysis technique at different deposition temperatures. The structural studies indicate that films are polycrystalline and the crystallinity increase with increasing the deposition temperature. EDS analysis for all films show that the chemical composition of prepared thin films is a function in the deposition temperature. The film prepared at high temperature was found to be nearly stoichiometric comparing to the film prepared at lower deposition temperature. The optical studies of indicated that films exhibit direct and gap which is strongly dependent on the deposition temperature. The electrical conductivity of sprayed $AgInSe_2$ thin films is found to increase with increasing the deposition temperature. The electrical transport of our films was studied in temperature interval from 448 K to 573 K. this study reveals that exist only one mechanism for conduction which is due to the thermoionic emission.

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