WALAILAK JOURNAL
http://wjst.wu.ac.th Engineering and Physical Sciences

Study on Physical Properties of $In_x Se_{1-x}$ Thin Films Synthesized by Vacuum Evaporation Method

Mahdi Hasan SUHAIL[1], Issam Mohammed IBRAHIM[1] and Asmiet RAMIZY[2,*]

Department of Physics, College of Science, University of Baghdad, Iraq
Department of Physics, College of Science, University of Anbar, Iraq

([*]Corresponding author's e-mail: mhsuhail@yahoo.com, asmat_hadithi@yahoo.com)

Received: 23 December 2012, Revised: 30 May 2014, Accepted: 28 June 2014

Abstract

Indium Selenide (In_xSe_{1-x}) thin films were synthesized in a sealed ampoule in a vacuum of 10^{-2} Torr using high purity elemental indium and selenium with different x concentration (0, 10, 15 % at.wt.) using vacuum evaporation technique. The structural properties of In_xSe_{1-x} alloys for (x = 10 and 15 % at. wt.) were examined by x-ray diffraction and exhibited a polycrystalline structure with hexagonal unit cell. The effects of the indium concentration and post deposition heat treatment on the structural and optical properties of the films were studied. The direct band gap of In_xSe_{1-x} thin films were estimated in the range (2.35 - 3.95) eV and the energy gap (E_g^{opt}) increases with increasing annealing temperatures. Optical constants (included refractive index (n), extinction coefficient (k), and real (ε_r) and imaginary parts (ε_i) of dielectric constant) for the above films were calculated. The results were discussed in detail in relation with film recrystallization during the heating process.

Keywords: Indium Selenide, vacuum evaporation, annealing, energy gap, optical constants

Introduction

III-VI semiconductor compounds such as InSe, GaSe and GaS have gained attention in recent years for optoelectronic applications [1]. Being layered-type semiconductors, their 2-dimensional structure and their resulting anisotropic properties are of particular interest. In these materials, inter-layer interactions are very weak compared to those in a single layer. It is known that the semiconductor applications are strongly influenced by the presence in the forbidden gap of the energy levels arising from impurities and structural defects [2]. Furthermore, the numbers of defects present in the amorphous structure, changes due to post deposition heat treatment [3]. Hence, systematic studies on the InSe thin films properties based on substrate temperature during the deposition and post-deposition processing must be made.

InSe layered semiconductors have been a promising material in thin film and single-crystalline form because of certain properties that make it attractive for device applications. Each layer is formed in packets of 2 In and 2 Se sublayers and the interlayer (Se-Se) bonding is of the van der Waals type, while inside the layers the bonding is largely covalent. Due to this bonding scheme, no dangling bonds exist at the surface which is an ideal condition for fabricating metal-semiconductor or p-n heterojunctions. Thus, the interfaces between such layered materials are unstrained even for the relatively high lattice mismatches [4]. The possibility of obtaining p and n-type conduction with doping makes InSe is a promising material for p-n heterojunction device structures with a low density of interface states [5-7]. Moreover, InSe is an appropriate material for photovoltaic conversion [8-9]. The structural of the InSe thin films, which strongly affect the device performance, depend on the deposition techniques and conditions [10-13]. The structural and physical properties of InSe differ widely in literature [14]. Different crystal structures such as hexagonal, rhombohedral and monoclinic forms have been reported by various workers [15].

The aim of this study is to experimentally investigate the structural and optical properties In_xSe_{1-x} films synthesized by vacuum evaporated method. The influence of the indium concentration and post deposition heat treatment on the structural and optical properties of the films was investigated. A correlation between the temperature dependence of the optical and the structural characteristic of the films were established.

Materials and methods

In_xSe_{1-x} alloys was synthesized using high purity element Indium and Selenium with purity of (99.9999 %) with different x content of (x = 0, 10, 15 % at. wt.) weight per cent of the elements are placed in a quartz ampoule, the quartz ampoule was cleaned carefully with water and alcohol, respectively to remove dust, grease, and other possible contaminants, which is evacuated to a vacuum of 10^{-2} Torr and then sealed. The sealed ampoule is placed in a furnace, and heated at a rate of 60 °C per hour in steps up to 900 °C. The ampoule is maintained at this temperature for about 8 h and then allowed to cool slowly to room temperature. The structure of the In_xSe_{1-x} alloys was examined by x-ray diffraction for different composition of alloy. In_xSe_{1-x} thin films with (x = 0, 10, 15 % at. wt.) of 50 nm thickness were prepared using thermal evaporation by continuously feeding power to a heated molybdenum boat of melting point of the materials. At this temperature, instantaneous evaporation of the material will take place. Corning glass slides substrates were used, and the distance of the source to substrate was 25 cm. The evaporation carried out using Edward coating unit (model E306A). During the evaporation of the films, the pressure in the system was 10^{-5} Torr. All samples were prepared under constant condition: pressure, rate of deposition (4 - 6 Å/sec), substrate temperature (room temperature) and thickness of 50 nm.

Finally, all prepared films were received thermal treatment under vacuum of 10^{-2} Torr at different temperature (323 and 348 °C) for 1 h. The structures of the In_xSe_{1-x} films have been examined by X-ray diffractions (XRD-6000 SHIMADZU). Optical measurements on the In_xSe_{1-x} thin films were performed on a UV/Visible sp.2102 spectrophotometer in the region 300 - 800 nm. The absorption coefficient (α) was calculated from absorption spectrum by using the following equation.

$$\alpha = 2.303\frac{A}{t} \tag{1}$$

where t is the thickness of the film and A is the absorbance.

The relation between (αhυ) and photon energy (hυ) was examined for different value of (r) to determine the type of the optical transition.

$$(\alpha h\nu) \approx (h\nu - E_g)^r \tag{2}$$

Optical constants included the refractive index (n), extinction coefficient (k), and real (ε_r) and imaginary parts (ε_i) of dielectric constant. The n can be calculated from the following equation.

$$n = \left[\frac{4R}{(R-1)^2}\right]^{\frac{1}{2}} - \frac{(R+1)}{(R-1)} \tag{3}$$

where R is the reflectance and given by the equation.

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{4}$$

The extinction coefficient (imaginary part of the refractive index), which is related to the exponential decay of the wave as it passes through the medium can be determined by using equation.

$$K = \frac{\alpha\lambda}{4\pi} \tag{5}$$

The ε_r and ε_i can be calculated by using equations.

$$\varepsilon_r = n^2 - k^2 \tag{6}$$

$$\varepsilon_i = 2nk \tag{7}$$

Result and discussions

Figure 1 shows X-ray diffraction of In_xSe_{1-x} alloys at (x = 10 and 15 % at. wt.) declared sharp diffraction peaks located at 23.42, 29.61 and 43.47 ° which showed the polycrystalline structure with hexagonal unit cell as compared with the American Standard for Testing Material (ASTM) cards. The strong diffraction peak at 2Θ = 45.45 ° corresponds to diffraction from the (110) planes while the other peaks at 2Θ = 26.02 and 50.05 ° are the result of diffraction from the (101) and (114) planes, respectively. According to XRD results the InSe films are polycrystalline (the hexagonal system) [16]. Noticeable remark from **Figure 2** is the increases in the polycrystalline degree which is obvious from the increase of peak heights in the diffraction pattern of the alloy for x = 15 %.

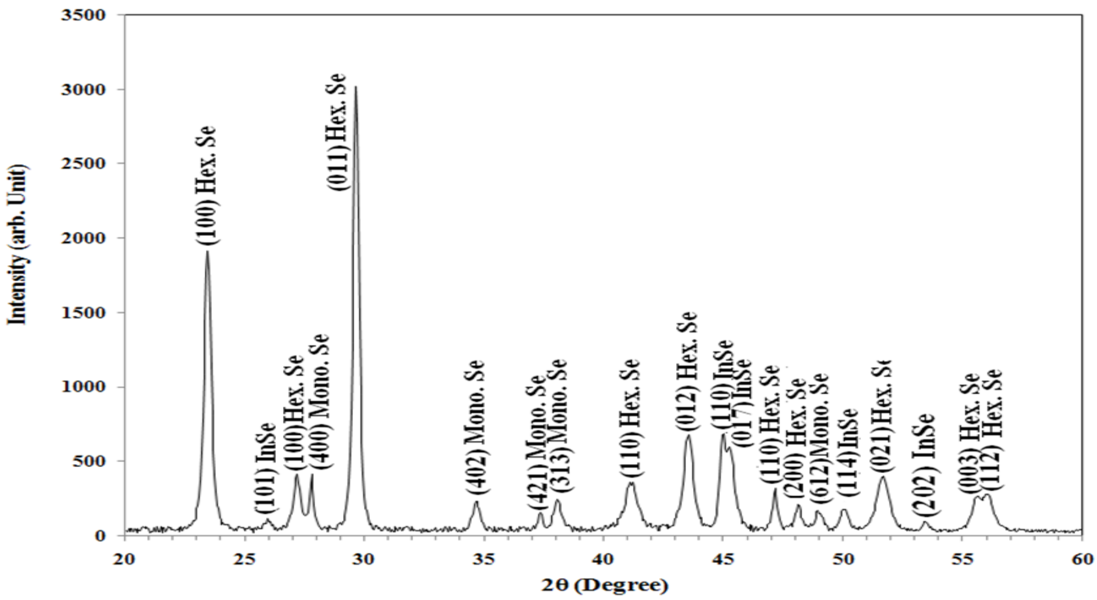

Figure 1 X-ray diffraction for In_xSe_{1-x} alloys with In content in the range (x = 10 % at. wt.).

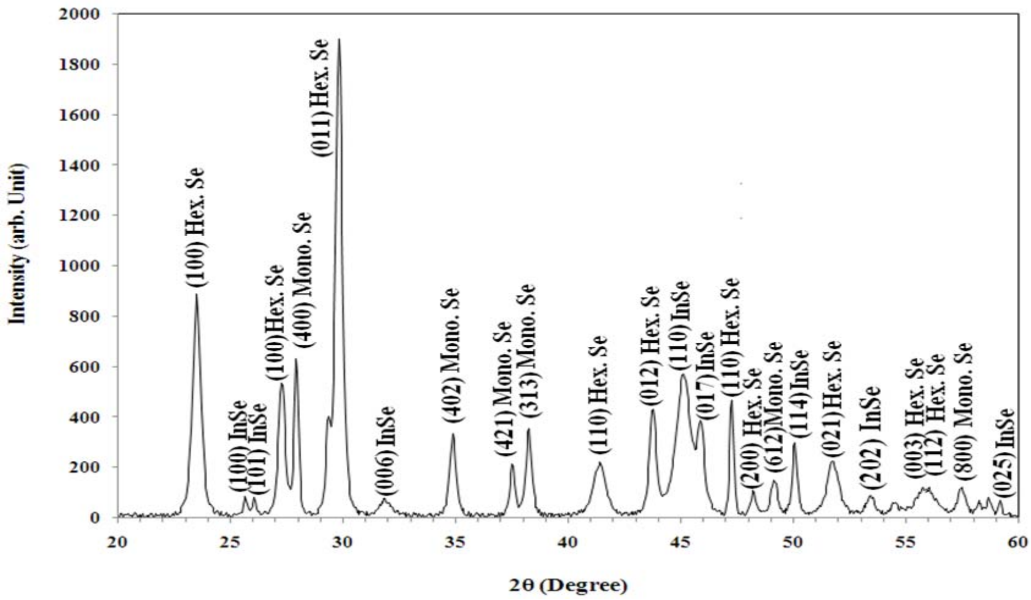

Figure 2 X-ray diffraction for In_xSe_{1-x} alloys with In content in the range (x = 15 % at. wt.).

The structural of InSe thin films obtained by the thermal evaporation technique were investigated. The results indicated that as-grown films have a non-crystalline structure and heat treatment results in a transformation to polycrystalline state. The diffraction patterned of prepared thin films of In_xSe_{1-x} for (x = 10 % at. wt.) for thickness (50 nm) at different annealing temperatures (323 and 348 K) is plotted in **Figure 3** and shows that the structure is amorphous. The heating process of such films leads to an improvement of the arrangement of indium and selenium atoms in the film crystallites and transformation into polycrystalline state which is due to the recrystallization process during the annealing of the film.

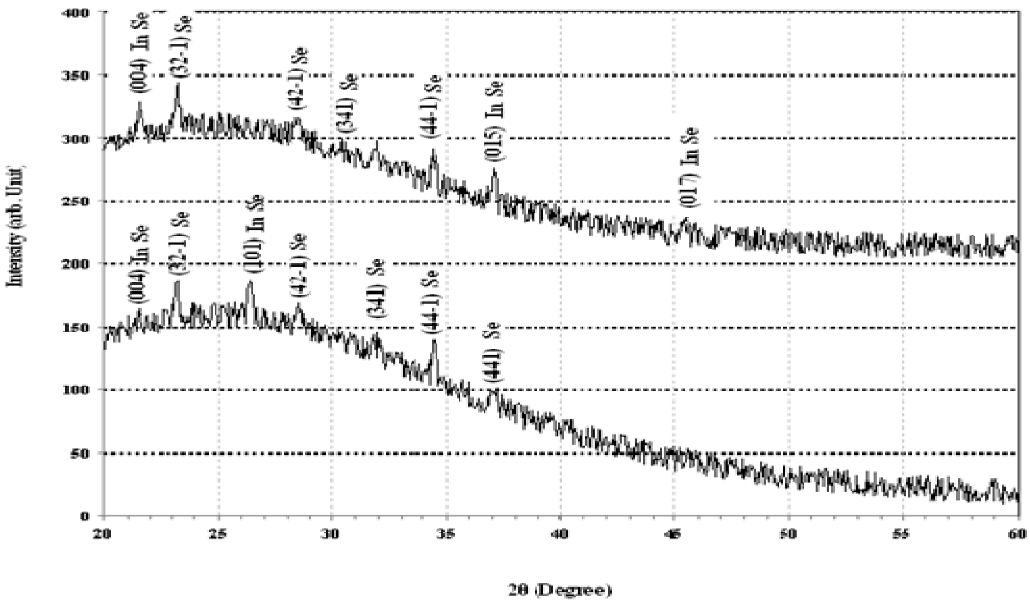

Figure 3 X-ray diffraction for In_xSe_{1-x} films with In content in the range (x = 10 % at. wt.) and different annealing temperatures (323 and 348 K).

Figure 4 shows SEM photographs deposited films with various particle sizes. It is observed that the surface morphology of the films with temperature of 348 K shows very rough surface. The grain size is increased gradually by increasing annealing temperature. These facts are also confirmed by the X-ray diffraction.

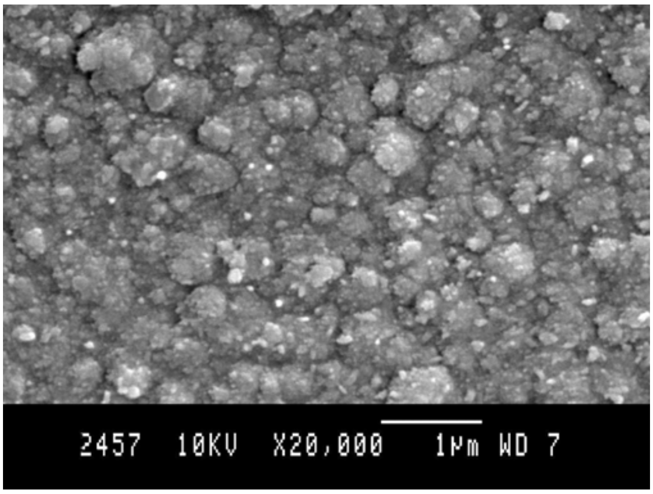

Figure 4 SEM micrograph of the surface for In_xSe_{1-x} films deposited onto heated substrates (348 K).

The transmittance and absorbance spectra of In_xSe_{1-x} films (x = 0, 10, 15 % at. wt.) annealed at 300, 323 and 348 K are shown in **Figures 5 - 7**. It could be observed that the peak of transmittance spectra of In_xSe_{1-x} thin films shift toward the longer wavelength with increasing annealing temperature. Below 350 nm, there is a sharp fall in transmittance of the film because of its high energy gap value which return to strong absorbance of the films in this region. The film deposited with higher annealing temperatures shows a higher transmittance compared to increase in concentration. This results agreed with the absorbance spectra obtained in other works [16].

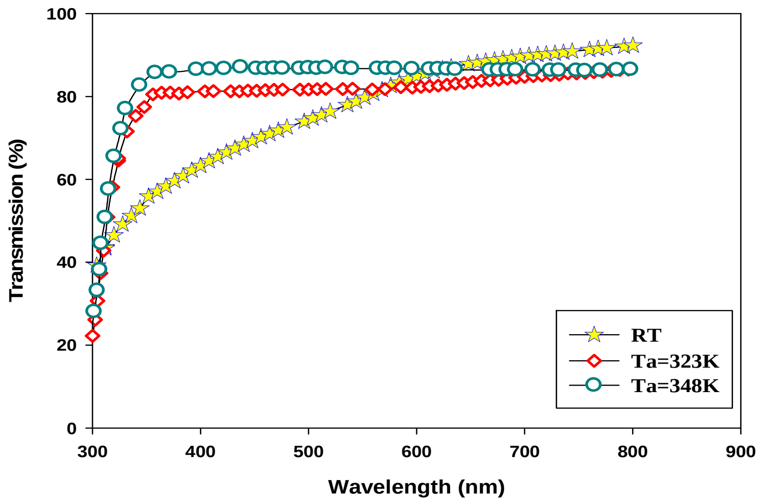

Figure 5 Transmittance spectra of In_xSe_{1-x} films with In content (x = 0 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

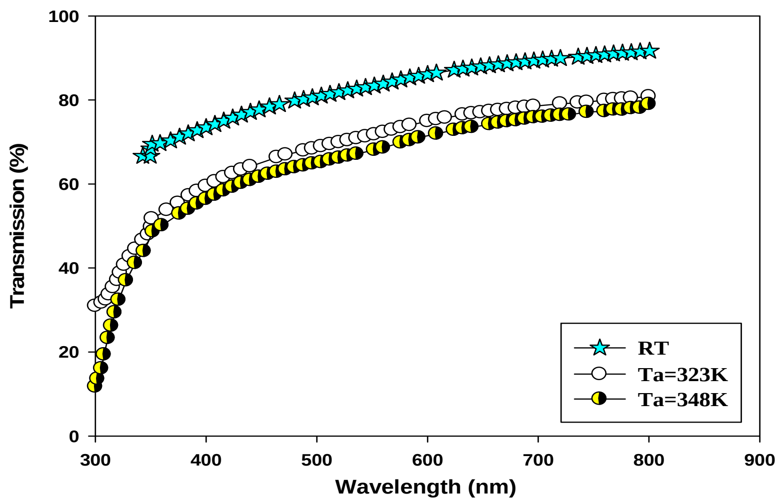

Figure 6 Transmittance spectra for In_xSe_{1-x} films with In content at (x = 10 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

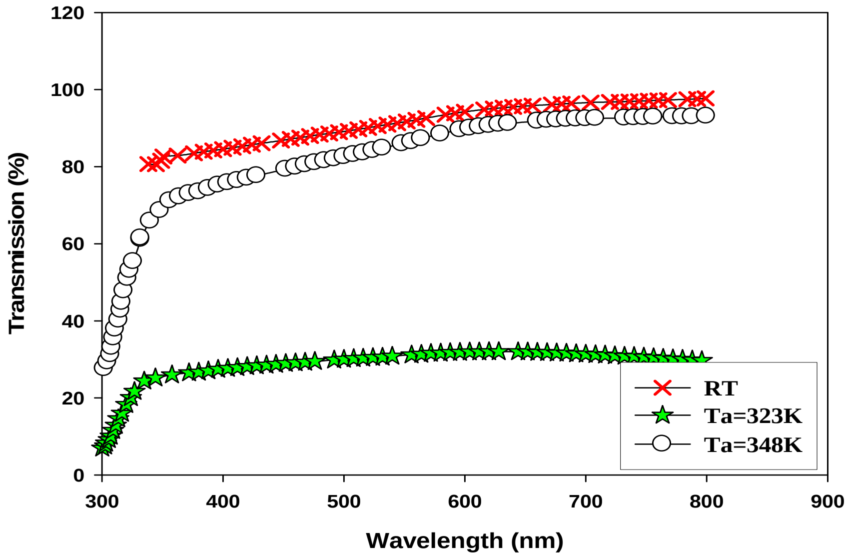

Figure 7 Transmittance spectra for In_xSe_{1-x} films with In content at (x = 15 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

Figures 8 - 10 show the variation of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) for In_xSe_{1-x} thin films. The best fit to the experimental data was obtained for n = 1/2. This agrees with the fact that InSe is a semiconductor material with a direct band gap. This means that the fundamental absorption edge can be described by the direct-allowed transition. The optical energy gap values for films deposited at room temperature 3.54 eV and post deposition heat treatment are 3.97 and 3.98 eV at annealing temperature equal to 323 and 348 K respectively. This result agrees with the literature [17-19]. The presence of a high concentration of localized states in the band structure is responsible for the low value of Eg^{opt} for room temperature. In the process of heated treatment (i.e., in polycrystalline films) the unsaturated defects are gradually producing a large number of saturated bonds. The reduction in the number of unsaturated defects decreases the density of localized states in the band structure, consequently increasing the optical gap [20,21].

The value of the optical energy gap is decreased with increasing the concentration of In content for all samples and this may be due to the increasing grain size and the decrease in defect states near the bands and this in turn decreased the value of Eg^{opt}. The reduction in the number of unsaturated defects reduces the density of localized states in the band structure, consequently increasing the optical gap [12]. The value of Eg^{opt} decreases with increasing the concentration (3.54 - 2.35 eV) for all samples and this may be due to the increasing grain size and the decrease in defect states near the bands which in turn reduce the value of Eg^{opt}. The optical band gap was found to increase after the heat treatment. This may be explained that the heat treatment made In_xSe_{1-x} samples less absorbing or more transparent to the incident light.

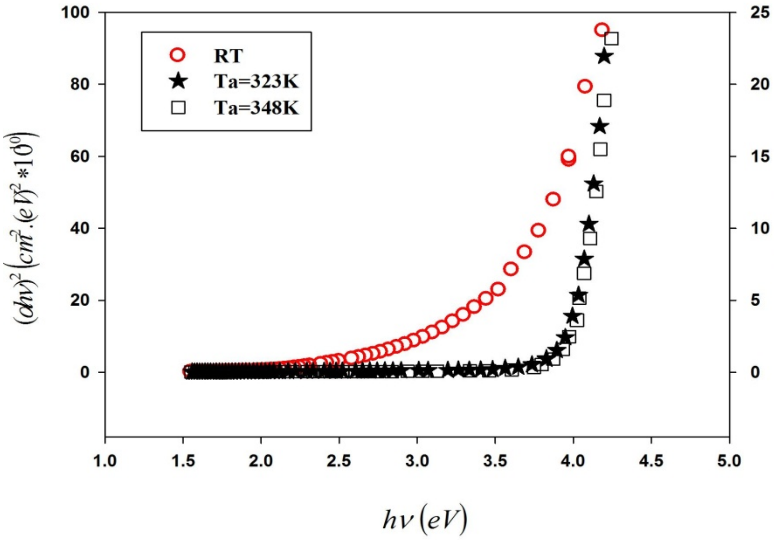

Figure 8 Variation of $(\alpha h\nu)^2$ vs $h\nu$ In_xSe_{1-x} films with In content at (x = 0 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

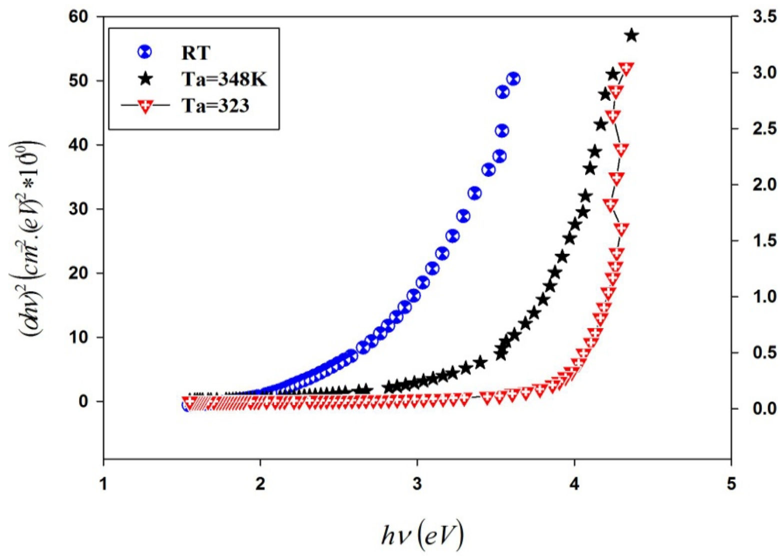

Figure 9 Variation of $(\alpha h\nu)^2$ vs $h\nu$ In_xSe_{1-x} films with In content at (x = 10 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

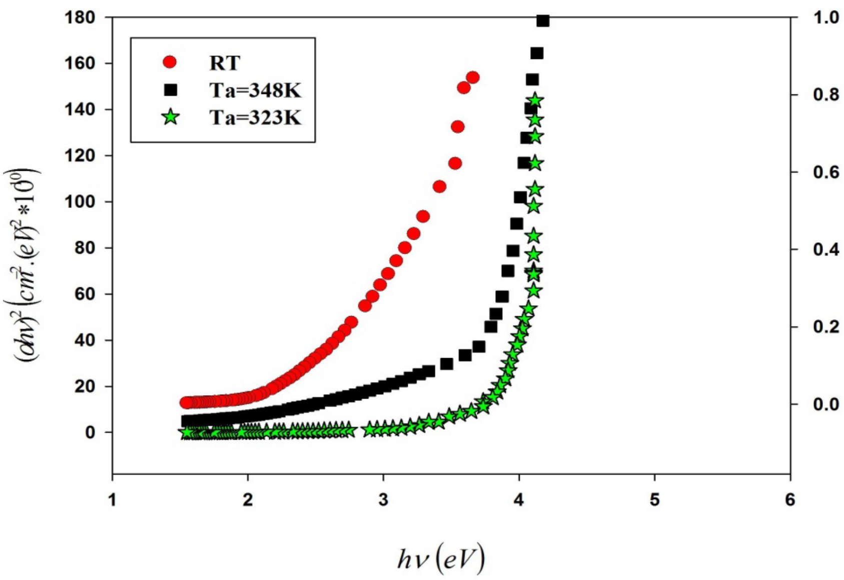

Figure 10 Variation of $(\alpha h\nu)^2$ vs $h\nu$ In_xSe_{1-x} films with In content at (x = 15 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

The optical behavior of a material is generally utilized to determine its optical constants. **Figures 11 - 13** shows the values of n for the In_xSe_{1-x} films as a function of wavelength with various annealing temperatures and concentration of indium. At a lower wavelength region, the n increases and remains constant at higher wavelength region. The increase of n in the lower wavelength region may be due to the strong effect of surface and volume imperfections on the microscopic scale [22].

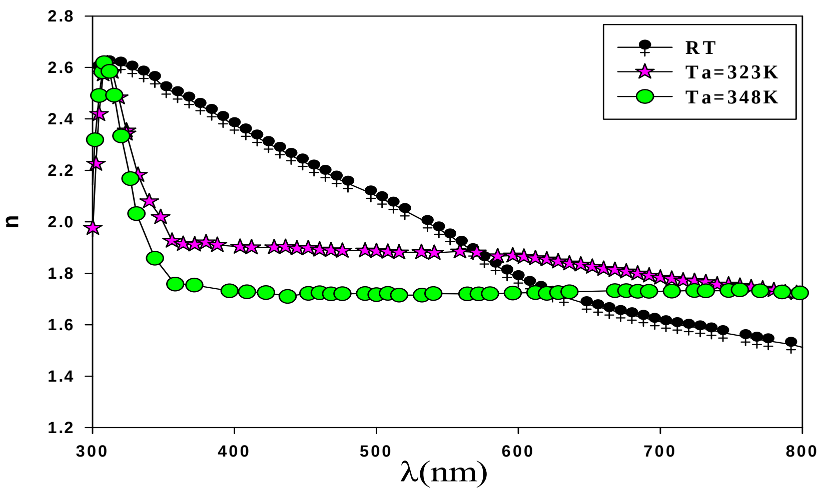

Figure 11 n of In_xSe_{1-x} films with In content at (x = 0 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

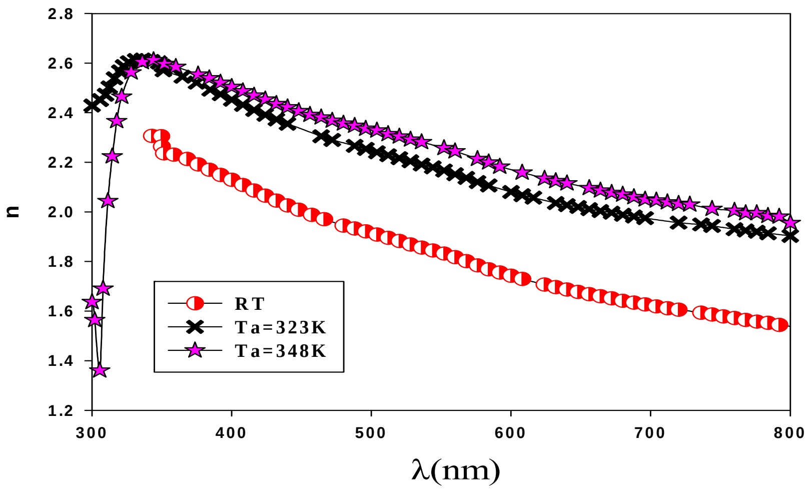

Figure 12 n of In_xSe_{1-x} films with In content at (x = 10 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

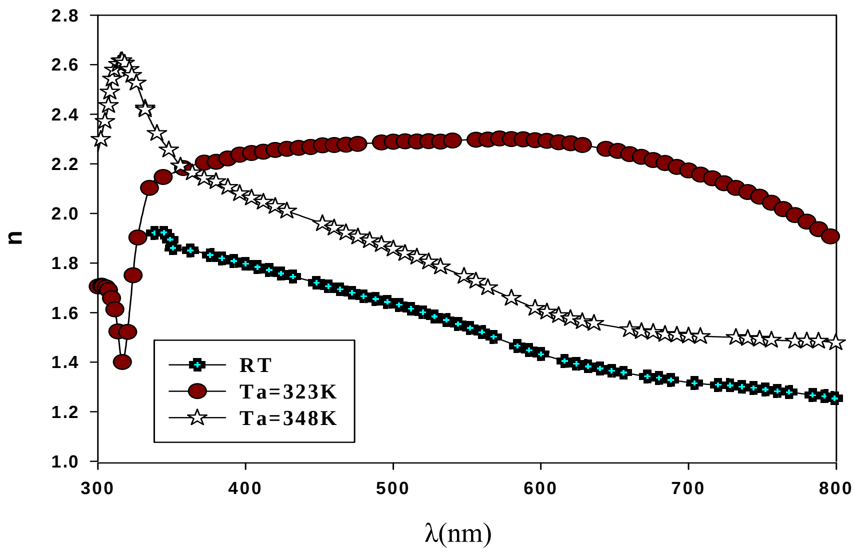

Figure 13 n of In_xSe_{1-x} films with In content at (x = 15 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

The values of k for In_xSe_{1-x} thin films as a function of wavelength with various annealing temperatures is shown in **Figures 14 - 16**. We noticed that the increase of k with increasing of photon energy because the increasing of absorption coefficient. This means that direct electronic transition happens in these films. The behavior of k is nearly similar to the corresponding absorbance and absorption coefficient for In_xSe_{1-x} thin films at different annealing temperatures. It could see that the k at 350 nm increase with annealing temperatures as shown in **Table 1**.

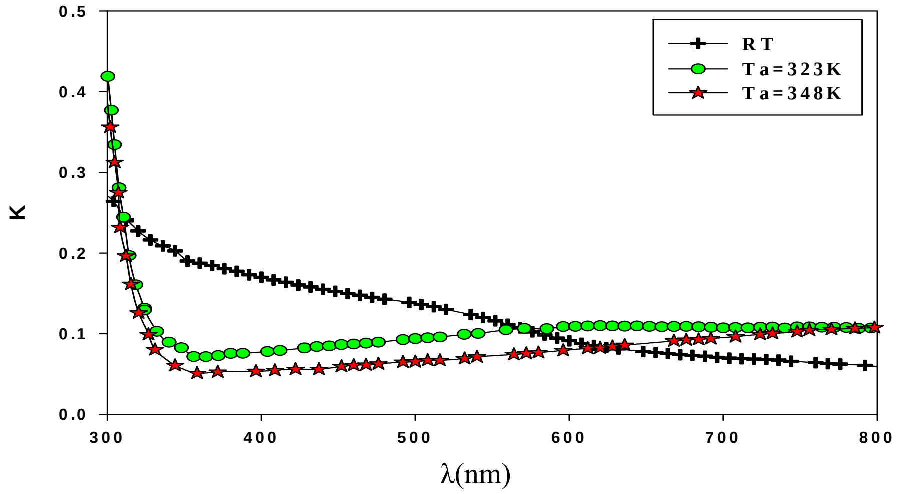

Figure 14 k of In_xSe_{1-x} films with In content at (x = 0 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

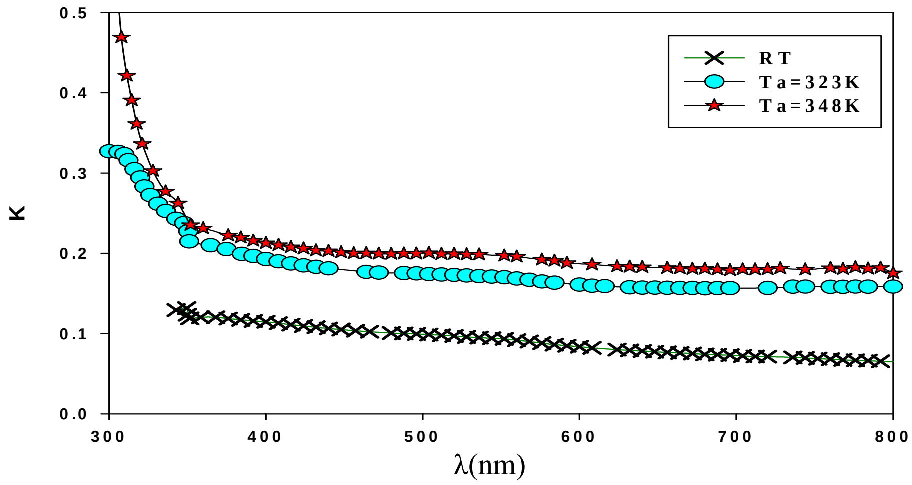

Figure 15 k of In_xSe_{1-x} films with In content at (x = 10 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

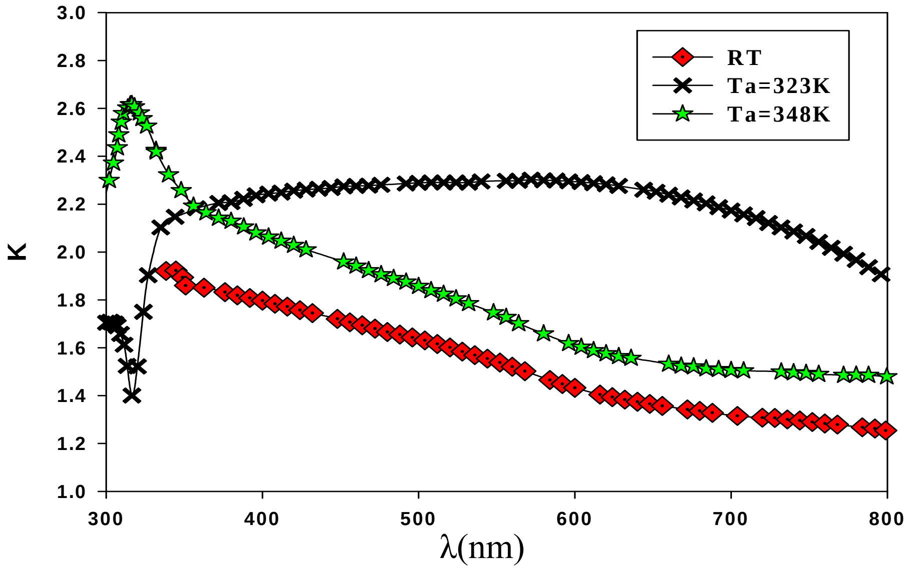

Figure 16 k of In_xSe_{1-x} films with In content at (x = 15 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

Figures 17 - 22 respectively show the variation of ε_r and ε_i as a function of wavelength. The behavior of ε_r is similar to n, while ε_i depends mainly on α. For In_xSe_{1-x} thin films, ε_r is decreased with the increase in annealing temperature, while ε_i increase with increasing annealing temperatures. The variations of ε_r and ε_i were increased with increasing annealing temperatures. The variation of the ε_r depends on the value of the n. By contrast, the ε_i depends mainly on the k that is related to the variation of absorption coefficient. The variation in the energy gap and optical constants is summarized in **Table 1**. The values of Eg^{opt} and the k increase while the values of refractive index decrease with increasing of concentration and annealing temperatures. The ε_r was increased similar to k while the ε_i behaves like n.

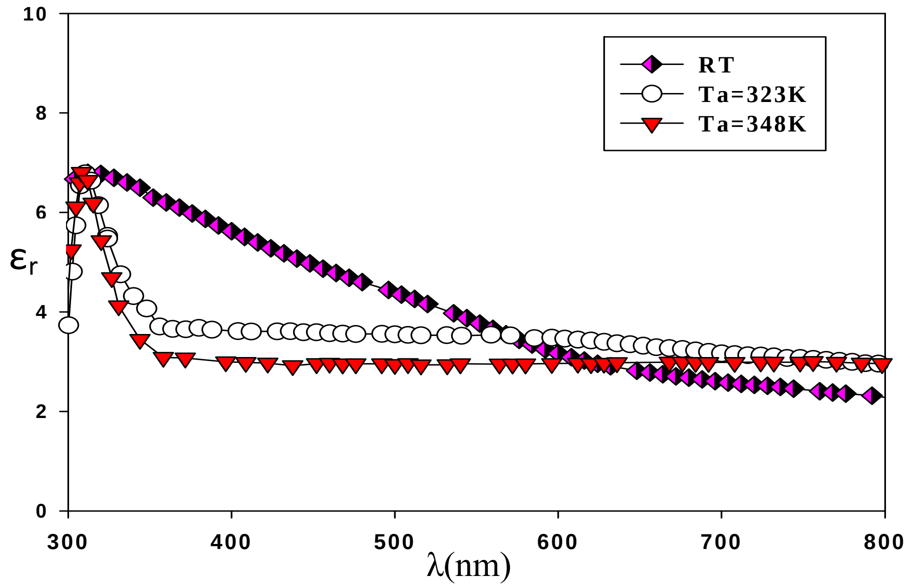

Figure 17 ε_r of In_xSe_{1-x} films with In content at (x = 0 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

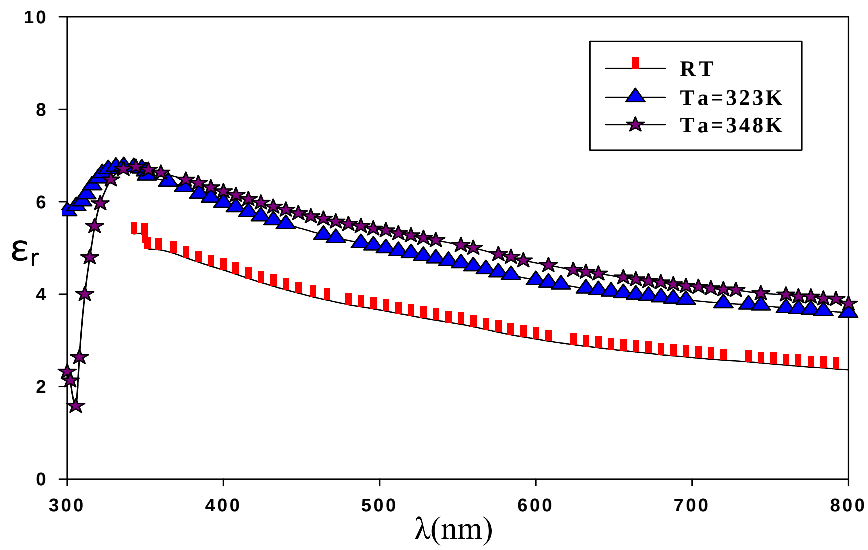

Figure 18 ε_r of In_xSe_{1-x} films with In content at (x = 10 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

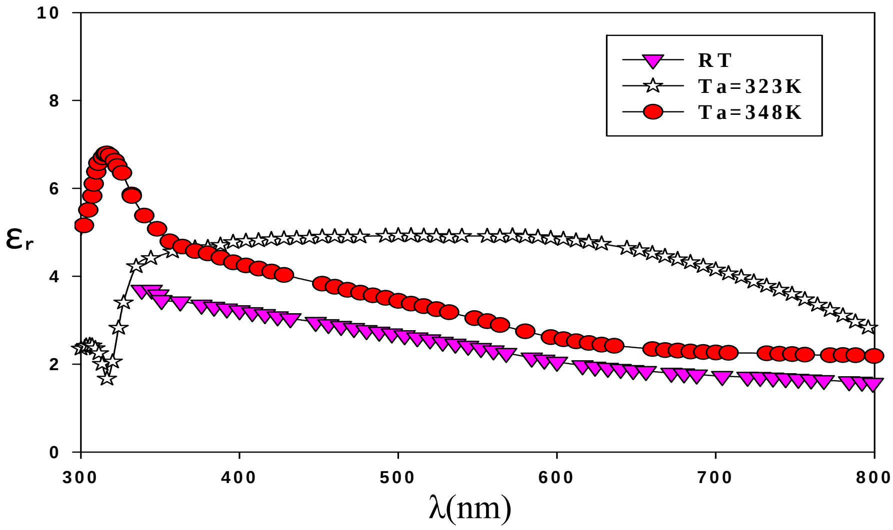

Figure 19 ε_r for In_xSe_{1-x} films with In content at (x = 15 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

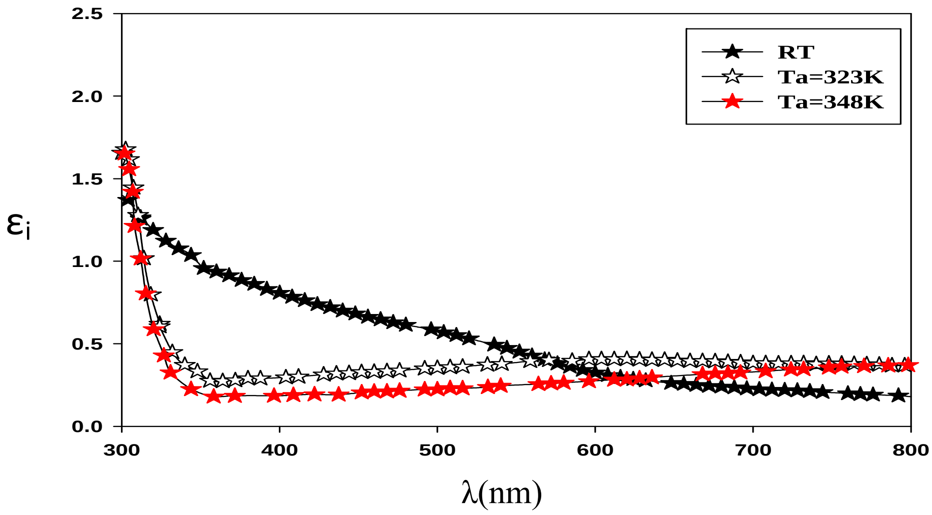

Figure 20 ε_i of In_xSe_{1-x} films with In content at (x = 0 % at. wt.) and different annealing temperatures (RT, 323 and 348 K).

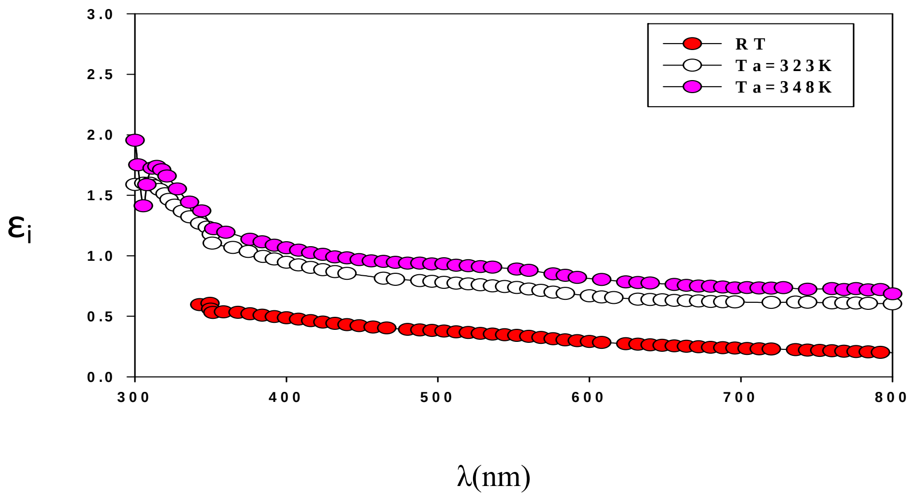

Figure 21 ε_i of In_xSe_{1-x} films with In content at (x = 10 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

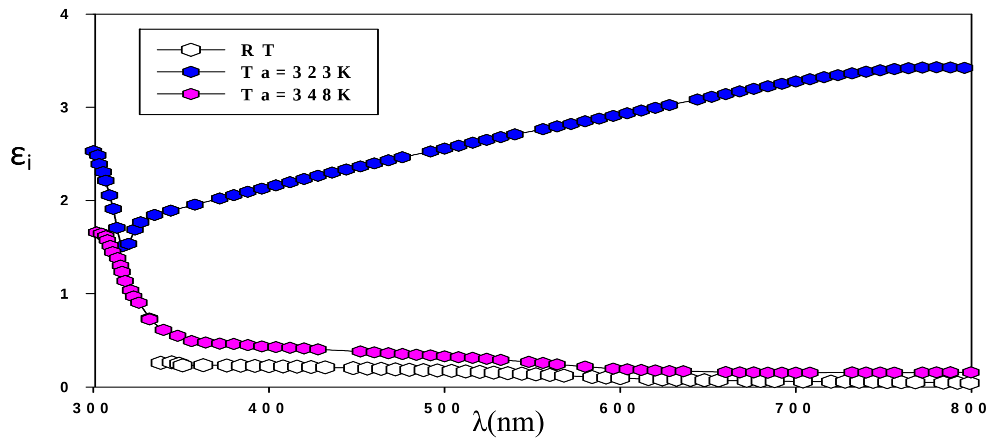

Figure 22 ε_i of In_xSe_{1-x} films with In content at (x = 15 % at. wt.) with different annealing temperatures (RT, 323 and 348 K).

Table 1 Energy gap (Eg^{opt}), refractive index (n), extinction coefficient (k) and real (ε_r) and (ε_i) imaginary of dielectric constants as a function of concentration and annealing temperature.

T_a (K)		x = 0 % In	x = 10 % In	x = 15 % In
RT	Eg^{opt} in eV	3.54	2.6	2.35
323		3.97	3.39	3.69
348		3.98	3.54	3.8
RT	n	2.7	2.6	2.70
323	at λ = 550nm	2.7	2.6	2.25
348		2.7	2.4	1.80
RT	k	0.26	0.12	0.5
323	at λ = 550nm	0.4	0.35	0.66
348		0.42	0.5	0.75
RT	ε_r	6.8	5.4	3.8
323	at λ = 550nm	6.77	6.85	4.8
348		6.74	6.7	6.8
RT	ε_i	1.4	0.6	0.3
323	at λ = 550nm	1.65	1.6	1.5
348		1.6	1.9	1.65

Conclusions

In_xSe_{1-x} films prepared by vacuum evaporation method and annealed at 323 and 348 K exhibited a polycrystalline structure. Optical studies showed that direct band gap values of In_xSe_{1-x} films was increased after the heat treatment because the heat treatment made In_xSe_{1-x} samples more transparent or less absorbing to the incident light. The obtained results revealed that the structural and the optical of the films were strongly influenced by the annealing temperatures during deposition process.

References

[1] C DeBlasi, G Micocci, A Rizzo and A Tepore. Large InSe single crystal grown from stoichiometric and non- stoichiometric melts. *J. Crystal Growth.* 1982; **57**, 482-6.

[2] M Parlak and C Ercelebi. The effect of substrate and post annealing temperature on the electrical properties of polycrystalline InSe thin films. *J. Mater. Sci. Mater. Electron.* 1999; **10**, 313-9.

[3] S Chaudhuri, SK Biswas and A Choudhury. The effects of heat treatment on the structural properties of amorphous In_{30} Se_{70} films. *Phys. Stat. Sol.* 1988; **109**, 511-6.

[4] A Segura, JP Guesdon, JM Besson and A Chevy. Photoconductivity and photovoltaic effect in InSe. *J. Appl. Phys*. 1983; **54**, 876-88.

[5] T Matsushita, TT Nang, M Okuda, A Suziki and S Yokota. Photovoltaic effect of amorphous In_xSe_{1-x}-Sn_{O2} heterostructure. *Jpn. J. Appl. Phys*. 1976; **15**, Article ID 901.

[6] J Martinez-Pastor, A Segura, JL Valdes and A Chevy. Electrical and photovoltaic properties of indium-tin-oxide/p-InSe/Au solar cells. *J. Appl. Phys.* 1987; **62**, 1477-83.

[7] C Tatsuyama, T Tanbo and N Nakayama. Heteroepitaxy between layered semiconductors GaSe and InSe. *Appl. Surf. Sci*. 1989; **41-42**, 539-43.

[8] R Rousina. Influence of deposition temperature on the crystallization of thermally evaporated indium selenide thin films. *J. Mater. Sci. Lett.* 1988; **7-8**, 893-4.

[9] Y Hasegava and Y Abe. Electrical and optical characteristics of a schottky barrier on a cleaved surface of the layered semiconductor InSe. *Phys. Stat. Sol.* 1982; **70**, 615-21.
[10] MD Guilio, G Micocci, A Rizzo and A Tepore. Photovoltaic effect in gold-indium selenide Schottky barriers. *J. Appl. Phys*. 1983; **54**, Article ID 5839.
[11] JC Bernede, S Marsillac, A Conan and A Goday. The influence of microcrystalline inhomogeneities embedded in amorphous In_xSe_{100-x} films on their electrical and optical properties. *J. Phys.: Cond. Mater*. 1996; **8**, Article ID 3439.
[12] M Parlak and C Erçelebi. The effect of substrate and post-annealing temperature on the structural and optical properties of polycrystalline InSe thin films. *Thin Solid Films* 1998; **322**, 334-9.
[13] SM Yu, JH Yoo, SP Patole, JH Lee and JB Yoo. The effect of pressure and growth temperature on the characteristics of polycrystalline In_2Se_3 films in metal organic chemical vapor deposition. *Elec. Mater. Lett*. 2012; **8**, 245-50.
[14] A Chevy, A Kuhn and MS Martin. Large InSe monocrystals grown from a non-stoichiometric melt. *J. Cryst. Growth* 1977; **38**, 118-22.
[15] E Mooser. *Physics and Chemistry of Material with Layered Structures*. Reidel, Dordrecht, 1976.
[16] MA Afifi, NA Hegab and AE Bekheet. Effect of annealing on the electrical properties of ln_2Se_3 thin films. *Vacuum* 1995. **46**, 335-9.
[17] C Julien, M Eddreif, K Kambas and M Balkanski. Electrical and optical properties of In_2Se_3 thin films. *Thin Solid Films* 1986; **137**, 27-37.
[18] K Bindu, C Sudhakartha, KP Vijayakumar, T Abe and Y Kashiwaba. Structural, optical and electrical properties of In_2Se_3 thin films formed by annealing chemically deposited Se and vacuum evaporated In stack layers. *Appl. Surf. Sci*. 2002; **191**, 138-47.
[19] ABA Ei-Moiz, MA Hefni, FM Reicha and MM Hafiz. Optical investigations on In_xSe_{1-x} thin films (II). *Phys. B Cond. Mater*. 1993; **191**, 303-11.
[20] M Parlak. The effect of substrate and post-annealing temperature on the structural and optical properties of polycrystalline InSe thin films. *Thin Solid Films* 1998; **322**, 334-9.
[21] HT Ei-Shair and AE Bekheet. Effect of heat treatment on the optical properties of In_2Se_3 thin films. *J. Phys. D: Appl. Phys*. 1992; **25**, Article ID 1122.
[22] B Samanta, SL Sharma and AK Chaudhuri. Optical andmicro structural properties of $Cd_{0.8}$ $Zn_{0.2}$ Te thin films. *Indian J. Pure Appl. Phys.* 1994; **32**, 62-7.