

Effect of annealing on thin film AgInSe₂ solar cell

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AgInSe₂ (AIS) thin films solar cell involving of n-type AgInSe₂ and Si of p-type substrate by using thermal evaporation method. The influence of annealing of the preparation AgInSe₂ were considered to find the best properties of solar device. Thin film AIS have been deposited under the vacuum of 1.5×10^{-6} Torr with (400) nm thickness at R.T and annealing temperatures (473,573) K. Polycrystalline tetragonal structure for AIS thin films from XRD and increasing of surface roughness from AFM, energy gap values decreasing with increasing annealing temperatures, all films were negative type, I-V characteristics show increasing of efficiency with increasing of annealing temperatures.

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1. Introduction

Silver Indium Diselenide is a ternary semiconductor material. These compounds are analogues to binary zinc blende II-VI. Silver based chalcopyrite semiconductor has as better candidates for solar cell fabrication [1]. I-III-VI₂ semiconductors Group for example AgInSe₂, AgInS₂ AgInTe₂ involve two metals and one chalcogen [2] The prominent member of the chalcogenide semiconductor family I-III-VI₂ is AgInSe₂, have their semiconductor which agreement alternatives for suitable band-gap energies, the attention of much recent research because of their excellent electrical and optical properties, very significant application in optical devices (linear and nonlinear), photovoltaic solar cell, NIR applications in addition to the preparation of solar cells device and Schottky diode [3], AgInSe₂ has a middle energy gap as compare with AgInS₂ and AgInTe₂ and so finds applications in solar cell [4]. thin films AIS are N type of semiconducting naturally [5]. The material modification by several external energy sources like laser irradiations [6] thermal annealing [7] γ irradiations [8] and proton irradiation [9]. brings significant changes in their structural and optical properties [10] direct gap semiconductors [11] lies between 0.8 and 2.0 eV [12] the crystal structure of AIS is tetragonal structure chalcopyrite with the lattice constant $a = b = 6.102 \text{ \AA}^\circ$ and $c = 11.69 \text{ \AA}^\circ$ [13]. high optical absorption (10^{-5} cm^{-1})[14]. Thin film of AgInSe₂ has been deposited by several methods such as spray pyrolysis technique [12,13] pulsed electrodeposition technique [15]. hybrid sputtering/evaporation process [16]. co-evaporation [11], sol-gel spin-coating technique [17]. reactive evaporation indicate that the incorporation[18], DC magnetron sputtering[19], chemical bath deposition [20], thermal evaporation with annealing [21], electrodeposition process [22], by Simple Chemical Method [23], hot-press method [24]. Bridgman technique[25]. This work concentrate for on fabrication of solar cells of AgInSe₂ by vacuum evaporation method and study the concentrate on the effect of annealing (473,573) K on their description using XRD, AFM, optical measurement, Hall Effect, and I-V of AgInSe₂ film and the interconnection between these parameters.

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2. Experimental

The ternary compound Silver Indium Diselenide AgInSe₂ alloy was synthesized from high purity (99.99%) Silver (Ag) Indium (In) and selenium (Se) elements stoichiometric proportions by weight (1:1:2) then mix these three elements and put them in an evacuated tube of quartz when a pressure of (4.5*10⁻⁴ mbar), heated up to (1100 K) was higher than the melting temperature of AgInSe₂ (1050 K) [10] in electric oven for six hours then alloy left to cool to room temperature. Observation of the structure by X-ray diffraction (XRD). Deposition of thin films AIS by vacuum thermal evaporation in glass substrates at R.T with 400 nm thickness, then annealing at (473,573) K in an electric furnace for 60 minutes. to study the properties the manufacturing thin film solar cells. X-ray diffraction was used to examination the compound formation used to study the structural of these films by detailed 2Θ from 20° to 80 °with interval of 0.05°, Scherer's Formula used to calculate the crystalline size of the films [26, 27]. The surface morphology, roughness and Grain Size of AIS were shown to be affected by annealing temperature using atomic force microscopy. The optical properties of thin film prepared, transmission and absorption spectrums in the range between 400 to 1000 nm has been noted, lambert law and Tauc equation have been used to determine the absorption coefficients α and the energy gap (E_{gap}) respectively from absorption spectrum [28,29,30]. The consequences of Hall Effect were showed types of thin films of AIS thin film has been achieved by Van der Pauw (Ecopia-HMS -3000). As a final point Shockley equation used to the I-V characteristics [31].

3. Results and discussions

Figure (1) shows the pattern for AIS thin films at R.T and (473,573) K when the thickness (400) nm deposition on glass substrate, this figure shows that the AIS thin film have the polycrystalline tetragonal structures.

The XRD shows that all the films have tow peak when $2\Theta \approx 25.7260$ when the preferred orientation (112)[1,12], and another peak appear at 2Θ equal to 42.970. Table (1) display the peaks experiential in films, this result matched with the ICDD 00-038-0952 card standard value, the films have an improvement crystalline and the peak main intensity of (112) was growth with annealing temperatures [14]. No other crystalline phase where absence of any other diffraction peaks indicates that. Crystallite size become larger when increased the annealing temperatures.

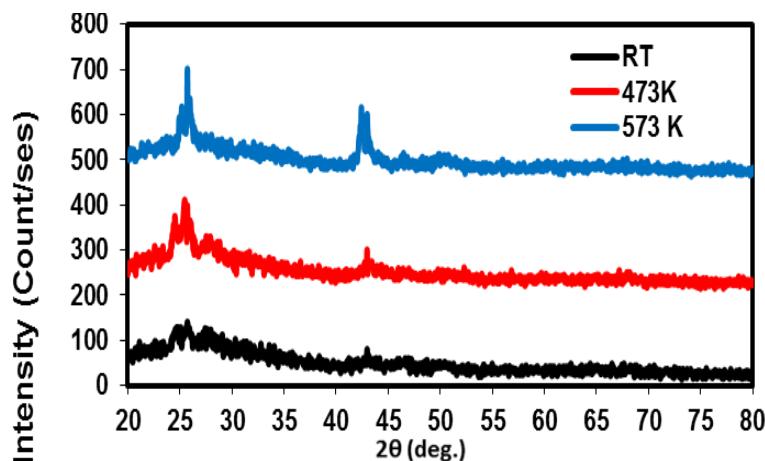


Fig. 1. XRD pattern for thin film AIS at R.T and (473,573) K.

Table 1. Experimental XRD data for thin films AlS at R.T and (473,573) K.

Thin Films	d(Std.) (Å)	d(Exp.) (Å)	2θ (Std.) (Deg.)	2θ (Exp.) (Deg.)	hkl	FWHM (deg.)	C.S (nm)
AgInSe₂ RT	3.46	3.4651	25.726	25.7	112	1.000	8.5149
	2.103	2.1012	42.97	42.95	204		
AgInSe₂ (Bi) RT	3.46	3.4573	25.726	25.75	112	0.975	8.7338
	2.103	2.1017	42.97	43	204		
AgInSe₂ (Bi) T=573 K	3.46	3.4573	25.726	25.75	112	0.471	18.0805
	2.103	2.1017	42.97	43	204		

Figures (2) present the AFM images of thin films with different annealing temperatures t=400nm. It is seen that all films surfaces exhibit a large number of grains of small size and uniform distribution. This confirms the result obtained from the XRD analysis, which indicates that all films have a polycrystalline structure. From Table (2), by annealing temperature, the average grain size is increased. This increase is expected due to the increase in the crystallite size of thin film. This result agrees with [21] for heat treatment AIS thin films.

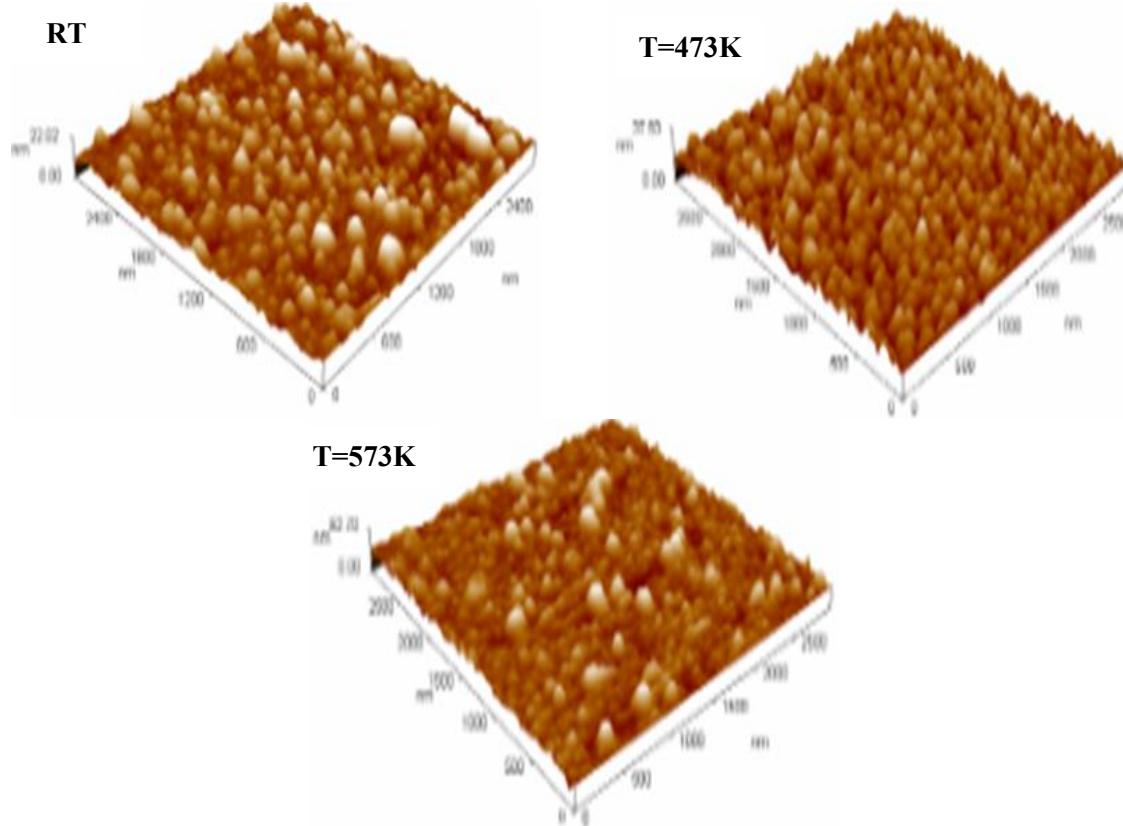


Fig. 2. 3D (AFM) of thin films AlS at R.T and (473,573) K.

Table 2. AFM analysis data for AlS at R.T and (473,573) K.

Thickness (400nm)	Grain Size (nm)	Surfaces roughness (nm)	Root mean Sq. (nm)
R.T	45.53	1.25	2.51
473	47.25	3.6	4.43
573	49.52	3.7	5.01

The increasing of transmittance spectra with increasing of wavelength display in figure (3) for all AIS thin films with different annealing temperatures at R.T and (473,573) K. The higher transmittance at R.T in the visible region this can be credited to decrease in the light absorption and reflection which lead to decrease in losses of light scattering[32]. The coefficient of absorption figure (4) value depending on the absorption spectrum and using Lambert Law [28,29]. The energy gaps of AIS is direct and this agrees with [11]. it can be concluded from the value of absorption coefficient larger than $\alpha > 104\text{cm}^{-1}$. The absorption coefficient of the AIS films is increasing in the visible spectrum region with increasing the annealing temperatures.

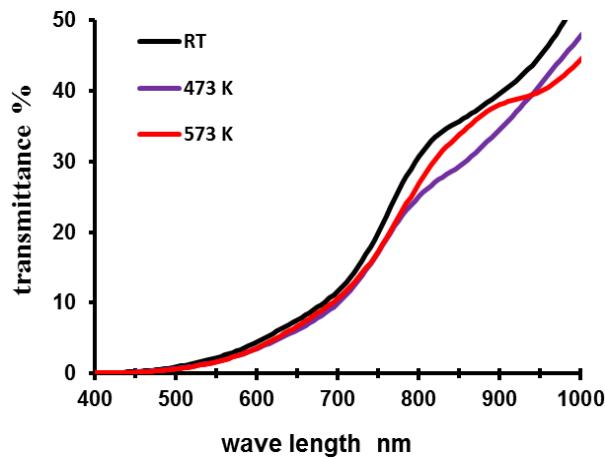


Fig. 3. Transmittance spectra vs. wave length of thin films AIS at R.T and (473,573) K.

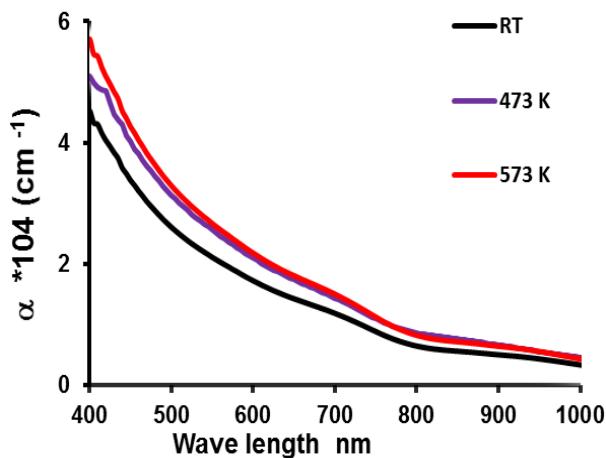


Fig. 4. The α vs. Wavelength of as prepared AIS at R.T and (473,573) K.

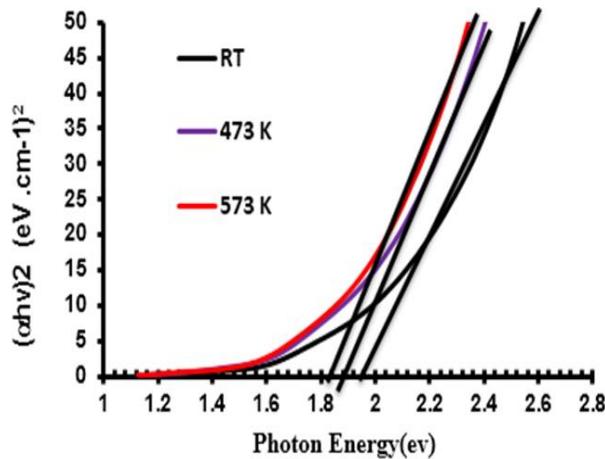


Fig. 5. $(\alpha h\nu)^2$ vs. $h\nu$ plot of as prepared of thin films AlS at R.T and (473,573) K.

Figure (5) and Table (3) shows the optical properties and the effect of annealing temperatures on the type and value of optical energy gap (E_{gopt}) for AIS is determined using Tauc Equation, the allowed direct transitions occur in thin film. This result agrees with MAHMOUD and SAYED [12]. The energy gap decrease this behavior may be attributed to the advance in the films crystallite size. The calculated energy gaps are listed in Table (3).

Table 3. The optical parameters $\lambda=500\text{nm}$ of thin films AlS at R.T and (473,573) K.

Thickness(400 nm)	E_g^{opt} (eV)	$\alpha \times 10^4 \text{ cm}^{-1}$
R.T	1.95	2.61
473	1.85	3.14
573	1.82	3.5

The type and concentration of the charge carrier and Hall mobility of annealing temperatures thin films have been estimated from Hall effect measurements, the calculated values are listed in Table (4). From this Table, one can be noticed that the value of Hall coefficient for all examined AIS thin films are negative which means that all the prepared samples exhibit n-type conductivity, i.e. the conduction is dominated by electrons. This is due to the donor centers formed during the deposition. This result agrees with previous investigations [5,33].

Table 4. Electrical parameters from Hall effect measurements for AIS thin films at R.T and (473,573) K.

Thickness(400 nm)	R_H	$N_D (\text{cm}^{-3})$	$\mu_H(\text{cm}^2/\text{V.S})$	$\rho(\Omega.\text{cm})$
R.T	-1973.47	3.167×10^{15}	37.6342	52.43
473	-852.3115	7.332×10^{15}	129.5513	6.578947
573	-656.3747	9.522×10^{15}	386.6047	1.697793

Figure 6 shows the characteristics of I-V calculated using Shockley equation of industrial AIS/Si heterojunction with different annealing temperatures (illumination and dark) conditions. All results for this investigation showed in Table (5), the values of current density began to

increase with the increase of the annealing temperatures when the incident photopower (100mw/cm²).

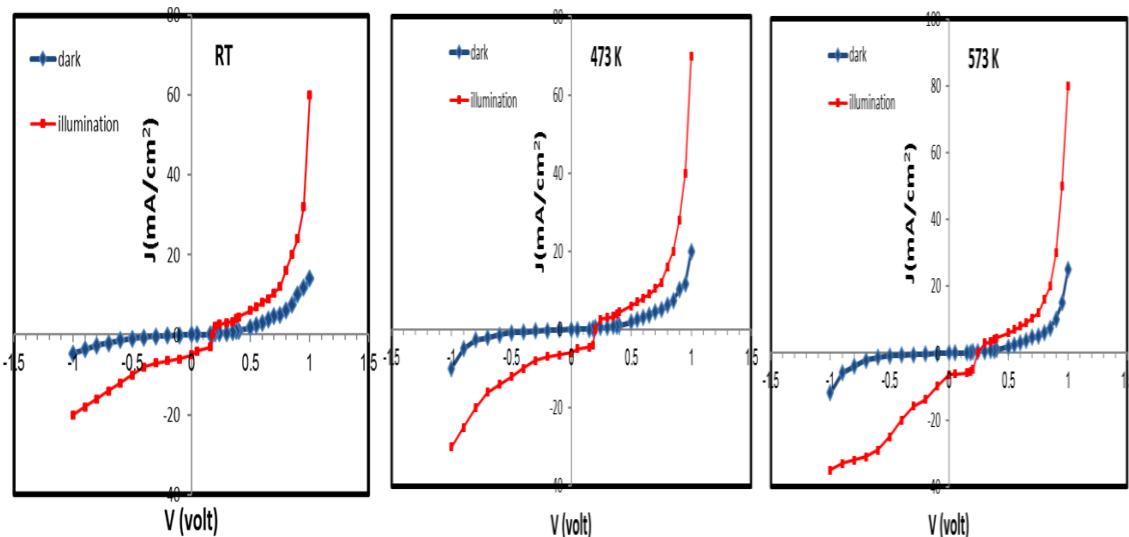


Fig. 6. I-V characteristic for AIS/Si under illumination and dark solar cell AIS at R.T and (473,573) K.

Table 5. Solar cell parameters of AIS /Si heterojunction at R.T and (473,573) K.

Thickness(400 nm)	V _{oc} (V)	J _{sc} (mA/cm ²)	V _{max} (V)	J _{max} (mA/cm ²)	FF	η %
R.T	0.18	5	0.16	3	0.533333	0.48
473	0.2	6	0.18	4	0.6	0.72
573	0.24	6.5	0.2	5	0.641026	1

This is due to the consequence of decreasing the energy gap values, the increase of the value of open circuit voltages with the increase of the annealing temperatures, that is mean increased of efficiency result of increase the absorption coefficient, grain size and roughness[34].

4. Conclusions

Un doped chalcopyrite, AgInSe₂ with annealing temperatures films were well synthesized by thermal evaporation method with film thickness (400nm). Our findings show that the polycrystalline of tetragonal with (112) orientation crystal structure AgInSe₂ thin film from XRD. The grain size rising from XRD with annealing temperatures at (473,573) K. From the optical studies the 573 K AgInSe₂ promoted a decreased band gap in comparison with the RT and 473 K the absorption coefficients increasing. The ability to improve growth and quality of the grains structure, the Hall effect show all the thin films from n-type, this study suggested AIS thin film is a very promising materials for high performance thin film solar cell.

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