Abstract
Sb-doped AgInSe2 (AIS: 3%Sb) thin films were synthesized by thermal evaporation with a vacuum of $7 \times 10^{-6}$ torr on glass with (400+20) nm thickness. X-ray diffraction was used to show that Sb atoms were successfully incorporated into the AgInSe2 lattice. Then the thin films are annealed in air at 573 K. XRD shows that thin films AIS pure, AIS: 3%Sb and annealing at 573 K are polycrystalline with tetragonal structure with preferential orientation (112). raise the crystallinity degree. The Absorption spectra revealed that the average Absorption was more than 60% at the wavelength range of 400–700 nm. UV/Visible measure shows the lowering in energy gap to 1.4 eV for AIS: 3%Sb at 573 Kt his energy gap making these samples suitable for photovoltaic application, The electric property was better when AgInSe2: 3%Sb at 573 K, thin films were of donor type and the concentration of electrons in them increased with increasing Sb doped and annealing temperature.

Keywords: AgInSe2, Antimony, AIS: 3%Sb thin films, XRD, Optical parameters.

1. Introduction
The chalcopyrite thin films like AgInSe2 which have tetragonal crystallizes and is a crystal structure for AgBi2S3 where (A= Ag, Cu, B= Ga, Al, In and C= Se, S, Te). These compounds are analogs to binary zinc blend II-VI. Silver-based chalcopyrite semiconductor has as better candidates for solar cell fabrication [1]. Ternary Silver Indium Diselenide (AIS) is a typical n-type semiconductor[2,3] that possesses direct gap energy[4] lies between 0.8 and 2.0 eV [5] high optical absorption ($10^{-5}$ cm$^{-1}$), (AgInSe2) is the best-promised absorber materials for photovoltaic cell [6]. In many works doping AIS with different elements such as boron (B)doping on AgInSe2 by ion implantation and heat-treatment technique desired behaviors for photoconductive of the B- AgInSe2 thin film when 473K [7]. The influence of germanium(Ge) doping on the AgInSe2 thin film properties has been studied with good optical transmittance spectra and the conductivity from type [2]. The electrical conductivity enhancements about
three orders by doping Tin (Sn) in the Ag sites in n-type, the increased conductivity for the films shows the Sn in AgInSe2 film as better applicants for fabrication of p–n junction in PV [8]. Found that the effects of Zinc (Zn) doping in AgInSe2 the Fermi level tend to shift toward the conduction band when Zn is a substitute for the Ag and forms the active donor defects, increasing the carrier concentration ND and decreasing the lattice thermal conductivity by modifying the crystal structure [9].

Several techniques used to fabrication AIS, such as spray pyrolysis technique [10,11], reactive evaporation [8], pulsed electrodeposition technique [12], co-evaporation [13], sol–gel spin-coating technique [14], hybrid sputtering/evaporation process [15], DC magnetron sputtering [16], chemical bath deposition [17], hot-press method [18], thermal evaporation with different ion uences [19], thermal evaporation with annealing [20], electrodeposition process [21], Bridgman technique [22]. Simple Chemical Method [23]. the crystal structure of AIS is tetragonal structure chalcopyrite with the lattice constant a = b = 6.102 Å° and c = 11.69 Å° [11]. AgInSe2 blended organic–inorganic solar cells were fabricated and obtained was efficiency of 0.2% [24] Doping of Antimony (Sb) in AIS occupies the cation (Ag or In) site, rather than the anion (Se) site since the relative electronegativity of Sb (2.05) compared to those of Ag (1.93) or In (1.78) or Se (2.55), 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 radius of Antimony is close to the ionic radius of Ag, In and Se ions. Sb is suitable dopant for AIS because the Sb ionic radii (0.9 Å) while Ag $^{+1}$ (1.29Å), In $^{+3}$ (0.94Å), Se $^{-4}$ (0.56Å) [25,26]. This study aims to concentrate on the effect of (Sb) doped on the optical structural properties and all Effects of AgInSe2 film and the interconnection between these parameters.

2. Experimental

From highly purity (99.99%) of Silver (Ag) Indium (In) and Diselenide (Se) elements with stoichiometric proportions (1:1:2) to prepare: 3%Sb thin films, these elements were put in a quartz tube with a vacuum (4.5×10$^{-4}$ mbar), these three elements heated up to (1100K) was higher than the melting temperature of AgInSe2 (1050 K) [19]. In an electric furnace for six hours in the end the alloy is left to cool to room temperature. AIS: 3%Sb thin films (pure and doped at 573K) were deposited by the thermal evaporation method (6×10$^{-6}$ torr) on glass substrates with 400 nm thickness. 3%Sbdoping methods were carried out by using the thermal diffusion at 473 K in an electric furnace for 60 minutes. X-ray diffraction has been used to study the structure of these films by detailed 2Ө from 20° to 80° with intervals of 0.05°, Scherer’s Formula was used to calculate the crystalline size of the films [27, 28]:

$$C.S = \frac{0.9\lambda}{B\cos\theta}$$

where 0.9 is the shape factor and B (FWHM). is the width of the diffraction peak at half maximum intensity.

The optical interferometer method was used to determine the thickness of AgInSe2: 3%Sb samples. Optical properties of thin film preparation, transmission and absorption spectrums in the range between (400 to 1000) nm have been noted, and lambert law and Tauc equation have been used to determine the absorption coefficients $\alpha$ and the energy gap (Eg$^{opt}$) respectively from the absorption spectrum [27,29]:

$$\alpha h\nu = D (h\nu - E_g)^r$$

$$\alpha = 2.303 \frac{A}{t}$$
where $D$ is a constant depending on the temperature and the properties of the valence & conduction bands and $\alpha$: the absorption coefficient, $h\nu$ the incident photon energy,$r$: is a parameter for the type of the optical transition. $A$: absorbance, $t$: thickness.

Optical Constants such as $k$: extinction coefficient, $n$ refractive index, real part $\varepsilon_r$ & imaginary part $\varepsilon_i$ of dielectric constant can be considered by the relations below: [30,31,32]:

\[ k = \frac{\alpha \lambda}{4\pi} \] (4)

\[ n = \left[ \frac{4R}{(R-1)^2} - k^2 \right]^{1/2} - \frac{(R+1)}{(R-1)} \] (5)

\[ \varepsilon_r = n^2 - k^2 \] (6)

\[ \varepsilon_i = 2nk \] (7)

The Hall Effect results showed the type of thin film of AgInSe$_2$: 3%Sb has been calculated by the relations below[31]:

\[ R_H = \left( \frac{V_H}{I_x} \right) \frac{t}{B_z} \] (8)

\[ p = \frac{1}{qR_H} \] (p – type) (9)

\[ n = -\frac{1}{qR_H} \] (n – type) (10)

When The Hall coefficient ($R_H$), electric current ($I_x$) and Hall voltage ($V_H$), magnetic field ($B_z$).

3. Result and Discussion:

Figure (1) displays XRD for AISpure and AgInSe$_2$: 3%Sb doped at RT and 573 K when the thickness (400) nm deposition on glass substrates, All the samples show polycrystalline for films have tetragonal structural with main to distinguishable peak when $\theta \approx 25.726^\circ$ when the preferred orientation (112)[1,10]and anther peak appear at 20 equal to 42.97 $^\circ$ when the orientation (204). Table (1) show our study, the comparison with the ICDD 00-038-0952 card standard value very good matched, the degree of crystalline increasing when AgInSe$_2$: 3%Sb dopant and annealing at 573 K. Peak main intensity of (112) was increased with the addition of 3%Sb comparison with that for AgInSe$_2$ and shifts approximately 3$^\circ$ to lower 20 angle in comparison with that for AgInSe$_2$ because that the Sb atomic “radius” (0.9 Å) smaller than that for In (0.94 Å) and Ag (1.29Å). The increase of intensity refers to include of Sb atom in the progress to the growth of crystallinity. No diffraction peak related to Sb was observed from the XRD patterns. It was illustrated that Sb ion replaces or enters the interstitials of AIS as shown in the same Table. The FWHM decreases with Sb content added so subsequently the crystallite size is increased as calculated by equation (1). The effect of annealing at 573 K& 1h 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 be attributed to the nucleation formation.
Figure 1. XRDPattern for pure AIS film, AIS: 3%Sb doped and AgInSe2: 3%Sb doped after annealing to 
T=573 K.

Table 1. Data of XRD for pure AgInSe2 film, 3% (Sb) and 3% (Sb) at T=573 K.

| Thin Films | d(Std.) (Å) | d(Exp.) (Å) | 2θ (Std.) (Deg.) | 2θ (Exp.) (Deg.) | hkl | FWHM (deg.) | C.S (nm) |
|------------|-------------|-------------|------------------|------------------|-----|-------------|---------|
| pure       | 3.46        | 3.4651      | 25.726           | 25.7             | 112 | 1.000       | 8.5149  |
|            | 2.103       | 2.1012      | 42.97            | 42.95            | 204 |             |         |
| 3% (Sb)    | 3.46        | 3.4918      | 25.726           | 25.5             | 112 | 0.317       | 26.8505 |
|            | 2.103       | 2.0994      | 42.97            | 43.05            | 204 |             |         |
| 3% (Sb)    | 3.46        | 3.4373      | 25.726           | 25.9             | 112 | 0.231       | 36.8788 |
| T=573 K    | 2.103       | 2.1092      | 42.97            | 42.85            | 204 |             |         |

Figure (2) and Table (2) show the optical properties and the effect of 3% (Sb) and annealing 
573K on transmittance and absorbance spectra of thin AIS films in the range 400-1000 nm. It is 
observed that the absorbance of all thin films increases with decreasing the wavelength. This 
may be due to decreasing the corresponding transmittance with decreasing the wavelength. 
The type and value of optical energy gap ($E_g^{opt}$) for AIS, 3% (Sb) and annealing at 573K thin 
films are determined using Tauc equation (2), the allowed direct transitions occur in a thin 
film. This result agrees with R. Panda et al.[19]. The absorption coefficients ($\alpha$) which were 
of order $10^4$ in these films were calculated from the absorbance spectra.

It is obvious from Figure (3) that the energy gap decreased to 1.4(eV) which has significant 
for optoelectronic device applications. This behavior may be attributed to the advance in the 
film's crystallite size. The calculated energy gaps are listed in Table (2). The value of the 
refractive index (n), the extinction coefficient (k) and the real and imaginary parts of the 
dielectric constant ($\varepsilon_r$, $\varepsilon_i$) for AIS thin film are calculated from equations (3-7). The calculated 
values of optical constant at the wavelength ($\lambda$) equal to 500nm are listed in Table (2). The 
refractive index n is a significant parameter for optical material and application. The values of 
n decrease with doping 3% (Sb) and annealing temperature (in the visible region) due to a 
decrease in the corresponding reflection and attributed to an increase in the carrier 
concentrations in AIS thin film, this result agrees with Suresh Pal et al.[32]. The extinction 
coefficient increases as seen in Table (2) takes the same behavior as the absorption coefficient 
because the extinction coefficient is directly related to the absorption of the light as in equation 
(4). The fundamental electron excitation spectrum of the film was termed using the frequency 
dependency of the complex dielectric constant. The real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) parts of the 
dielectric constant are related to the n and k values and the value of $\varepsilon_r$ and $\varepsilon_i$ at $\lambda=500$nm
decreases because the behavior of \( \varepsilon_r \) is similar to that of the \( n \) equation (6), while the behavior of \( \varepsilon_i \) is similar to that of \( k \) because it mainly depends on the \( k \) value equation (7). The effect of doping 3\% (Sb) and annealing on the value of \( \varepsilon_i \) were smaller than that of the pure thin film, which indicates a small dielectric loss.

**Figure 2.** Transmittance and Absorption with wavelength for pure AgInSe2 film, AIS: 3\% Sb doped and AIS: 3\% Sb doped after annealing to \( T=573 \) K.

**Figure 3.** The \( \alpha \) vs. Wavelength and \((\alpha h\nu)^2\) with \( h\nu \) plot of as prepared pure AgInSe2 film, AIS: 3\% Sb doped and AIS: 3\% Sb doped after annealing to \( T=573 \) K.
Table 2. The optical parameters ($E_{g}^{opt}$, α, n, k, εr and εi) for pure AIS film, AgInSe2: 3% Sb doped and AgInSe2: 3% Sb doped after annealing to T=573 K, where λ=500nm.

| Thickness (400nm) | $E_{g}^{opt}$ (eV) | α×10$^4$ cm$^{-1}$ | n | k | εr | εi |
|-------------------|--------------------|---------------------|---|---|----|----|
| pure              | 1.96               | 2.61                | 3.7 | 0.103 | 14   | 0.77   |
| 3% (Sb)           | 1.75               | 3.58                | 2.55 | 0.14 | 6.52 | 0.72 |
| 3% (Sb) T=573 K   | 1.4                |                      |     |      |      |      |

Figure 4. Variation of refractive index, Extinction coefficient, of the real and imaginary part of dielectric constant with wavelength for pure film, AgInSe2: 3% Sb doped and AgInSe2: 3% Sb doped after annealing to T=573 K.
The type concentration of the charge carrier, resistivity and Hall mobility for pure, 3% Sb doped and AgInSe2: 3% Sb doped after annealing to T=573 K thin films have been estimated from Hall effect measurements, the calculated values are shown in Table (3). From this Table, one can be noticed that the value of the Hall coefficient for all examined AgInSe2 and 3% Sb doped 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 [2,3].

Moreover, it is seen that the carrier concentration increases with increasing annealing temperature due to an increase in the film grain size which leads to a decrease in the density of grain boundaries and thus reduces the electron trapping probability. As a result, the number of collisions between carriers will increase, which leads to a decrease in their mobility with increasing the annealing temperature.

| Thin Films | R_H (cm^3/C) | N_D (cm^-3) | \( \mu_H \) (cm^2/V.s) | \( \rho(\Omega.cm) \) |
|------------|--------------|-------------|-------------------------|---------------------|
| pure       | -1973.47     | 3.167*10^{15} | 37.6342                 | 52.43               |
| 3% (Sb)    | -0.117261    | 5.33*10^{19}  | 3.022983                | 0.03879             |
| 3% (Sb) T=573 K | -0.092183     | 6.78*10^{19}  | 2.703724                | 0.034095            |

4. Conclusions

Pure tetragonal AgInSe2: 3% Sb doped and AgInSe2: 3% Sb doped after annealing to T=573 K films were well synthesized by a thermal evaporation method. The grown AIS thin films were then doped with Sb at temperature 473 K by a thermal diffusion process. After doping, the crystallinity of the thin film was improved. Our findings show that the polycrystalline of tetragonal with (112) orientation crystal structure AgInSe2 thin film from XRD. The grain size rose from XRD with 3% Sb doping. From the optical studies the 3% Sb doping into AgInSe2 promoted a decreased band gap in comparison with the undoped AgInSe2, the absorption coefficients increasing. The ability to improve the growth and quality of the grains structure, the Hall effect shows the conductivity type of the grown films remained n-type and the enhancement in the optical properties highlights 3% Sb doped AgInSe2 to be applied as an absorber layer in films making these films suitable for photovoltaic application.

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