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International Journal of Current Engineering and Technology
E-ISSN 2277 – 4106, P-ISSN 2347 - 5161

Available at http://inpressco.com/category/ijcet

Research Article

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Accepted 15 Nov 2014, Available online 20 Dec2014, **Vol.4, No.6 (Dec 2014)**

Abstract

The pure and Sb doped GeSe thin films have been prepared by thermal flash evaporation technique. Both the structural and optical measurement were carried out for as deposited and annealed films at different annealing temperatures.XRD spectra revealed that the all films have one significant broad amorphous peak except for pure GeSe thin film which annealed at 573 K, it has sharp peak belong to orthorhombic structure nearly at $2\theta=33^o$. The results of the optical studies showed that the optical transition is direct and indirect allowed. The energy gap in general increased with increasing annealing temperature and decreased with increase the ratio of Sb dopant. The optical parameters such as refractive index, extinction coefficient and real and imaginary parts of dielectric constants for these films have been investigated, and it was found that the films affected by changing the ratio of Sb dopant and heat treatment .

Keywords: *Chalcogenide semiconductors, optical parameters, Ge-Se system, Sb dopant films.*

1. Introduction

The Ge-Se system belongs to IV-VI compound semiconductors. Such a system is now considered among the most important chalcogenides glasses (M.Alisa *et al*, 2003).

Chalcogenide glasses always contain one or more chalcogen element, sulphur, selenium or tellurium in combination with elements from IVth,Vth or VIth group of the periodic system of elements (D.Lezal *et al*, 2004). Chalcogenide glasses attract interest of many researchers due to their uniguephysico-chemical properties, e.g., high infrared transparency, non-linear optical properties, photo-induced phenomena etc.(J.Orava *et al*, 2009).

Today we need more sensitive, rapid and miniaturized detection system, capable of real-time pollutant detection. Therefore, integrated optical devices are increasingly being used for opto-chemical sensing applications. The characteristics of Ge-As-Se,Ge-As-Se-Te and Ge-Sb-Se chalcogenide thin films make them good candidates for realization of opto-chemical sensors (V.Balan *et al*, 2004).Properties of Ge-Se as amorphous chalcogenide semiconductors have been extensively used to understand the behavior in these materials (A.Alnjjar, 2009).

In recent years much attention has been paid to a-Ge-Se chalcogenide semiconductors as they are very promising materials for opto-electronic application (R.Pan *et al*, 2009).Hafiz *et al*. reported thermal annealing near the crystallization temperature causes a decrease in the indirect optical gap for the $Ge_{20}Se_{80}$ film (M.Hafiz *et al*,2007).Thin films of Ge-Se system prepared by different methods such as: conventional melt quenching (H.Lee *et al*, 2003), thermal evaporation (A.Thakur *et al*, 2007,A.Bard *et al*, 2009), radio-frequency sputtering (J.Choi *et al*, 1996).

The study of doped amorphous semiconductors is becoming of great interest scientist. It was believed earlier that impurities have little effect on the properties of amorphous semiconductors as each impurity atom can satisfy its valance requirements by adjusting its nearest-neighbor environment (S.Fouad *et al*, 2008).

The properties of chalcogenide glassy semiconductors are usually affected by the addition of impurities as a third element (S.S.Fouad *et al*, 2008).

The properties of chalcogenide materials such optical, electrical and physical properties can be controlled by changing their chemical composition (N.Mehta *et al*, 2004).When doped with metal impurities, these materials become multipurpose by the modification of their properties (A.Badaoui *et al*, 2013).

In this paper, we present result of structural and optical properties of GeSe and GeSe:Sb thin films with different ratio of Sb dopant (5% and 10%) which treated at different annealing temperatures.

2. Experimental Parts

Bulk GeSechalcogenide glass was prepared by melt-quenching technique from pure 5N elements (which were weighted according to demanding atomic ratio and sealed in quartz ampoule at 10^{-2} mbar pressure. The ampoule was putted into a rocking furnace and heated at 1230 K for four

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houre. The GeSe and GeSe:Sb thin films of thickness 300nm were prepared by thermal flash evaporation from bulk sample in a residual pressure of 10^{-5} mbar,on glass substrates at 393 K with rate 2 nm/sec.

A post deposition annealing was performed in vacuum at different annealing temperatures (373, 473, 573 K) for an half hour.

X-ray diffraction data of studied samples were obtained with diffractometer using Cu Kα radiation operated at 40 kV and 30 mA ,with scanning angle 20^o-60^o. The inter planer distance d (hkl) for different planes was measured by Bragg's law:

$$2d\sin\theta = n\lambda \tag{1}$$

Where n is the reflection order.

The absorbance and transmittance were recorded at room temperature using a double-beam spectrophotometer model (UV-Visible 2601) in the wavelength range 300-1100 nm ,using blank substrate as the reference position.

The absorption coefficient (α) was calculated using the formula:

$$\alpha = 2.303\frac{A}{t} \tag{2}$$

Where t is the film thickness and A is the optical absorbance

The dominant feature of the energy dependence of the absorption coefficient is the onsets of absorption near the region of interband transition from valence to conduction bands. The energy dependence of absorption coefficient (α) near the band edge for band to band and exciton transition could be described by Tauc formulas (L.Kazmerski, 1980):

$$\alpha h\upsilon = B_o(h\upsilon - E_g)^{1/r} \tag{3}$$

Where, B_o is a constant inversely proportional to amorphousity , hν is the photon energy (eV), E_g^{opt} is the optical energy gap (eV) ,and r is constant and may take values 2, 3,1/2, 3/2 depending on the material and the type of the optical transition. r is equal to 2, 1/2, 3 or 3/2 for the indirect allowed, direct allowed, indirect forbidden and direct forbidden transitions respectively (A.Qasrawi, 2005).

The optical behavior of a material is generally utilized to determine its optical constant [refractive index (n), extinction coefficient (k) and, real (ε_r) and imaginary parts (ε_i) of dielectric constant]. The refraction index value can calculate from the formula (T.S.Moss, 1959):

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

Where, R is the reflectance, and k is the extinction coefficient.

The absorption coefficient is related to k by:

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

Where, λ is the wavelength of the light.

The dielectric constant can be introduced by (L.Kazmerski, 1980):

$$\varepsilon = \varepsilon_r - i\varepsilon_i \tag{6}$$

where, $\varepsilon_r = n^2 - k^2$ (7)

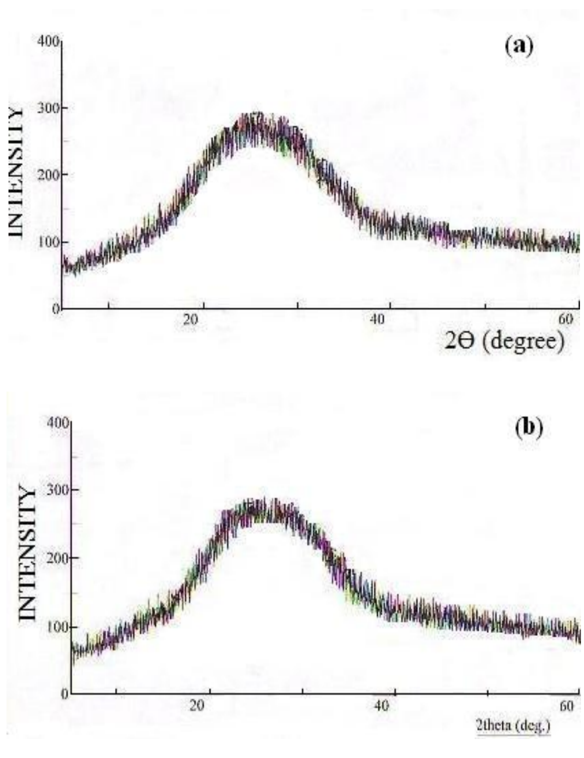
$$\varepsilon_i = 2nk \tag{8}$$

3. Results and Discussions

The structure of undoped and Sb doped GeSe thin films were studied in order to get an idea about the structural changes induced by heat treatment.

The X-ray Diffraction spectra of the films showed one broad diffusion band in the range of 2θ ~ 15-35^o for all samples as shown in Fig. (1), which is characteristic for high- disordered amorphous materials. Similar results were found by Alias *et al*. (M.Alisa *et al*, 2003), and Orava *et al* (J.Orava *et al*, 2009).

The one exception was for pure GeSe thin films which annealed at 573 K as illustrated in Fig.(2) , it has sharp peak nearly at 2θ=33^o , which correspond to reflection from (004) plane of orthorhombic phase .It is obvious from Figure (2) there is no peak appeared in the spectra of GeSe:Sb films, this means that Sb dopant increase the amorphous-crystalline transformation point. Sehly found that the GeSeSb films annealing at temperature higher than *T*g (*T*g = 439.8 K), enough vibrational energy is present to break some of the weaker bonds, thus introducing some translational degrees of freedom to the system. The additional degrees of freedom result in an increase in the heat capacity. Crystallization via nucleation and growth becomes possible and depends on annealing temperature (A.Abu-Sehly, 2000).



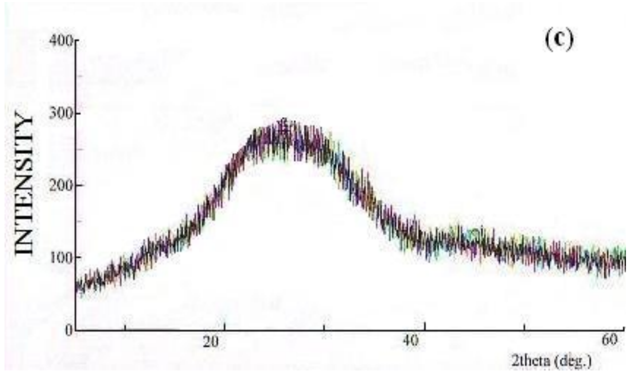


Fig. 1XRD pattern of as depositedGeSe and GeSe:Sbthin films with various ratio of Sb.(a) Sb=0 (b) Sb=5% (c) Sb=10%

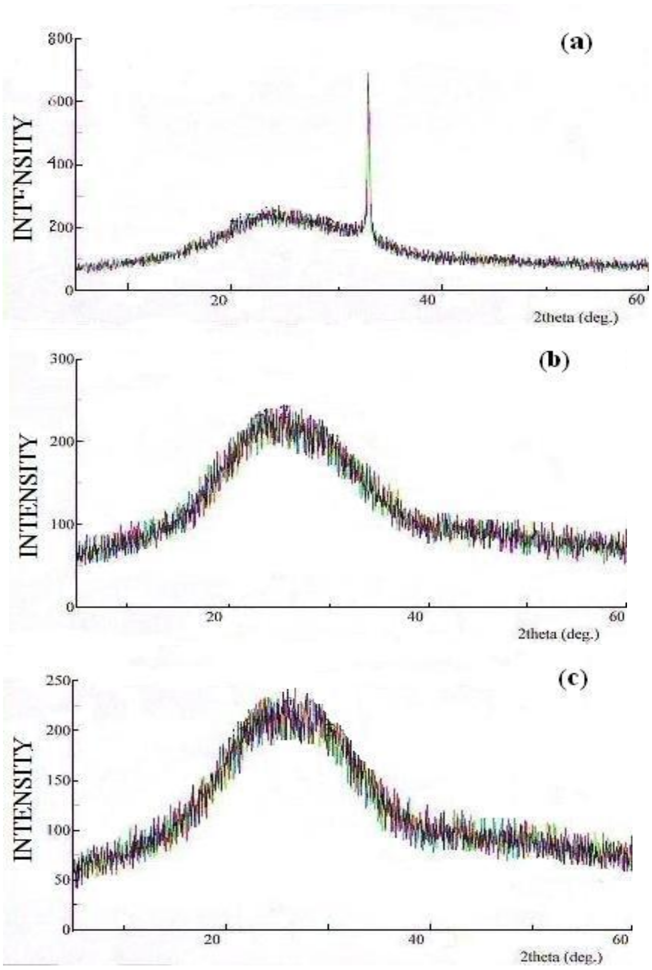


Fig. 2XRD pattern of GeSe and GeSe:Sb thin films at Ta=573 K with various ratio of Sb. (a) Sb=0 (b) Sb=5% (c) Sb=10%

The optical properties which include band gap, refractive index ,real and imaginary parts of dielectric constant, also the extinction coefficient are the most significant parameters in amorphous semi-conducting thin films. So, an accurate measurement of the optical constants is extremely important. Chalcogenide glasses have been found to exhibit the change in refractive index under the influence of light, which makes it possible to use these materials to record not only the magnitude but also the phase of illumination (J.Choi *et al*, 1996).

The transmittance and absorpttance spectra have been measured for as deposited and annealed GeSe, GeSe:5%Sb, GeSe:10%Sb thin films .

The variation of transmittance as a function of wavelength for undoped and doped GeSe thin films with 5% and 10% Sb were shown in figure (3) a , b and c respectively.
It is clear from these figures that as deposited films exhibit a low transmittance that not exceeds 54% at the visible rang of wavelength (300-700nm), where the transmittance decreases to 39.5% and 33% for Sb doped films. While it increases to 78.5% when the films annealed at 573K.

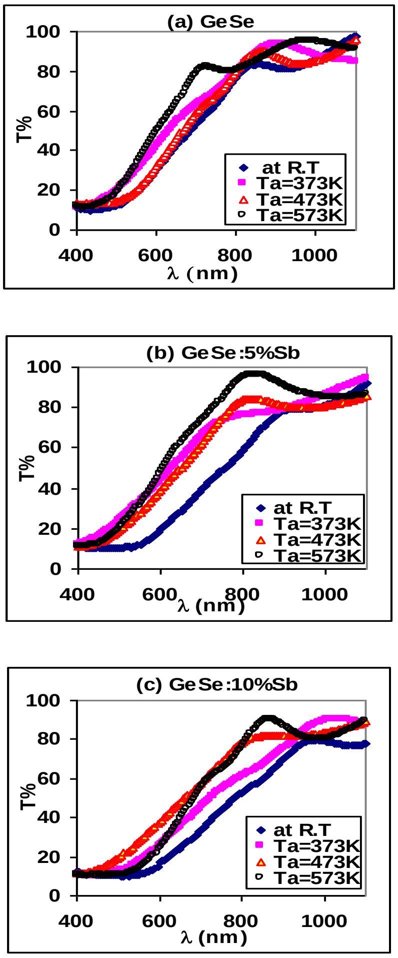


Fig. 3 Transmittance vs. wavelength at different annealing temperatures for(a) GeSe films (b) GeSe:5%Sb (c) GeSe:10% Sb.

The values of the absorption coefficient were calculated for all the samples by using eq.(2) over the investigated range of the incident photon energy 1.12 to 4.13 eV.

The relation between α and hυ was described for the investigated films (see figure (4)). A blue shift in the absorption edge towards higher band gap is noticed to undoped and Sb doped GeSe films with increasing the annealing temperature. This suggests the increase in optical band gap energy. contrast notice was observed by Abu-Sehly (A.Abu-Sehly, 2000) who studied the effect of annealing temperature on the optical properties of GeSeSb films and he found that the optical energy gap decrease with increasing annealing temperature.

The same figure suggests that the absorption coefficient of as deposited GeSe and doped films with Sb exhibits no long band tail at the long wavelength region of the incident photon energy range. The tailing of the band states into the gap width may be induced from a small concentration of free carriers resulting from screened coulomb interaction between carriers that perturbs the band edges, where there is no absorption tail exhibited in this figures. In the region of the photon energy, that has values greater than those of the exponential edge region do, the absorption coefficient linearly increases with increasing the incident photon energy (high absorption region) (J.Choi *et al*, 1996).

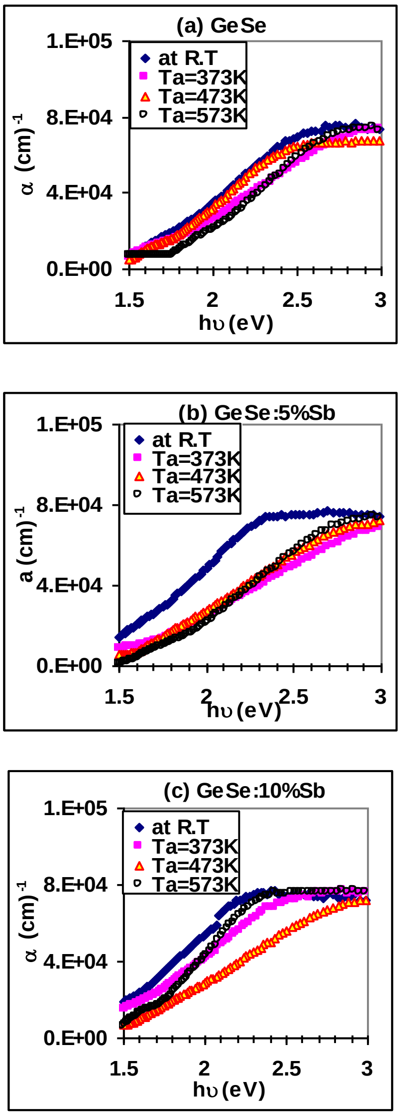


Fig.4 The relation between absorption coefficient and wavelength at different annealing temperatures for(a) GeSe films (b) GeSe:5%Sb (c) GeSe:10% Sb

The band gap can be obtained from extrapolation of the straight-line portion of the $(\alpha h\nu)^{1/r}$vshv plot to hv = 0. It is observed that for all the films, the best straight line is obtained for r equal to 1/2 , 2 which is expected for direct and indirect allowed transition.

The optical energy gaps of GeSe, GeSe:5%Sb, GeSe:10%Sb thin films have calculated from the absorption and transmission measurements, we deduced that there are two kind of optical types transition allowed direct and indirect typesas shown in figures (5) and (6) respectively.

All the undopedGeSe and doped films with various values of Sb ratio show the same behavior, that the optical energy gaps decreases with the increasing of the value of Sb for all annealing temperature, this means that the increase of Sb leads to an increase in the density of localized states in the band tail and consequently reduced the band gap(J.Choi *et al*, 1996), Another explanation for the reduction of E_g value could be the generation of charged defects in the band-tail regions, which leads to narrowing of the band gap (N.Mehta *et al*, 2004).

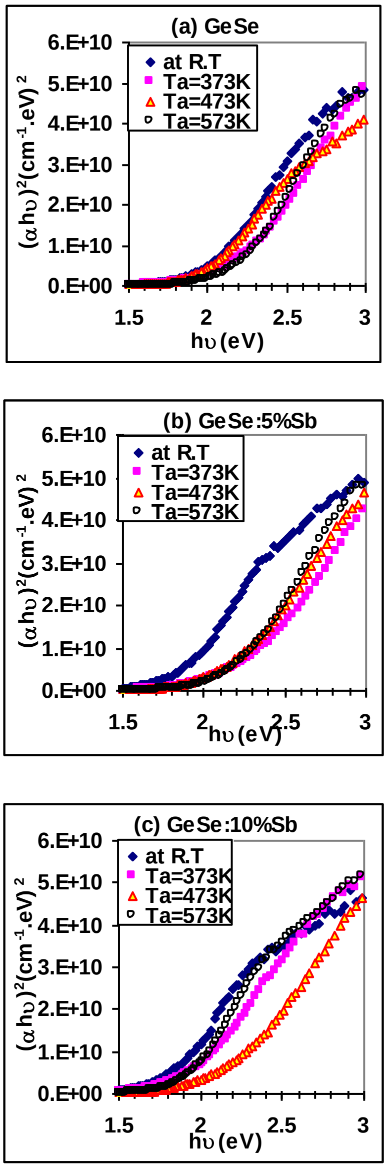


Fig.5 $(\alpha h\upsilon)^2$ vs. $(h\upsilon)$ plots at different annealing temperatures for(a) GeSe films (b) GeSe:5%Sb (c) GeSe:10% Sb.

Table 1 The direct and indirect optical energy gap values for undoped and doped GeSe thin films annealed at different annealing temperature

	direct optical energy gap (eV)			indirect optical energy gap (eV)		
Ta (K)	GeSe	GeSe:5%Sb	GeSe:10%Sb	GeSe	GeSe:5%Sb	GeSe:10%Sb
303	1.95	1.85	1.8	1.7	1.63	1.5
373	2.0	2.18	1.9	1.8	1.69	1.6
473	2.2	2.2	1.92	1.82	1.7	1.62
573	2.25	2.22	2.0	1.88	1.82	1.73

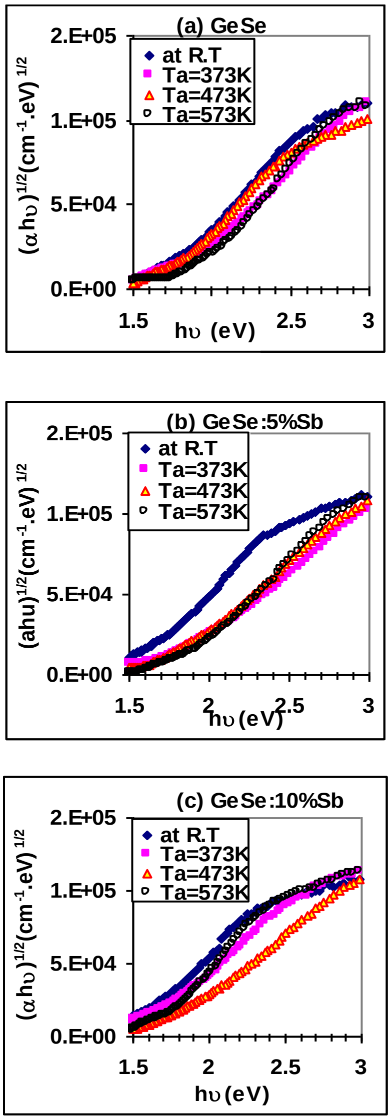


Fig. 6$(\alpha h\upsilon)^{1/2}$ vs. (hυ) plots at different annealing temperatures for(a) GeSe films (b) GeSe:5%Sb (c) GeSe:10% Sb.

For undopedGeSe and doped with variation of Sb ratio (5% and 10%) thin films, the samples have the same behavior with the heat treatment that, the optical energy gaps increases with the increasing the annealing temperature, due to, decrease the density of states, this decrease was attributed to the conversion of some bipolaron states (D^+, D^-) into single-polaron state(D^o) according to the relation $[D^+]+[D^-]\rightarrow 2[D^o]$ (N.Mehta *et al*, 2004).

The general features of the density of states of amorphous solids can be understood from the model proposed by Mott and Davis. During thermal annealing at temperatures below the glass transition temperature *T*g, the unsaturated defects are gradually annealed out producing a larger 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 (K.Shimakawa *et al*, 1993).The direct energy gap larger than indirect due to transition from band to band in the first one.

One of the most important optical constants of a material is its refractive index, which in general depends on the wavelength of the electromagnetic wave.

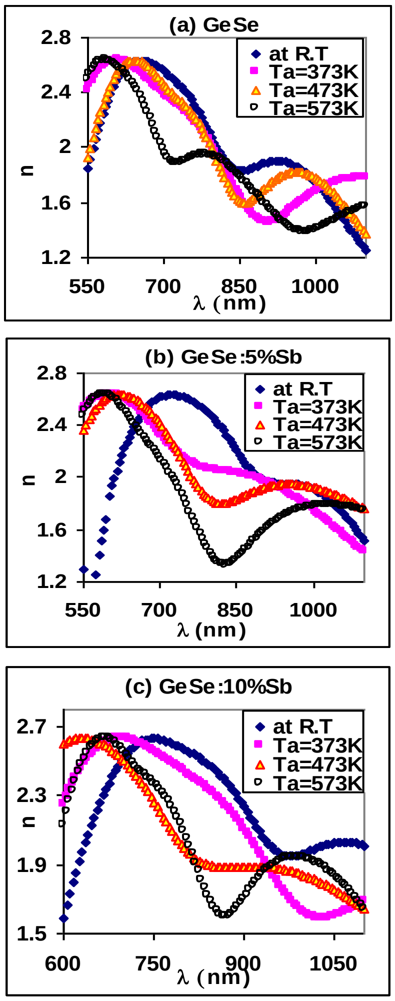


Fig.7 The refractive index vs. the wavelength at different annealing temperatures for(a) GeSe films (b) GeSe:5%Sb (c) GeSe:10% Sb.

Figures (7 a, b, and c) show the variation of refractive index of as deposited pure and doped GeSe films and annealed at different annealing temperature with the wavelength . It is interesting to see that the refractive index decreases when the annealing temperature increases and increases when the Sb ratio increases. This behavior is due to the inverse relation between the refractive index (n) of a semiconductor and the energy band gap (E_g) as mentioned by Moss who suggested that n and E_g related by n^4E_g= constant (constant is about 100eV) (J.Singh, 2006).

The behavior of extinction coefficient (k) is nearly similar to the corresponding absorption coefficient as shown in figures (8 a, b, and c).It is obvious from these figures that k in general decrease with increasing the annealing temperature and increases when the films doping with Sb as illustrated in table (2).

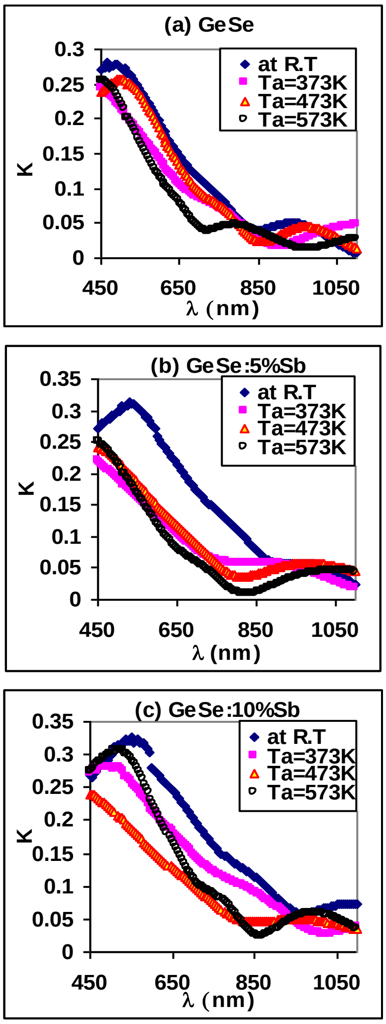


Fig.8 The extinction coefficient vs. the wavelength at different annealing temperatures for(a) GeSe films (b) GeSe:5%Sb (c) GeSe:10% Sb.

The complex dielectric constant is a fundamental material property, the real part of it is associated with term of how much it will slow down the speed of light in the material and the imaginary part gives that how a dielectric absorb energy from electric field due to dipole motion.

The variation of real (ε_1) and imaginary (ε_2) dielectric constants with different annealing temperatures are shown in figures (9) and (10). The behavior of ε_1 is similar to refractive index because the smaller value of k^2 comparison of n^2, while ε_2 is mainly depends on the k values, which are related to the variation of absorption coefficient. In general the dielectric constants decrease with T_a , while they increase with increasing Sb dopant.

The dielectric constant ε_1 increase with increasing of Sb content since the dielectric constant provides an insight into the nature of bonding in the system, also the increase in Sb causes the system to become more flexible, i.e. the number of the weak bonds increased (Sb-Sb) bonds, which are more responsive to the electric field than the stronger bonds(Ge-Ge) (N.Mehta *et al*, 2004).

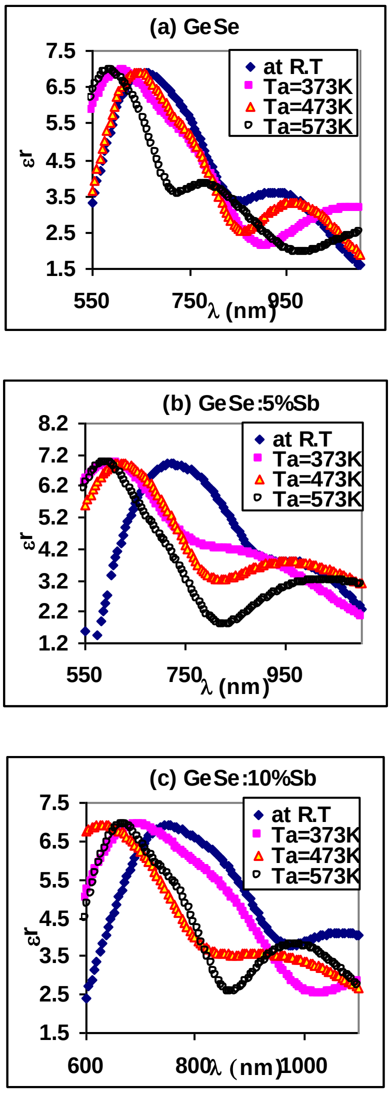


Fig.9ϵ_r vs. the wavelength at different annealing temperatures for(a) GeSe films (b) GeSe:5%Sb (c) GeSe:10% Sb.

The optical properties parameters including , absorption coefficient, refractive index, extinction coefficient , real and imaginary part of the dielectric constant at wavelength equals to 750 nm for GeSe and GeSe:Sb thin films treated at different annealing temperature are listed in table (2).

Table 2 The optical parameters for GeSe and GeSe:Sb thin films at different annealing temperature (λ =750 nm)

GeSe					
T_a(K)	**α ×10^4(cm^{-1})**	**n**	**k**	**ε_r**	**ε_i**
303	1.49	2.373	0.089	5.627	0.422
373	1.22	2.242	0.072	5.024	0.325
473	1.28	2.273	0.076	5.162	0.346
573	0.701	1.912	0.041	3.654	0.16
GeSe: 5%Sb					
303	2.38	2.61	0.141	6.794	0.74
373	1.05	2.145	0.062	4.6	0.267
473	0.949	2.083	0.056	4.339	0.235
573	0.593	1.826	0.035	3.335	0.129
GeSe: 10%Sb					
303	2.74	2.631	0.163	6.898	0.861
373	2.07	2.558	0.123	6.529	0.63
473	1.26	2.263	0.074	5.117	0.339
573	1.49	2.373	0.089	5.627	0.422

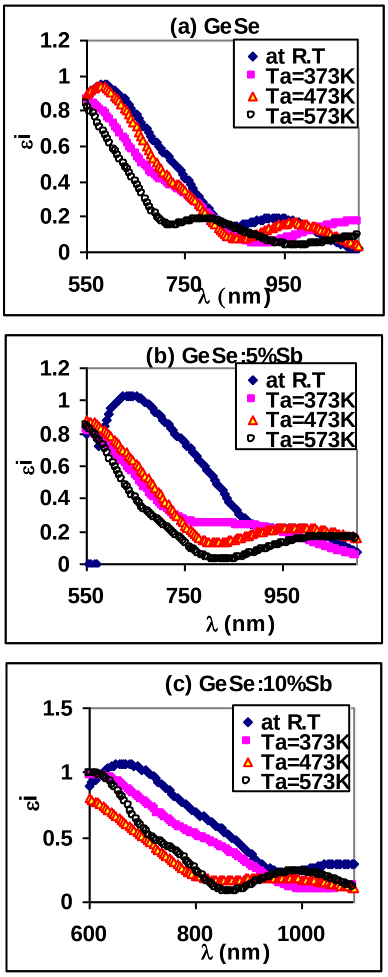


Fig.10ϵ_i vs. the wavelength at different annealing temperatures for(a) GeSe films (b) GeSe:5%Sb (c) GeSe:10% Sb.

Conclusions

The effect of post deposition annealing treatment and the Sb dopant ratio on the structural and optical properties of thin GeSe films deposited by thermal flash evaporation technique were studied. All samples have one broad diffusion band except the undopedGeSe films which annealed at 573 K has sharp peak, this means the structure transform to crystalline structure at this degree.

The optical transition calculations show that the films have direct and indirect allowed optical energy gap , where the optical band edge shift towards lower energies when Sb ratio increase and to higher energies when the films annealed at different annealing temperature for the mention range. The refractive index and the extinction coefficient increase with the increasing the Sb dopant ratio and decrease when the films annealed at different annealing temperature .

References

Alias, M.F., Makadsi ,M.N. and Al-Ajeli , Z.M. (2003), The influence of Ge content and annealing temperature on the d.c and a.c conductivity of Ge_xSe_{1-x} thin films , Turk J.phys, 27, pp 133-143.

Lezal,D. , Pedlikova, J. and Zavadil, J. (2004), Chalcogenide glasses for optical and photon application, Chalogenide Letters, 1(1), pp 11-15.

Orava,J. , Kohoutek, T. , Wagner, T. , Cerna,Z., Benes, L. , Frumarova, B. and Frumar, M. (2009), Optical and structural properties of Ge-Se bulk glasses and Ag-Ge-Se thin films , J. of non-crystalline solids, 355, pp1954-1954.

Balan ,V. , Vigreux, C. ,and Pradel,A. (2004), Chalcogenide thin films deposited by radio-frequency sputtering, J. of optoelectronics and Advance Material , 6(3), pp 875-882.

Alnjjar, A.A. (2009), The role of thermal treatment on the optical properties of $Ge_{0.15}Se_{0.85}$ system, J.Renewable energy, 34, pp 71-74.

Pan, R.K. , Tao, H.Z., Zang, H.C. and Zhang,, X.J. (2009), Annealing effect on the structure and optical properties of GeSe2 and GeSe4 films prepared by PLD , J.of alloys and compounds, 484, pp 645-648.

Hafiz ,M.M., Othman, A.A., El-Nahass, M.M.-,and Al-Motasem-A.T. (2007), Composition and thermal-induced effects on the optical constants of $Ge_{20}Se_{80-x}Bi_x$ thin films , Physica B: Physics of Condensed Matter, 390, pp 348-355.

Lee ,H. Y., Wookim, J., Chumg, H. B. (2003), Evaluation for photo-induced changes of photoluminescence and optical energy in amorphous $Se_{100-x}Ge_x$ (x=5,25 and33) thin films , J.of Non-Crystalline Solids, 315, pp 288-296.

Thakur,A., Singh, G., Saini, G.S.S., Goyal, N. ,and Tripathi, S.K.(2007), Optical properties of amorphous $Ge_{20}Se_{80}$ and $Ag_6(Ge_{0.20}Se_{0.80})_{94}$ thin films, Optical Materials, 30, pp 565-570.

Bard, A.M., Wahaab, F.A. and Ashraf, I.M. (2009), Influence of temperature on charge transports and optical parameters for the $Ge_{15}Sb_5Se_{80}$ amorphous thin films, International J. of Physical Sciences, 4(5), pp 313-320.

Choi, J., Singh, A. , Davis, E.A. and Gurman ,S.J. (1996), Optical properties and structure of unhydrogenated hydrogenated and zinc-alloyed a-Ge_xSe_{1-x} films prepared by radio-frequency sputtering, J.of Non-Crystalline Solid, 198-200, pp 680-683.

Fouad ,S.S., Fadel, M., Abd.El-Wahabb, E. (2008), A detailed comparison between the hopping conductivity and theoretical data of the Ge_xSe_{100-x} glassy system, J.of Ovonic Research, 4(3), pp51-60.

Atyia ,H.E., Farid ,A.M. ,and Hegab, N.A. (2008), AC conductivity and dielectric properties of amorphous $Ge_xSb_{40-x}Se_{60}$ thin films, Physica B, 403, pp3980-3984.

Mehta ,N., Zulfequar, M., and Kumar A. (2004), Crystallization kinetics of some Se-Te-Ag chalcogenide glasses , J .Optoelectron Adv. Mater, 6, pp441-448.

Badaoui ,A. ,and Belhadji, M. (2013), Thermal stability and Tg characteristics of GeTeSb glasses, Physical Review &Research International, 3 (4), pp 416-424.

Kazmerski , L. (1980), Polycrystalline and Amorphous Thin Films and Device , Academic Press.

Qasrawi, A. F. (2005), Refractive index, band gap and oscillator parameters of amorphous GaSe thin film, Cryst. Res. Technol., 40, pp 610-614.

Moss ,T.S. (1959) Optical Properties of Semiconductors .

Abu-Sehly ,A. A. (2000), Optical constants and electrical conductivity of $Ge_{20}Se_{60}Sb_{20}$ thin films , Journal of Materials Science, 35, pp 2009- 2013.

Shimakawa, K., Kondo, A., Hayashi, K., Akahori, S., Kato, T., Elliot, S.R. (1993), Photoinduced metastable defects in amorphous semiconductors: communality between hydrogenated amorphous silicon and chalcogenides , J. Non-Cryst. Solids, 387, pp 164–166.

Singh ,J. (2006), Optical properties of condensed matter and application, John Witey and sons , Australia.