Influence of Al dopant on structural and optical parameters of $AgInSe_2$ thin film

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Chalcopyrite thin films ternary Silver Indium Diselenide AgInSe2 (AIS) pure and Aluminum Al doped with ratio 0.03 was prepared using thermal evaporation with a vacuum of $7*10^{-6}$ torr on glass with (400) nm thickness for study the structural and optical properties. X-ray diffraction was used to show the inflance of Al ratio dopant on structural properties. X-ray diffraction show that thin films AIS pure, Al doped at RT and annealing at 573 K are polycrystalline with tetragonal structure with preferential orientation (112). raise the crystallinity degree. AFM used to study the effect of Al on surfaces roughness and Grain Size Optical properties such as the optical band gap, absorption coefficient, Extinction coefficient, refractive index, real and imaginary part of dielectric constant were calculated to inspect the influence of the Aluminum on the optical Parameters of AIS thin film. UV/Visible measure show the lowering in energy gap to 1.35 eV for AgInSe2: Al at 573 K this energy gap making these samples suitable for photovoltaic application.

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1. Introduction

The chalcopyrite is a chemical composition of AgInSe2 which have tetragonal crystallizes and is a crystal structure for $A_IB_{III}C_{2VI}$ (A= Ag, Cu, B= Ga, Al, In and C= Se, S, Te). Silver based Chalcopyrite semiconductor has advantages over Cu based compounds like [1] The energy gap of AIS films is wider than CIS and close to the optimum solar spectrum. The melting point of AIS film is lower than CIS which make them commercially more preferable over CIS. They can also be the type of conductivity as n-type or p-type depending on the type of majority carrier either electron or hole [2]. (AIS) is the best promising absorber materials for photovoltaic cell, because (AIS) have optimum direct energy gap, high optical absorption (_10^{-5} cm^{-1})[3]. Melting point and band gap energy of AgInSe2 is better than CuInSe2 for solar cell applications [1] direct gap semiconductors [4] lies between 0.8 and 2.0 eV [5] the crystal structure of AIS is tetragonal structure chalcopyrite with the lattice constant a =b= 6.102 A° and c = 11.69 A° [6]. Several techniques used to manufacture AIS, such as co-evaporation [4], spray pyrolysis technique [5,7]. sol–gel spin-coating technique [6]. chemical bath deposition [8], electrodeposition process [9], reactive evaporation indicate that the incorporation[10], DC magnetron sputtering[11], pulsed electrodeposition technique[12] thermal evaporation with annealing [13], by Simple Chemical Method [14], thermal evaporation with different ion uences [15]. Bridgman technique[16] hybrid sputtering/evaporation process[17]. hot-press method [18]. The effect of different material doped on $AgInSe_2$ characterization thin films were investigated by various researches such as the influnce of germanium(Ge) doping on the AgInSe2 thin film properties has been studied good optical transmittance spectra and an increased of n-type conductivity compared with the pure [19]. The effects of boron (B)doping on AgInSe2 by ion implantation and heat-treatment technique with different annealing temperatures 473, 573 and 673K on the electro-optical and electrical properties of thin films, desired behaviours for photoconductive of the B- AgInSe2 thin film when 473K [3].

Found that the effects of Zinc (Zn) doping in AgInSe2 the Fermi level tend to shift toward the conduction band when Zn substitute for the Ag and form the active donor defects Zn_{Ag}^{1+}, increasing the carrier concentration N_D and decreasing the lattice thermal conductivity by

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modifying the crystal structure [20]. The electrical conductivity enhancements about three orders by doping Tin (Sn) in the Ag sites in n-type while the Selenium (Se) sites in p-type, the band gap with temperature in the Sn doping films, the increased of the conductivity for the films shows the Sn in AIS film as better applicants for fabrication of p–n junction in PV and in thermoelectric material for power generation application [10]. AgInSe2 thin film solar cells with efficiency of 5% were prpaer by Thermal Evaporation [13], Zinc-diffused silver indium selenide with efficiency of 3.07% [21], AgInSe2 blended organic–inorganic solar cells were fabricated obtained was an efficiency of 0.2% [22]. In this study the doping of Aluminum (Al) in AIS occupies the cation (Ag or In) site, rather than anion (Se) site, since of the relatively small electronegativity of Al (1.61) compared to those of Ag (1.93) or In (1.78), the anticipate a mainly formation of the mono valence Al_{Ag}^{1+} or Al_{In}^{-1} defects that act as an active donor or acceptor respectively. The ionic radii is a major factor uses for choosing applicable contribution materials[23]. Structural, optical and electrical properties of AIS film could be controlled for example the ionic radii of Al doping being smaller than the ionic radius of Ag, In and Se ions. Al is suitable dopant for AIS lattice because the lower ionic radii Al (0.53Å) than Ag^{+1} (1.29Å) , In^{+3} (0.94Å), Se^{-4} (0.56Å) [23,24].

The aim of this study is to focus on the effect of (Al) dopant on the structural and optical propertie of AIS film and the interconnection between these parameters.

2. Experimental

AgInSe2 alloy was synthesized of ternary compound Silver Indium Diselenide from highly purity (99.99%) Silver (Ag) Indium (In) and Diselenide (Se) elements with stoichiometric proportions (1:1:2) after that these elements were putting in evacuated quartz tube (4.5×10^{-4} mbar), after that these three elements melt at temperature (1100 K) was higher than the melting temperature of AgInSe2 (1050 K) [15] in oven for six hours in the end the alloy left to cool. By the thermal evaporation method, thin films of AgInSe2 were deposited on glass substrates from powder of alloy placed in a molybdenum boat with thickness of 0.4 µm. The thin films of AIS pure and Al doped (AIS: Al) with ratio 0.03 were syntheses on glass by thermal evaporation with vacuum system of 6×10^{-6} torr. Al doping methode was carried out by useing the thermal diffusion at 473 K in an electric furnace for 60 minutes. X-ray diffraction was used to examination the compound formation with (λ = 1.5418 Å) 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 [25, 26]. The surface morphology, roughness and Grain Size of AIS were shown to be affected by Al doping content and annealing temperature using atomic force microscopy. The optical interferometer method used to determined the thickness of AIS and AIS: Al samples. 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 (Eg^{opt}) respectively from absorption spectrum [27,28]. Optical Constants the refractive index, the extinction coefficient, the real and imaginary part of dielectric constants can be considered [29, 30,31].

3. Result and Discussion

Fig.(1) displays XRD for $AgInSe_2$ pure and doped at RT and annealing at 573 K when the thickness (400) nm deposition on glass substrate, this figure shows polycrystalline for the $AgInSe_2$ films have tetragonal structure with main peak when $2\theta \approx 25.726^o$ when the preferred orientation (112)[1,2] and anther peak appear at 2θ equal to 42.97 ^{o}. Table (1) show our study, the compare with the ICDD 00-038-0952 card standard value found very good matched, the degree of crystalline increasing when Al ratio dopant and annealing at 573 K. Peak intensity of (112) was increased with add of Al. This increasing of intensity refer to include of Al atom in the In vacancies progress to growth of crystallinity. It can see that the thin films crystal structure and their orientation remain the same after adding Al with 0.03 ratio, but there is a shift in the positions of the diffraction peaks to lower angle. The relation between the FWHM of majority peak and Al content is shown in the same Table. The FWHM decreases with Al content add so the subsequently the crystallite size is increased.

When annealed at 573 K 1h. it is noticed that the behavior of annealed thin films is similar to that of as deposited thin films. However, annealed thin films show higher crystalline quality compared to as deposited thin films this may attributed to the nucleation formation.

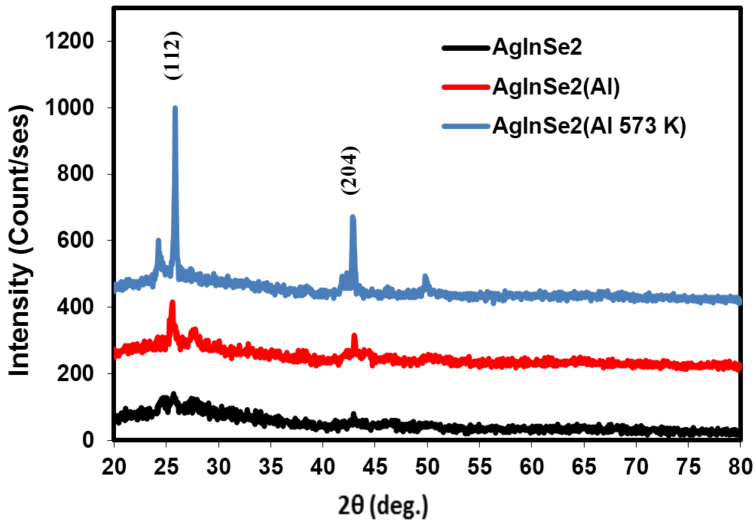

Fig. 1. Pattern of XRD for pure $AgInSe_2$ film, doped Al and doped Al after annealing to T=573 K.

Table 1. XRD data for pure $AgInSe_2$ film, doped Al and doped Al at T=573 K.

Thin Films	**d(Std.) (Å)**	**d(Exp.) (Å)**	**2θ (Std.) (Deg.)**	**2θ (Exp.) (Deg.)**	hkl	FWHM (deg.)	C.S (nm)
$AgInSe_2$ RT	3.46	3.4651	25.726	25.7	112	1.000	8.5149
	2.103	2.1012	42.97	42.95	204		
$AgInSe_2$ (Al) RT	3.46	3.4839	25.726	25.55	112	0.201	42.3521
	2.103	2.1046	42.97	42.95	204		
AgInSe2 (Al) T=573 K	3.46	3.4511	25.726	25.8	112	0.168	50.6984
	2.103	2.1092	42.97	42.85	204		

Figures (2) present the AFM images of AgInSe2 (Al) thin films. It is seen that all films surfaces exhibit a large number of grains of small size and uniform distribution. XRD confirms with the result obtained from AFM, which indicates that all films have a polycrystalline structure. From Table (2), by adding the Al 0.03content and annealing temperature. This increasing in grain size is expected due to the increasing in the crystallite size of thin film. This result agrees with Khudayer [13] for annealing of AIS thin films.

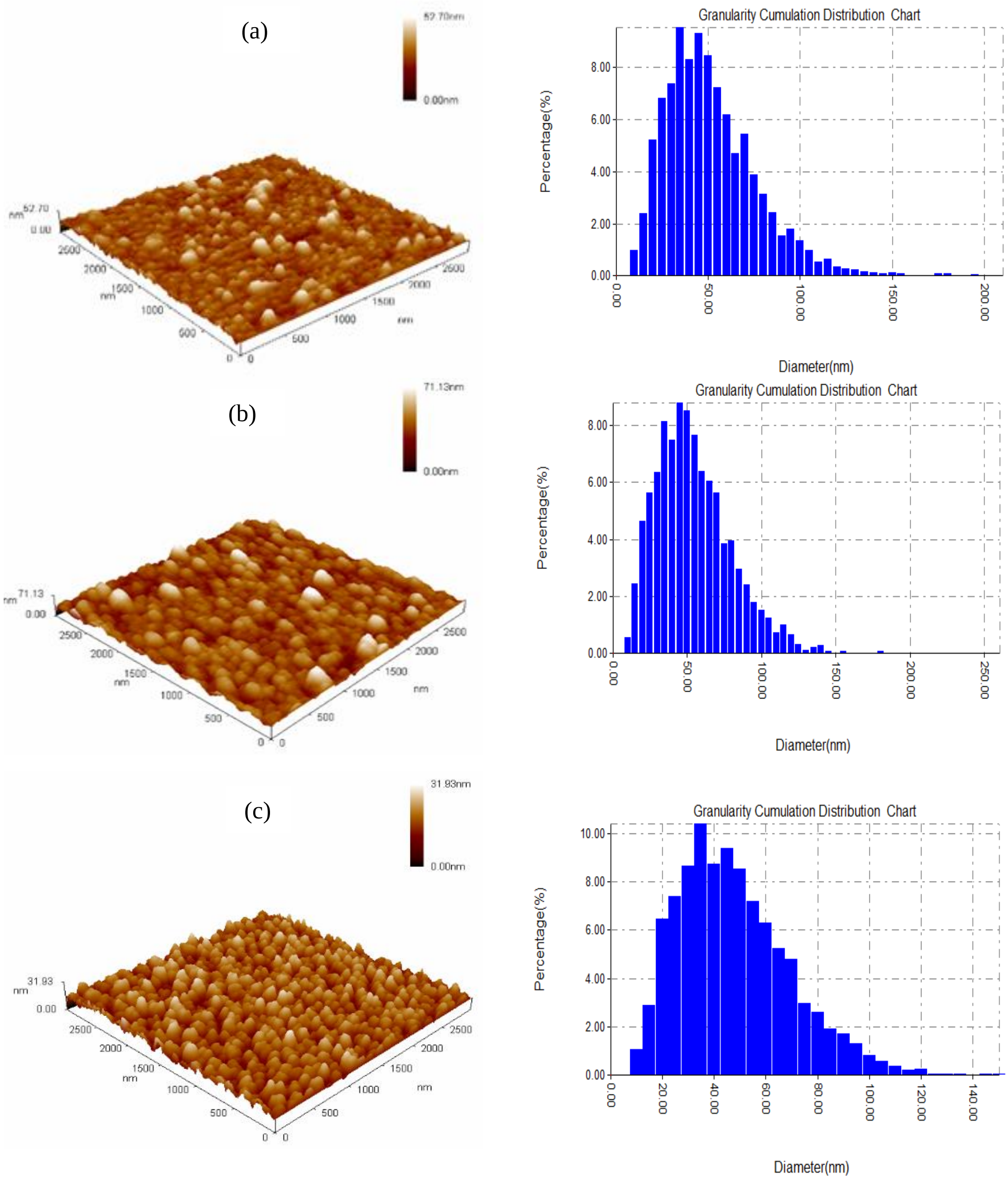

Fig. 2. AFM micrographs of $AgInSe_2$ thin films as a function of Bi content: (a) undoped AgInSe2, (b)3% Al and (c) 3% Al at T=573 K.

Figure (3) shows the effect of Al ratio and annealing 573K on transmittance and absorbance spectra of thin AIS films. It is observe that the absorbance of all thin films increases with decreasing the wavelength. This may be due to decrease the corresponding transmittance with decreasing the wavelength as shown in Figure (3).

From the same Figure shows the effect of doping AIS (Al) on absorbance of AIS thin film, While, the inflance of annealing temperature on thin AIS (Al) films absorbance, The optical transmittance clearly shown a shift in band edge because of the add Al and annealing in the visible range 400-700 nm. So, these films are a good candidate as absorber layer in solar cell due to their high absorbance in the visible regions.

The type and value of optical energy gap (**E_g^{opt}**) for AIS, AIS(Al) and annealing at 573K thin films is determined using Tauce Equation by plot the relation (αhυ)2, (αhυ)1/2, (αhυ)2/3 and (αhυ)1/3 with photon energy (hυ) and selecte the optimum linear parts. Only the first relation yield straight line, this means only the allowed direct transitions occur in this material. This result agrees with Rajani Jacob et. al. and R. Panda et. al.[10,15]. The $\mathbf{E_g^{opt}}$ has been determine by extrapolating the linear part of the plotted curve to the energy axis. The absorption coefficients (α) of these films was calculated from the absorbance spectra which was of order 10^4.

It is obvious from Figure (4) 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). The values of the refractive index (n), the extinction coefficient (k) and the real and imaginary parts of the dielectric constant (εr, εi) for AIS thin film show in Figure (5) . The calculated values of optical constant at wavelength (λ) equal to 500nm are listed in Table (3). The refractive index n is a significant parameter for optical material and application. The values of n decreases with doping Al and annealing temperature at wavelength of 500nm due to decrease the corresponding reflection and attribute to an increase in the carrier concentrations in AIS thin film. For the AIS thin film, the refractive index n in the visible region altered. One can be noticed that the extinction coefficient takes the similar behavior of the absorption coefficient because the extinction coefficient is directly related to the absorption of the light. The value of k increases as seen in Table (3). The fundamental electron excitation spectrum of the films was described by means of the frequency dependence of the complex dielectric constant. The real (εr) and imaginary (εi) parts of the dielectric constant are related to the n and k values. The variation of (εr) and (εi) parts of dielectric constant with λ for these thin films. From Table (3), the value of εr and εi at λ=500nm decreases because the behavior of εr is similar to that of n, while the behavior of εi is similar to that of k because it mainly depends on the k value. The value of εi of the AIS: Al thin film was smaller than that of the pure thin film, which indicates small dielectric loss in the AIS: Al thin film.

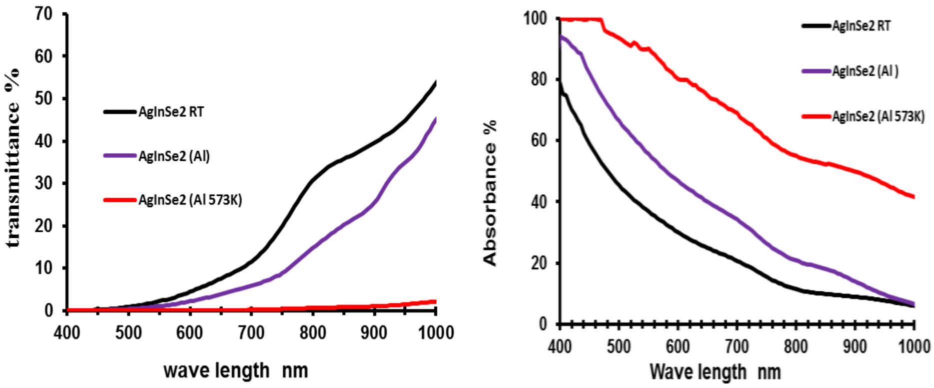

Fig. 3. Transmittance and Absorption vs. wave length for pure AgInSe2 thin film, doped Al and doped Al at T=573 K.

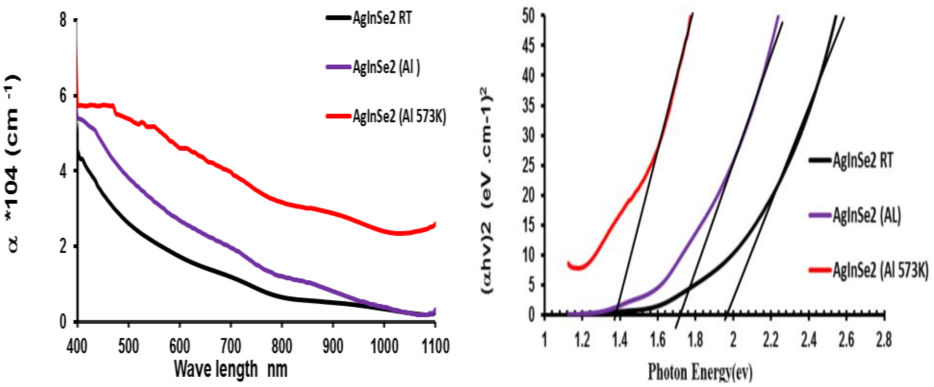

Fig. 4. The α vs. Wavelength and $(\alpha h\upsilon)^2$ vs. hυ plot of as prepared pure and doped Al and doped Al at T=573 K.

Table 3. The optical parameters (E_g^{opt}, α, k, n, εr and εi)for $AgInSe_2$: Al thin films where λ=500nm.

Thickness (400nm)	E_g^{opt} (eV)	α×10^4 cm^{-1}	n	k	εr	εi
$AgInSe_2$	**1.95**	2.61	3.7	0.103	14	0.77
AgInSe2 (Al)	**1.7**	3.8	2.36	0.15	5.5	0.71
AgInSe2 (Al) at T=573 K	**1.35**	5.8	1.34	0.21	1.75	0.57

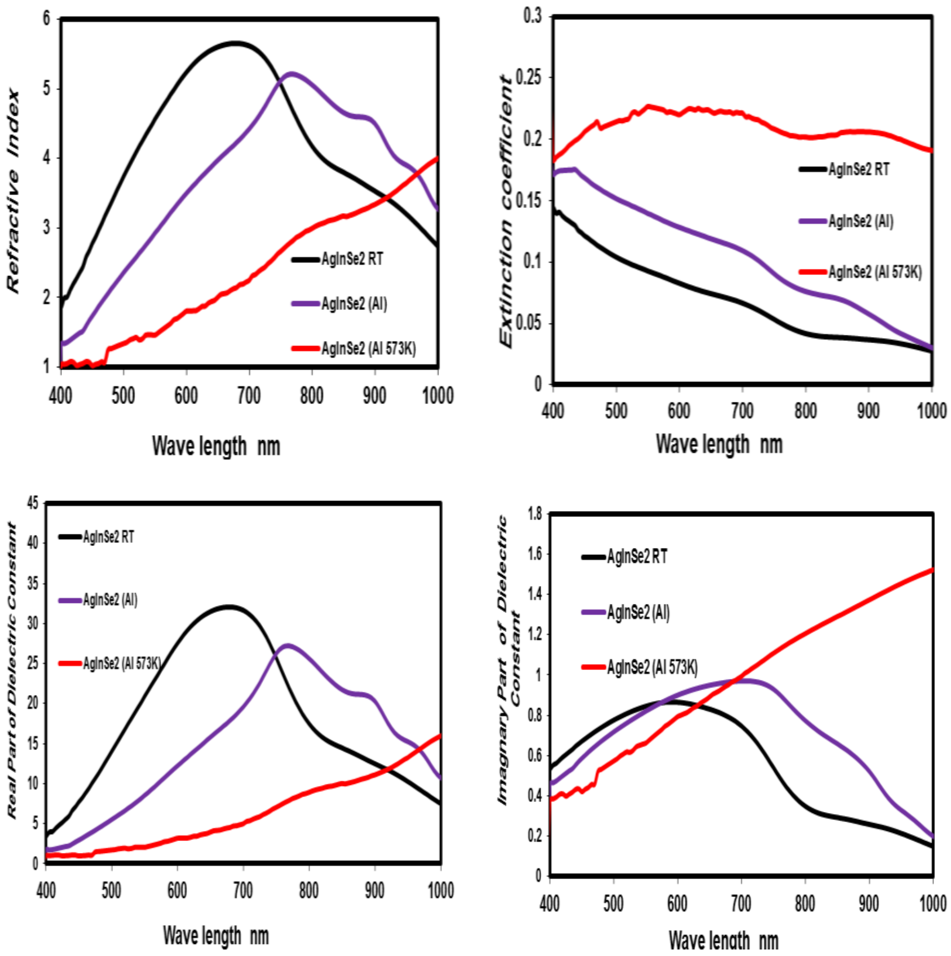

Fig. 5. Variation of refractive index, Extinction coefficient , of real and imaginary part of dielectric constant with wave lenghth for $AgInSe_2$ thin films.

4. Conclusions

Un doped, 0.03 of Al: $AgInSe_2$ and doped Al at T=573 K films were well manufacturered by thermal evaporation methoed. XRD shows the polycrystalline of tetragonal with (112) orientation crystal structure $AgInSe_2$ thin film. The crystallite and grain size increasing from analysed XRD and AFM with Al doping. From the optical studies the Eg decreases and absorption coefficients increasing. $AgInSe_2$ film produced at 0.03 of Al at T=573 K reveal a low value of transmition and high absorption making these filmes suitable for photovoltaic application.

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