Impact of the annealing temperature on the structural, morphology and optical properties of bilayer thin films In/Se prepared by thermal evaporation method

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Thermal evaporation in a high vacuum was utilized under a pressure of (10^{-5} m bar) to deposit indium selenium (In/Se) multilayer thin films on a glass substrate with a constant overall thickness of (350 nm). For (100,300°C)annealing temperatures results of (XRD) showed the appearance of the two compounds (In_2Se_3) and (In/Se), while the morphological tests showed that films had uniform and homogeneous surfaces free of voids and islands and spectral analysis (Uv.-Vis.) showed to anneal temperatures affect grain formation and grain splitting in the film. Increased annealing led to an increase in absorbance while decreasing the energy gap noting that the Hall effect tests showed that the prepared compound is of the type n-type.

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Keywords: Annealing temperature, Bilayer, In/Se multilayer, Thin film, Thermal evaporation

1. Introduction

II-VI and III-V compounded substances are used widely in modern technology [1]. Indium selenide is a direct bandgap semiconductor in the III-VI category of compound semiconductors. The fabrication of photovoltaic devices relies heavily on this material [2]. Solar cells, batteries, and optoelectronic devices could all benefit from the In/Se system's potential applications [3,5]. In/Se films have gotten a lot of attention recently as a potential new material for solar cells [6]. In terms of optical devices, selenium is among the most useful [7,8]. It is smaller, faster, and more efficient to use multilayer thin films in electronic [9]. An ionizing radiation detector could benefit from using indium selenide (In/Se), a layer-type semiconductor in chalcogenide compounds, which has a bandgap of roughly 1.3 eV and substantial structural anisotropy, making it suitable for solar cells [10].When working with In/Se photoconductive thin films, a straightforward procedure of consecutive thermal evaporation of the In and Se layers, followed by annealing, is all that is required. When it comes to device performance, it is well established that growth conditions and heat treatment have an enormous impact on the material's structural and electrical properties [11,12]. In this study, the thermal annealing-induced diffusion of the In layer into the Se material is used to analyze the evolution of different phases. and study the effect of annealing on the structural, morphological, and optical properties of In/Se.

2. Experimental work

Glass substrates have been coated with layers of selenium and indium to create a bilayer In/Se. Two steps of unloading are required for the locally made thermal evaporation system with excellent requirements. The first stage is that the air is withdrawn from the vacuum chamber through a mechanical rotary pump to reach pressure (10^{-2} m bar). Perini vacuum gauges are used to measure the pressure. Second, the diffusion pump is unloaded and the membranes are deposited on clean glass substrates, which are then used to create pure membranes under a pressure of (10^{-5} m bar). Placed in the substrate holder almost exactly on top of source material, ultrasonically cleaned glass substrate (9cm). For the overall thickness, the indium layer (150nm thick) was

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deposited on top of the 200nm thick se layer, making the total thickness of the two layers (350 nm). At temperatures between 100 and 300 degrees Celsius, they were annealed. X-ray diffraction Philips diffract meter modelPW1730(manufactured at US) results were used to determine the crystal structure of the composite thin films (In/Se) and to identify and describe their phase configurations at various temperatures. The prepared bilayer thin film and its schematic diagram is shown in figure 1. The surface morphology of the films was recorded with scanning electron microscope (TESCAN Mira3- Country: Czech Republic) .Optical characteristics were recorded using Model Lambda 850 (manufactured at US)Company Perkin Elmerat the range of (300-700)nm. The Hall effect was carried (Keithley type 616).

(a) *(b)*

Fig. 1. (a) Schematic representation of In/Se thin-film structure without Al contact.(b) Schematic representation of In/Se thin-film structure with Al contact.

3. Results and discussion

3.1. Structural analysis

Figure 2 displays the X-ray diffraction for films with thicknesses for layers of (In/Se bilayer) thin films. These films were formed on glass substrates in a high vacuum using thermal evaporation method. The total thicknesses of the films (350±20) nm. Thin films of In/Se can be grown at room temperature. According to the desired direction, the indium lattice plane (101), the sample was at 33.15° (2-theta) in the preferred direction. Compound Indium Selenide is formed at angles 36.51°, 37.65° and 69.15° and the planes (421),(106) and (802) respectively, prior to annealing. With the appearance of the constituent elements of this compound, selenium and indium, the composition of this compound became more complex. The peaks detected corresponding to the lattice plane at values of 2θ as shown in Table 1 before annealing. More In/Se and In_2Se_3 is produced at a high temperature. The prominent diffraction peaks 38.10° of the as-grown film correspond to the planes (106)Compound indium selenide after the film is annealed at (100°C).During the annealing of the thin films, we can also see that the appearance of the compound has increased significantly, along with the presence of selenium. the phase development of In_2Se_3 occurs, demonstrating that The In_2Se_3 and In/Se system is heat-diffusible thermally. The strength of the significant In/Se peak increased as the annealing temperature was increased from (100°C) to (300°C) for layers. Increasing the annealing temperature to 300 °C compounds with the same angles form, and the intensity of the peaks increases. It was noticed that when the temperature of annealing increased, an increase in the appearance of the compound was noted increasing the intensity of the compound. From XRD line broadening of the highest peak plane and depending on the Scherrer's equation[13,14]

$$D=\frac{K\lambda}{\beta cos\theta} \quad (1)$$

where k dimensionless form factor ,θ is Bragg's angle, β- is represent Full Width Half Maximum of highest intensity and λ-represent XRD wavelength that used. The normal value of the form factor, which is approximately 0.9. crystallite size (D) were determined. Due to the fact that the In_2Se_3 peak and the In/Se peak overlap with each other, it is impossible to quantify the crystallite size . Because of this, the annealing process causes an increase in the crystallinity of the film material while simultaneously causing a decrease in the number of crystal defects.

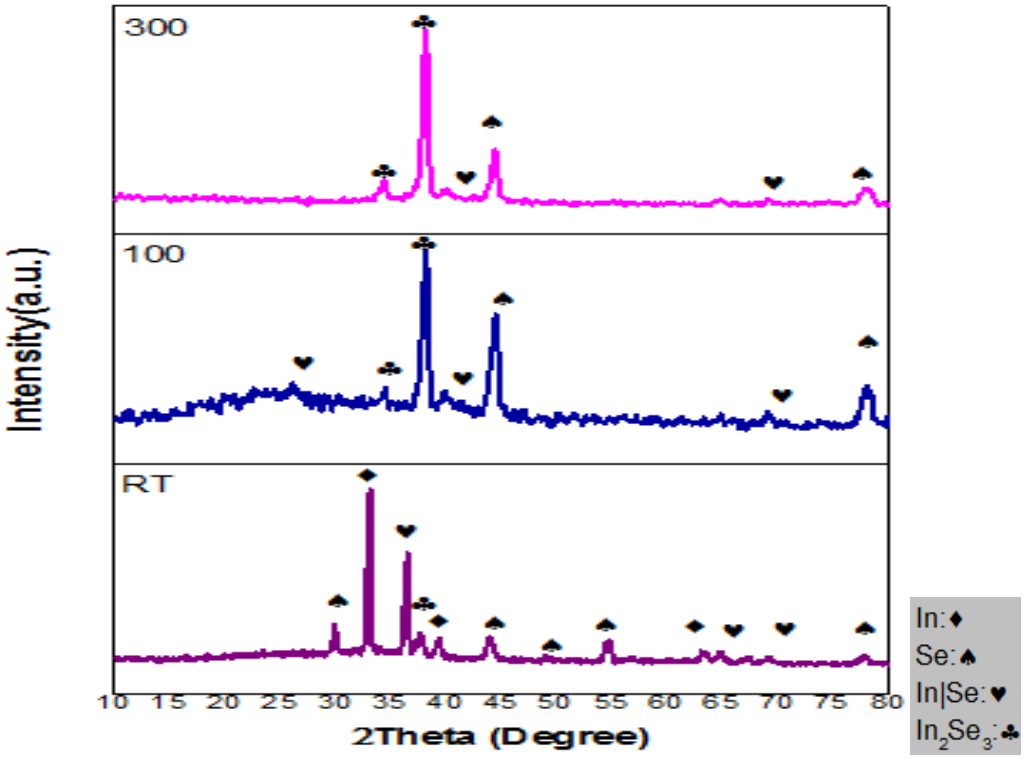

Fig. 2. XRD patterns of In/Se thin films at RT and annealing (100, 300°C).

Table 1.1. XRD analysis for In/Se thin films as deposited at room temperature

Sample	**as-deposited**					
Thicknesses Se:200,In:150	2θ (Deg.)	Miller indices	FWHM (Deg.)	d (A^o) Observed	d(A^o) Standard	JCPDS card number and Phase
Se	29.90 43.95 48.95 54.45 77.71	(101) (012) (110) (033) (120)	0.299 0.599 0.349 0.349 0.499	3.775 2.068 1.869 1.685 1.231	3.782 2.073 1.889 1.652 1.222	85-0569 86-2246 Hexagonal
In	33.15 63.15 39.35	(101) (103) (110)	0.249 0.399 0.349	2.723 1.465 2.288	2.716 1.470 2.298	85-1409 Tetragonal
In_2Se_3	37.65	(106)	0.549	2.406	2.410	00-012-0117 Hexagonal
In/Se	36.50 64.75 69.15	(421) (802) (950)	0.349 0.299 0.349	2.448 1.439 1.363	2.440 1.440 1.359	00-012-0118 Hexagonal

Table 1.2. XRD analysis for In/Se thin films annealed at 100, 300 °C for 60 min.

Sample	**annealed at 100 °C for 60 min**					
Thicknesses Se:200,In:150	2θ (Deg.)	Miller indices	FWHM (Deg.)	d (A^o) Observed	d(A^o) Standard	JCPDS card number and Phase
Se	44.40 77.75	(012) (120)	0.494 0.100	2.026 1.221	2.013 1.237	85-0569 86-2246 Hexagonal
In						85-1409 Tetragonal
In_2Se_3	34.35 38.10	(105) (106)	0.200 0.300	2.585 2.342	2.580 2.370	00-012-0117 Hexagonal
In/Se	28.90 39.85 69.05	(420) (620) (021)	0.212 0.510 0.110	3.207 2.250 1.354	3.140 2.300 1.353	00-012-0118 Hexagonal
Sample	**annealed at 300 °C for 60 min**					
Thicknesses Se:200,In:150	2θ (Deg.)	Miller indices	FWHM (Deg.)	d (A^o) Observed	d(A^o) Standard	JCPDS card number and Phase
Se	44.40 77.95	(012) (120)	0.012 0.301	2.043 1.226	2.013 1.237	85-0569 86-2246 Hexagonal
In						85-1409 Tetragonal
In_2Se_3	34.30 38.10	(105) (106)	0.400 0.450	2.613 2.362	2.580 2.370	00-012-0117 Hexagonal
In/Se	39.80 64.55 69.10	(620) (802) (950)	0.201 0.101 0.135	2.251 1.438 1.363	2.300 1.440 1.353	00-012-0118 Hexagonal

3.2. FE-SEM (Field Emission Scanning Electron Microscope)

FE-SEM diagnostic results for films placed on thermally evaporated glass bases were generated using the FE-SEM film deposition process. Figure 3a, shows that the films are usually homogenous, dense, and free of islands and voids on the surface, as microscopy can show. The annealing temperature affects surface morphology. There are no single particles in the films because they depict a more complicated nature. Larger grains are formed through the aggregation of tiny grains. The particles and nanorods have a variety of shapes and sizes. For as-prepared In/Se thin films, the surface of the samples normally has a uniform, dense, and void-free appearance shown in Figures (3 a,b,c). If mentioned thin films which are annealing at 300°C for 60 minutes represent the granules expanded larger and wider where the shape of a flower is similar to the shape of a cauliflower. As shown in Figures (3d). Granule diameter was determined at random using Digimizer's software. According to the results annealing at 300°C results in an increase in the diameter of the particles from (54.14nm at RT to109.65nm at 300°C) . This is that Clusters may form as a result of the agglomeration of particles that occurs during the heat treatment process. This conclusion is consistent with the results in Ref [15]. It is also shown that when annealing these films, the effect of annealing is clear on the resulting images, where we notice that there is an increase in the size of the grains, which can be attributed to the state of nucleation and growth as a result of the agglomeration of the grains.

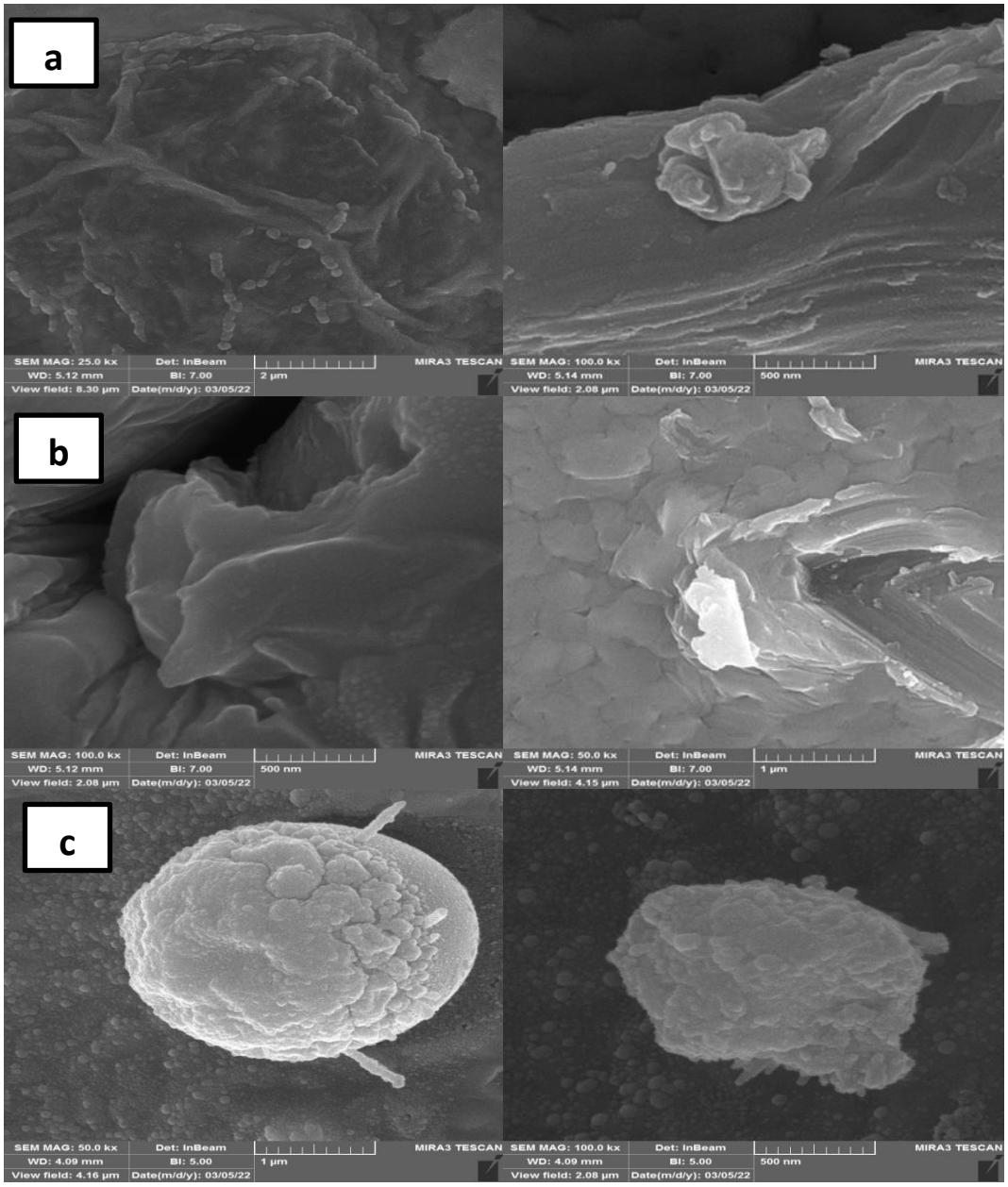

Fig. 3. FE-SEM images of In/Se for different annealing at: (a) RT, (b)100°C,(c) 300°C.

3.3. Optical analysis

The spectrometer was used to measure the optical absorbance of the as-prepared and annealed In/Se thin films. In order to figure out the energy of the optical band gaps, we used the Tauc relation [16]:

$$\alpha h\upsilon = B(Eg - h\upsilon)^{n} \tag{2}$$

The Eg is equal bandgap to the α absorption coefficient the frequency f, B is an invariant, and the number n is dependent on whether the interband transition is permitted (direct), prohibited (direct), permitted (indirect), or forbidden (indirect)[17]. The optical energy gap values (Eg) for In/Se thin films have been determined by plotting the relations of $(\alpha h\upsilon)^2$ versus photon energy (hv) and selecting the optimum curve. The value of the energy gap decreases slightly with increased annealing temperature shown in figure(4b), Where the decrease in the energy gap is shown in Table (2),So the energy gap values of this work give a good indicator that the direct transition

possibly occurs. The band gap narrows as the annealing temperature rises. Due to a decrease in grain boundary scattering, the XRD results may be supported. A drop in band gap energy may be attributable to grain growth and an increase in the localized grain boundary. Also, the formation of an alloy of indium and selenium due to the diffusion of indium into selenium is responsible for the decline. The absorption of In/Se was measured with different annealing temperatures. Figures (4a) show The examinations of the absorption spectrum showed that the absorbance of the prepared films increases with the increase in the annealing temperature, with an important note which is the effect of the absorption spectrum of the films prepared by the annealing process, as shown in the general behavior of the films after they are annealed, and this indicates that the annealing process has changed the nature of the bilayer, and the conditions became more favorable for the formation of the compound (In/Se).

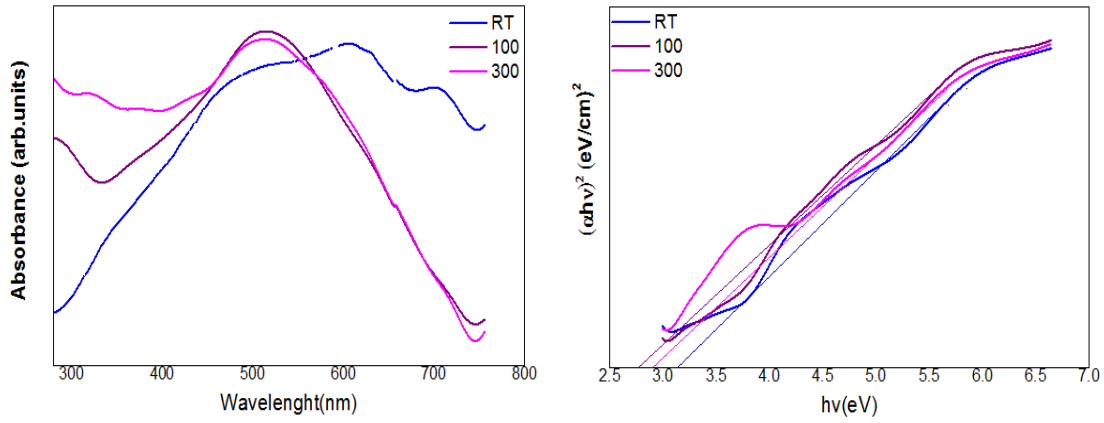

Fig. 4. (a) In/Se thin films at (100), (300), and without annealing have absorbance spectra plotted against wavelength; (b).The Energy Band Gap of In/Se of different annealing temperature

Table 2. Shows the values of energy gap of In/Se at RT and with annealing temperature.

Thickness (nm)	Temperature (°C)	Energy gap (eV)	Absorption edge(nm)
Se:200,In:150	RT	3.05	406
	100	2.91	426
	300	2.82	439

3.4. Electrical properties

3.4.1. (D.C) conductivity

In order to study conductivity mechanisms, it is convenient to plot logarithm of conductivity (ln σ) as a function of (T^{-1}) [i.e. ln σ=f(10^3/T)≡ Arrhenius plot]. However, the Arrhenius plot cannot be fitted by a single straight line. Figure(5) illustrates the resistivity of an In/Se film with a thickness of 350 nm. Calculations of the activation energy are performed at temperatures ranging from 388 to 440 K. The fact that the resistivity drops as the temperature rises is evidence of the semiconducting nature of the In/Se film [18]. In addition, it has been noticed that the variation is nonlinear. It has been determined that the activation energy is on the order of 0.42 eV**.** This conclusion is consistent with the results in Ref.[19]. This means, there are two activation energies Ea_1 and Ea_2 corresponding to at least one of the possible conduction mechanisms dominant at a respective temperature range. The first activation energy (Ea_1=0.42 eV)

within the range (390-410) K,, represents the transition process for carriers within localized states in the energy gap. This suggests the high density of localized states in the energy gap. The second activation energy (Ea_2=0.604 eV) within the range (400-410) K, represents the carrier's transport across the grain boundaries by thermal excitation.

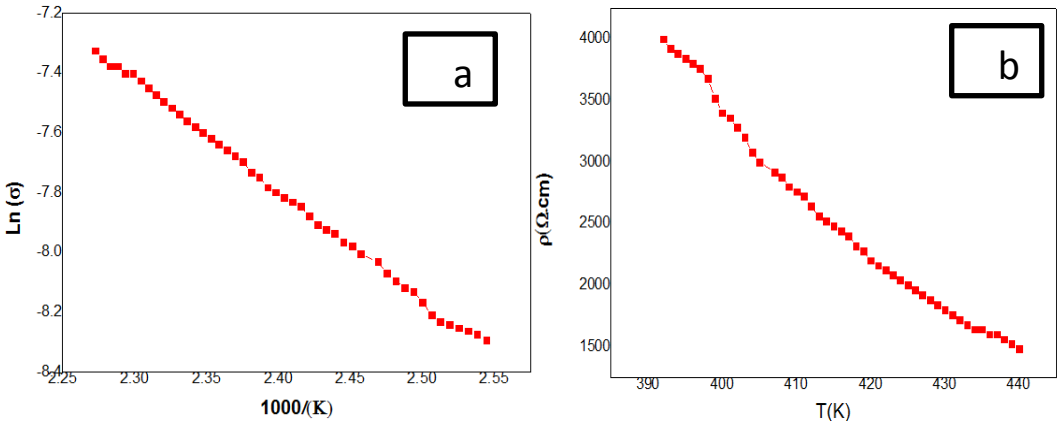

Fig. 5 (a)(p) Vs. T(K) of thin films In/Se; (b). (ln σ) Vs. 1000/T(K)) of thin films In/S.

3.4.2. Hall effect

Hall measurements for thin films In/Se bilayer deposited on glass substrates by thermal evaporation method were carried out at 300 ^{0}C temperature and showed the values of mobility, the concentration of carriers, and the Hall coefficient. The value of the Hall coefficient was (-2.76×10^6) for films are of n-type. Table (3) shows Hall parameters. This conclusion is consistent with the results in Ref.[20].

Table 3. Hall measurements at annealing Temperature (300 ^{o} C) (mobility, Concentration of carriers, type ,and Hall coefficient).

sample	**Mobility ($cm^2V^{-1}s^{-1}$)**	**Concentration of carriers$(nm)^{-2}$**	**Hall coefficient RH ($cm^{-3}C^{-1}$)**	**Type**
At 300 ^{o} C	8.14×10^1	-1.12×10^{12}	-2.76×10^6	n-type

4. Conclusion

An effective method for manufacturing In/Se bilayer membranes has been developed and proven successful. In accordance with the results obtained by using the thermal evaporation method, it was discovered that the phase of the compound was completed, as well as the preparation of the compound and that homogenous films could be generated by heating the bi-layer films to temperatures ranging between 100 and 300 degrees Celsius. Annealing at 300°C for 60 minutes results in the creation of a mixed-phase of In /Se and In_2Se_3 compounds, as well as a trace quantity of the element Se. The result of the annealing process is that the thin films become polycrystalline and the bandgap decreases to 2.82 eV.

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