Structural Properties of Ge$_x$Se$_{1-x}$ Thin Films Prepared by Semi-closed Space Technique

N.A. Bakr, M.S. Aziz* and M. Hammam**

Department of Physics, Faculty of Science, Mansoura University, Mansoura, Egypt
*Department of Physics, Faculty of Science, Mansoura University, Damietta, Egypt
** Department of Physics, Faculty of Science, Helwan University, Ain Helwan, Egypt

Bulk and thin film Ge$_x$Se$_{1-x}$ alloys have been prepared with $0.1 \leq X \leq 0.5$. The bulk materials were obtained by quenching from the melt. They have been used as source materials to produce thin film samples using the thermal evaporation method (semi-closed space technique). The composition of the obtained films was checked against the bulk ones by X-ray fluorescence (XRF) technique. X-ray diffraction patterns of the obtained compositions revealed the presence of some crystalline inclusions in the amorphous matrix for some compositions. Glass transition temperature measurements showed a maximum in the range $X=0.25$ to 0.32 where the glass forming ability is optimum. Measurements of the temperature dependence of the steady state dark current as a function of the Ge content has been recorded during heating and cooling cycles. A compensation effect has been found and characterized with two compensation temperatures, during the cooling cycle. Optical transmission, (UV) and infrared (IR), measurements have been performed. Energy band gap, width of the band tail and the refractive index have been calculated. Results have been interpreted in terms of the structural behavior of the samples under investigation in view of the models presented in literatures.

Introduction

Development of modern technology led to the appearance of new family of materials. Chalcogenide glass semiconductors are one of these families due to their interesting properties.

Selenium is considered to be one of the most important semiconductors due to its unusual crystal structure [1,2]. Amorphous semiconductors from Se-based systems such as Ge_xSe_{1-x} have attracted much attention in recent years. This family of chalcogenide glasses can provide an ideal system for investigation. The chemical composition and/or energy band structure changes as a result of introducing the Ge atoms into the Se matrix.

The melts of many IV-VI substances can be cooled to the glass state sufficiently rapidly to bypass crystallization. Recently it has been suggested that chalcogenide alloyed glasses may consist primarily of partially polymerized clusters, many of which resemble crystalline fragments [3].

The variation of the Ge_xSe_{1-x} structure is reflected in different properties such as the glass forming regions, glass transition temperature, photoluminescence, IR and Raman spectra and the optical properties [4-9]. Changing the physical properties of these materials at a specific composition reflects the most interesting information.

The glass transition has been treated by various theoretical approaches. It is suggested that this property is a first, second or even third-order transition [10]. Some authors have claimed that there is no true phase transition at all [11]. $Ge_x Se_{1-x}$ glasses in the range of $0.39<X<0.4$ are found to be the most chemically ordered, where they consist of both $GeSe_{4/2}$ and $Ge_2Se_{6/2}$ units. The structure of glass forming compound Ge_2Se_3 can be understood as three-dimensionally connected network of $Ge_2Se_{6/2}$ units which are constitutionally disordered forming charge defect centers [6]. According to Phillips et al. [12], the glass forming difficulty with X undergoes a minimum at $x{\approx}0.25$. Also, a maximum glass transition temperature has been observed at the stoichiometric composition, at $x=0.33$ [3,6,9,13] and 0.2 [7].

Optical properties of IV-VI compounds have been studied in various publications [5-9,14-16]. The optical band gap and the localized states width are found to depend on the composition. Unlimited data have been reported on the electrical conductivity and refractive index depending on the Ge content in the Ge_xSe_{1-x} alloy prepared by different techniques.

Still the properties of the prepared materials are highly dependent on the preparation conditions, leading to difference in the values of the parameter connected with electrical properties, optical properties, glass transition temperature, crystallization….etc.

Here, we investigate the effect of introducing Ge into Ge-Se systems on some thermal, electrical and optical properties of the compounds prepared by semi-close space technique [17,18]. This method has been applied to deposit films of various semiconducting materials. The main advantages of this technique are: its simplicity, its ability to keep the system pure, and that the chemical transport conditions are controllable to high extent.

Experimental

Bulk samples of the Ge_xSe_{1-x} with $0.1 \leq X \leq 0.5$, have been prepared by the conventional melt technique. Elements of the Ge and Se with purity 5N were mixed in sealed silica ampoules, slowly heated to 900°C, then the temperature was raised to 1000°C for 8 hours. Quenching was done in water at a cooling rate of about 100 K/min.

Thin film samples were deposited by the thermal evaporation (semi-closed space technique) of crushed bulk materials. The deposition was carried out under vacuum of about 10^{-5} torr by using Edward 360-A coating unit. The substrates used were corning 7059 glass slides. The distance between the crucible containing the crushed Ge-Se and the glass substrate was about 10 cm, so the temperature of the substrate could be increased slightly during the deposition. All the deposition parameters such as evaporation source temperature ($\approx$500°C) deposition time (~5 min), pressure and substrate-source distance (~10 cm) were kept constant, so that a comparison of results for different preparations could be made under the same conditions.

X-ray fluorescence XRF(ORTEC) measurements were carried out on both the bulk and thin film samples. The results confirmed the reproduction of the stoichiometry of the starting materials in the resulting films. On the other hand X-ray diffraction technique has been used to examine the amorphous and/or the crystalline state of the evaporated Ge_xSe_{1-x} films. Infrared studies for $Ge_x Se_{1-x}$ films were carried out using MATTSON 5000 FTIR spectrometer. The glass transition temperature (T_g) of the quenched ingots was determined by using the differential thermal analysis (DTA).

For electrical measurements, a co-planar geometry was used. The samples have been provided with indium electrodes because it is not easily

oxidized as Au and Al which may cause a thin insulating layer between the metal electrodes and the chalcogenide glass film [19]. Electrodes were evaporated on the Ge-Se films providing the gap. The active area of the sample was typically 1.0 x 10.0 mm^2. Two fine copper wires were attached to the electrodes by means of silver paste providing a good mechanical and electrical joint. DC conductivity measurements were performed at 100 V using a Keithely electrometer 485. To calculate the optical constants of the films, the spectral distribution of the absorbance were recorded at room temperature in the range 200-900 nm, using a Unicam UV2-100 spectrometer.

Results And Discussion

The X-ray diffraction patterns of Ge_xSe_{1-x} films with $0.1 \leq X \leq 0.5$, taken at room temperature, are illustrated in Fig. (1). The absence of any structure in the patterns of the evaporated films in the range $X=0.2$ to 0.32, confirm the amorphous nature of the evaporated material. At $X=0.1$ and 0.4, the patterns of the samples are characterized by the appearance of a week line at $2\theta=45°$, and for $X=0.5$, a defined crystalline diffraction lines appears in the range $2\theta=18°-60°$. This would be considered as an evidence for the formation of a partially crystalline phase in the material with these compositions.

Figure 2 shows the dependence of Tg(K) on the Ge atom content in Ge_xSe_{1-x} films. Adding of Ge atoms, in Se-rich region for $X \leq 0.2$, leads to a slow reduction of

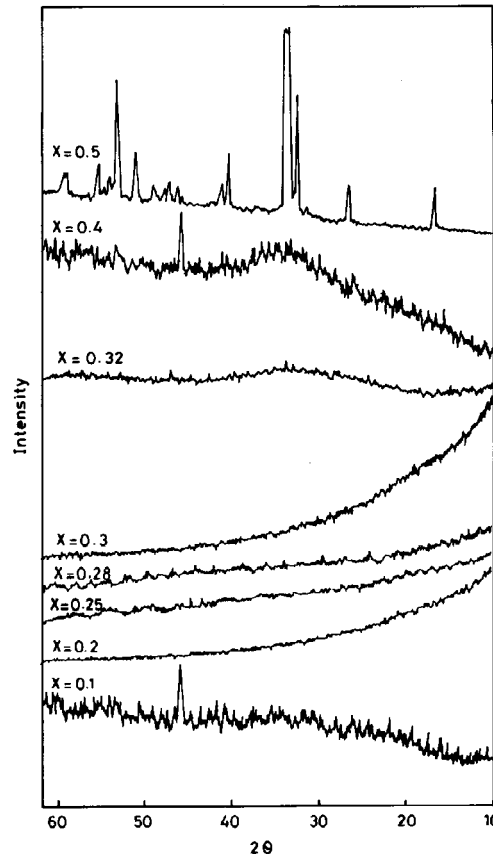**Fig. (1) :** X-ray diffraction pattern of as deposited Ge_xSe_{1-x} thin film $(0.1 \leq X \leq 0.5)$.

the glass transition temperature. This can be due to the increasing in the number of non-bridging Se atoms, which intern lead to weakening the bond in the amorphous network.

As the Ge atom content increases, 0.2<X<0.4, the glass transition temperature passes through a maximum, at X≈0.28, where each atom exhibits its normal valence and the glass forming ability is optimum. Tg values

Fig. (2) : Glass transition temperature as a function of Ge concentration in Ge_xSe_{1-x} alloys.

for X≤0.2 are in reasonable agreement with the values reported by other workers [20-22]. In the region X>0.2, Tg has a lower value than that reported before, which may be due to the difference in the preparation conditions. For higher Ge atom content, X>0.4 a remarkable increase in the glass transition temperature was observed, which can be attributed to the increase in the partially crystalline phase which leads to the possibility of increase the network structure.

The temperature dependence of the steady-state dark current (during heating cycle) as a function of Ge content in the prepared $Ge_x Se_{1-x}$ films is shown in Fig. 3a. It is observed that, as the Ge concentration increases, there is a change over from a metallic like behavior to a semiconducting type one due to the incorporation of Ge in the Se chain. On the other hand, Fig. 3b shows the temperature dependence of the steady-state dark current (during cooling cycles) as a
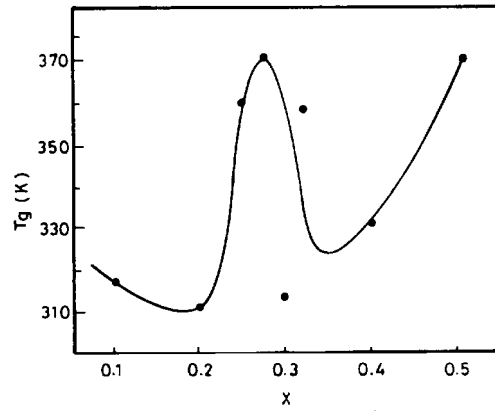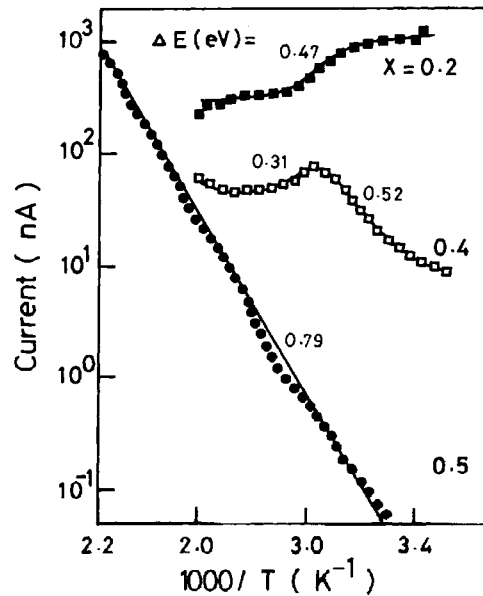

Fig. (3) : Temperature dependence of the steady state dark current of Ge_xSe_{1-x} during (a)- heating (b)- cooling cycles.

function of Ge content. The behavior is clearly thermally activated one, with single activation energy and can be described by the Arrehnius relation [1]:
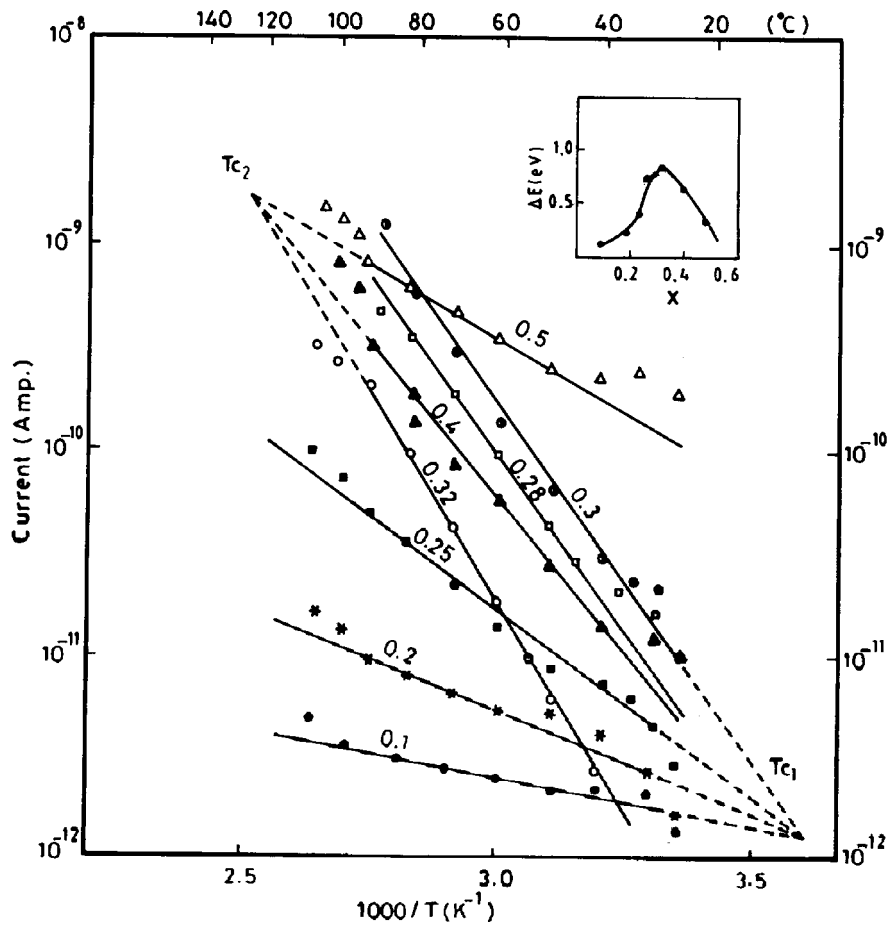

Fig. (3) : Temperature dependence of the steady state dark current of Ge_xSe_{1-x} during (a)- heating (b)- cooling cycles.

$$I = I_o \exp[-\Delta E/kT] \qquad (1)$$

where I_o is the pre-exponential factor, k-is the Boltzmann constant and ΔE- is the activation energy of the dark current. The activation energy ΔE for different compositions, calculated from the slopes of the curves in Fig. 3b, are illustrated in inlet of the figure. A maximum value of ΔE has been obtained at $X \approx 0.28$-3.2 which is in accord with that reported Shimizu [23] and in contrast with that reported by Adriaenssens [24] where a tendency towards higher activation energy with increasing Ge content is observed. As the conduction process is

characterized by a single thermally activated process, then the electric conduction is dominated by p-type electrical conduction [25] with one type of carriers which is due to holes [26]. Therefore ΔE can be taken as a measure of the location of the Fermi-level in the gap relative to the valence band edge.

On the other hand, it is clear form Fig. 3b that the relation between lnI vs 1/T passes through two common points. These are located at 400 K and 285 K. These points represent the compensation law for the samples under investigation. They depend on the Ge atom concentration on both sides of the stoichiometric composition of the Ge_xSe_{1-x} films. This compensation phenomenon is found to exist in any system contains elements moving within different energy barriers [27].

Further investigation have been done by measuring the IR transmission spectra of Ge_xSe_{1-x} as a function of composition. A defined band at 260 cm^{-1} has been detected. This band results from bond rearrangement with the formation of heteropolar Ge-Se bond [9]. The intensity of this band as a function of Ge content is illustrated in Fig. 4, with a maximum value at $X \approx 0.28$, where the number of Ge-Se bonds are maximized. This behavior provides an evidence for the mon-opolar Se-Se and Ge-Ge bonds

Fig. (4) : IR peak intensity at 260 cm^{-1} versus Ge content (x).

below and above the stoichiometric composition. Therefore, the two compensated temperatures Tc_1 and Tc_2 (obtained in Fig. 3) can be attributed to the formation of both Se-Se (in rich Se-region) and Ge-Ge (in rich Ge-region) bonds. Consequently, it is very important to reveal a correlation between the glass transition temperature and the compensation temperature. More study is needed for a complete discussion to understood the physical origin of that compensation phenomenon.

The effect of changing the germanium content in Ge_xSe_{1-x} films on its optical properties, has been discussed. The optical band gap (E_g), the width of the localized tail states (Urbach's tail) (E_u) and the width of the refractive index (n) can be calculated by measuring the optical absorption coefficient (α), using the equation [28,29]:
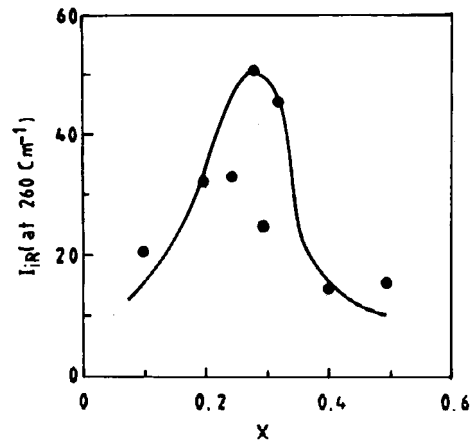
$$\alpha = 2.303/d \log (T_o/T) = 2.303 \ A/d \qquad (2)$$

where T_o and T are the intensity of the incident and transmitted light respectively, A-is the absorbance and d-is the film thickness. The optical absorption measurements of Ge_xSe_{1-x} films, for different compositions have been performed and analyzed to give a qualitative descriptions of the structural dependence near the band edge. A linear relation between $(\alpha h\nu)^{1/2}$ and the photon energy $(h\nu)$, is presented for different compositions as shown in Fig. 5, which indicates that the indirect band gap transitions are predominant [30]. The optical band gap (E_g) can be calculated from the extrapolation of the linear portions of the lines Fig. 5 to $(\alpha h\nu)^{1/2} = 0$ according to the relation [28-30]:

$$(\alpha h\nu)^{1/2} = B(E_g - h\nu) \qquad (3)$$

where B-, Tauc constant [15], is determined from the slope of the linear parts in Fig. 5. This constant represents the degree of randomness of the structure of the amorphous solids [28] and reflects the density of states deeper in the band [15]. It depends on the transition probability and the refractive index [28]. The obtained values of the constant B, as reported in Table (1) reaches its highest value in the range $0.10 < X < 0.28$. These values are in good agreement with those reported by Shirafuji [5]. In contrast, for a comparison with other authors, the variation of Tauc constant with the composition of Ge_xSe_{1-x} almost decreases linearly [15,31] and is independent of the chemical composition of the chalcogenide semiconductor films [32].
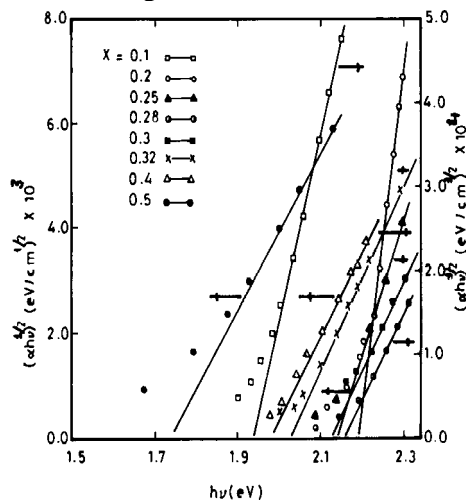

Fig. (5) : Plot of $(\alpha h\nu)^{1/2}$ versus incident photon energy $(h\nu)$ for different composition X.
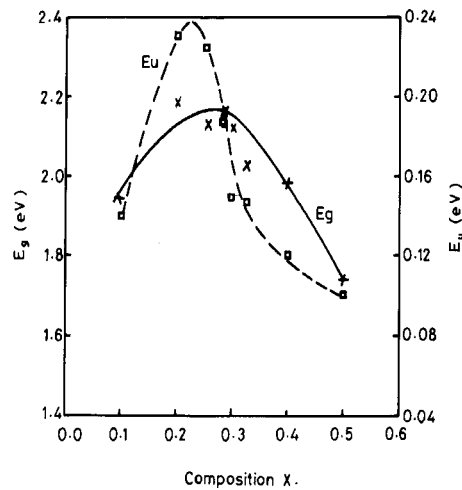
Fig. (6) : The optical band gap E_g and the band tail width E_u versus the Ge content in the Ge_xSe_{1-x} alloys

Figure 6 shows that the observed change in the optical band gap (E_g) as a function of the composition, exhibits a maximum near the value of X=0.28. This behavior was found to be in good agreement with these published in literatures [3,8,15], and corresponding to the stiochiometric composition. The width of the band tail [E_u] can be calculated from the Urbach's rule [33] (as the inverse of the slope of the linear part of the relation ln α versus hν).

Table (1)
Tauc constant of Ge_xSe_{1-x} at various germanium content X.

X	$B(cm^{-1}.eV^{-1})^{1/2}x10^4$
0.10	5.00
0.20	7.07
0.25	3.90
0.28	3.16
0.30	1.30
0.32	1.40
0.40	1.26
0.50	1.24

The relationship, as shown in Fig. 6 has a maximum value near the composition range X=0.20 to 0.25 and confirms the dependence of (E_u) on the Ge atom concentration. This result was found to be confirmed with that proposed by Zanin et al. [34], that the Urbach`s tail often arises from the electronic transitions between localized states where the density of these localized states is energy dependent. Davis and Mott [35] reported that this dependence is not valid for all disordered materials. As indicated from the above results, maximum values of the optical parameters (E_g) and (E_u) have been obtained near the stoichiometric compositions corresponding to 0.2 <X< 0.32. In this state, the Ge-Se system can be regarded as a mixture of different molecular species of both $GeSe_4$ and $GeSe_2$.

Chalcogenide glasses also have the ability to change their refractive index under the action of the band gap light. This is considered to be one of the most important properties for holographic optical components and devices [16]. In the spectral region of medium and weak absorption, only films with composition X=0.1, 0.2 and 0.3 exhibit remarkable interference effects that give rise to oscillation in the absorbance curve. Such interference fringes will allow the determination of the refractive index [32,36-40]. For other compositions, all the interference effects were destroyed and the spectrum showed a nearly smooth curve. The refractive index (n) of the samples with compositions at X=0.1, 0.2 and 0.3 can be calculated using the expression:

$$n = [N + (N^2 - S^2)^{1/2}]^{1/2}$$

where

$$N = 2S(T_M - T_m/T_M \cdot T_m) + (S^2 + 1/2)$$

T_M and T_m are the maximum and the corresponding minimum of the transition spectrum at constant wavelength. In this technique, the thickness of the substrate material should be several orders of magnitude thicker than the film thickness. A free interference transmission T_s has been obtained for the substrate alone and its refractive index S has been calculated using the relation [32,36,37]:

$$S = 1/T_s + (1/T_s^2 - 1)^{1/2}$$

Figure 7 illustrates the dispersion curve of the refractive index with wavelength (λ), from 600 to 800 nm, for different compositions of Ge_xSe_{1-x}. It is observed that, the refractive index has the normal dispersion, according to Cauchy formula [41,42], and is in good agreement with that obtained in literature [43]. So it can be stated that the change in the refractive index may be attributed to the transparency of the films which are related to the film compositions.
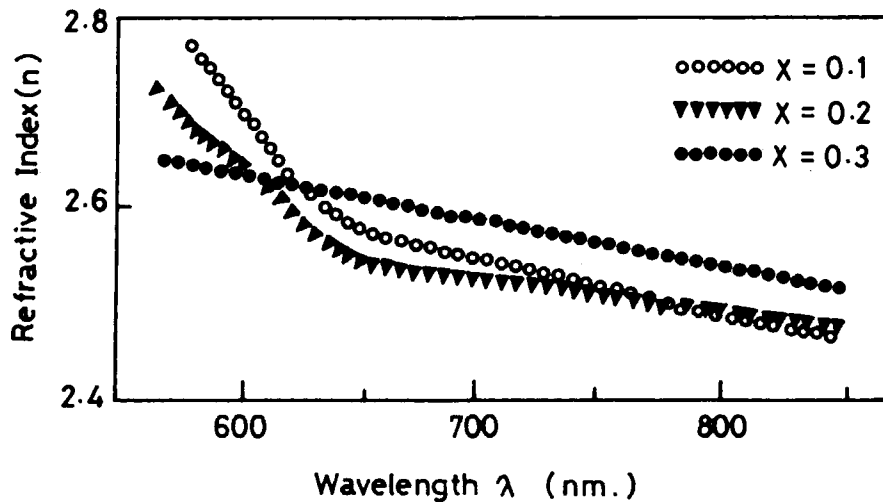

Fig. (7) : Refractive index (n) of the Ge_xSe_{1-x} alloys as a function of photon energy, at room temperature.

Conclusions

Addition of Ge atoms into Se-system matrix, to form a thin film of Ge_x-Se_{1-x} (0.1≤X≤0.5), prepared by semi-closed space technique, leads to a pronounced structural changes. X-ray and DTA measurements confirm the

stoichiometric composition at x≈0.28 characterized by the amorphous state and maximum glass transition temperature.

The temperature dependence of the steady state dark current, during the cooling cycle, reveal the appearance of the compensation law. Depending on the Ge concentration, two compensation temperatures are observed comparable to the glass transition temperature for both Se- and Ge-rich regions.

Data obtained from transmission measurements have been used to calculate the optical absorption coefficients and the refractive index. An indirect band gap transition was found to be dominant for different alloy compositions. The estimated band gap energy as a function of Ge content was found to exhibit a maximum at the composition X= 0.28, while the band tail width shows its highest value at 0.2 <X< 0.32. In addition the transparency and the refractive index of the films have been found to be strongly dependent on the film composition. These results have been attributed to the formation of some complex structures in the compounds.

Ge_xSe_{1-x} (0.1≤X≤0.5) Samples prepared by semi-closed space show a remarkable difference in electrical properties when compared with those prepared by other techniques. This difference can be arising from the change in the Fermi-level position and the appearance of the compensation law depending on the Ge content. On the other hand, no significant difference in the behavior of both thermal and optical properties was observed.

Acknowledgements

References

1. K.V.Reddy and A.K.Bhatnagat, J. Phys. D: Appl. Phys. 25, 1810, (1992).
2. J. Callaway, "Electron Energy Bands in Solids", p.103, (1958).
3. J.E. Griffiths, G.P.Espinosa,J.P.Remeika and J.C.Phillips, Solid State Communications, 40, 1077 (1981).
4. Y. Wada, Y. Wang, O. Matsuda, K. Inoue and K. Murase, J. Non-Cryst. Solids, 198-200, 732 (1996).
5. J. Shirafuji, Gi Il Kim and Y. Inuishi, Japanese Journal of Applied Physics 16(1), 67 (1977).
6. A. Feltz, H. Aust and A. Blayer, J. Non-Cryst. Solids 55, 179 (1983).

7. S. Asokan, G. Parthasarathy and E.S.R. Gopal, Phil. Mag. B. 57(1), 49 (1988).
8. K. Shimakawa, J. Non-Cryst. Solids, 43, 229 (1981).
9. E. Sleeckx, L. Tichy, P. Nagels and R. Callaerts, J. Non-Cryst. Solids 198-200, 723 (1996).
10. N.O. Birge and S.R. Nagel, Phy. Rev. Lett. 24(25), 2674 (1985).
11. S.P. Das, G.F. Mazenko, S. Ramaswamy and J.J. Toner, Phys. Rev. Lett. 54, 118 (1985).
12. J.C. Phillips, J. Non-Cryst. Solids 35 & 36, 1157 (1980).
13. P. Tronc, M. Bensoussan, A. Brenoc and C. Sebenne, Phys. Rev. B8, 5947, (1973).
14. K. Solomon, S. Rajagopalan, L.K. Molhotra, and K.L. Chopra, J. Appl. Phys. 54(2), 1048 (1985).
15. J. Choi, A. Singh, E.A. Davis and S.J. Gurman. J. Non-Cryst. Solids 198-200, 680 (1996).
16. A. Zekak, P.J.S. Ewen, C.W. Slinger and A.E. Owen, J. Non-Cryst. Solids 202, 122 (1996).
17. N.A. Bakr and F.M. Feodrov, J. Cryst. Growth 142, 298 (1994).
18. A. Yoshikawa and Y. Sakai, J. Appl. Phys. 15, 3521 (1974).
19. A.M. Wallace, A.E. Owen and J.M. Robertson. Phil. Mag. B, 38(1), 57 (1978).
20. A. Feltz and F.J. Lippmann, Z. Anorg. Ally. Chem. 298, 83 (1979).
21. R.Azoulay, H. Thibirge and A. Brenac, J. Non-Cryst. Solids 18, 33 (1973).
22. R.Ota, Y.Ymata, N.Soga and M.Kunugi, J.Non-Cryst. Solids 29, 67 (1978).
23. T.I. Shimizu, M.Kumeda and M. Ishikawa, J. Non-Cryst. Solids 33, 1 (1979).
24. G.J. Adriaenssens, A. Gheorghiu, C.Senemaud, N. Qamhia, N. Bolle, E. Sleeckx and P. Nagels, J. Non-Cryst. Solids 198-200, 675 (1996).
25. O. Matsuda et al. J. Non-Cryst. Solids 198, 68 (1996).
26. T.T. Nang, M.Okuda, T. Matsushita, S. Yokota and A. Suzuke,. Japan. J. Appl. Phys. 15, 849 (1976).
27. E. Peacock-Lopez and H. Suhl. Phys. Rev. B 26, 3774 (1982).
28. N.A. Bakr and M.I. Abdel-Hamid, J. Mat. Res. 10, 2653 (1995).
29. K.Sedeek, E.A.Mahmoud, F.S.Terra, A.Said and S.M. El-Din, J.Phys. D: Appl. Phys. 27, 156 (1994).
30. H.T.El-Shair and A.E. Bekheet. J. Phys. D: Appl. Phys. 25, 1122 (1992).
31. M.F. Kotkata, K.M. Kandil and M.L. Theye. J. Non-Cryst. Solids 164, 1259 (1993).
32. E. Marquez et al. J. Phys. D: Appl. Phys. 25, 535 (1992).
33. J. Tauc: Amorphous and Liquid Semiconductors, ed. J. Tauc (Plenum Press, New York 1974). Ch. 4.

34. M. Zanin and J. Tauc, J. Non-Cryst. Solids 23, 349 (1977).

35. E.A. Davis and N.F. Mott Phil. Mag. 22, 903 (1970).

36. R. Swanepoel, J. Phys. E: Sci. Instrum. 16, 1214 (1983).

37. R. Swanepoel, J. Phys. E: Sci. Instrum. 17, 896 (1984).

38. M. Hammam, Solid State Communications, 85, 401 (1993).

39. A.M. Goodman, Appl. Opt. 17, 2779 (1978).

40. T. Nakada, J. Appl. Phys. 46, 4857 (1975).

41. F.A. Jenkins and H.E. White "Fundamentals of Optics" (London: McGraw-Hill), 479 (1985).

42. S. Sakaguchi et al., J. Non-Cryst. Solids 196, 58 (1996).

43. S.S. Fouda, J. Phys. D: Appl. Phys. 1282 (1994).