The Optical properties of Bismuth - doped Germanium Selenide Semiconductor

S.K.J.Al-Ani*, M.N.Makadsi, S.S.Al-Rawi and N.Abbss
Department of Physics, College of Science, University of Baghdad, Baghdad – IRAQ.
*Present address: Faculty of Education – Seyoun Hadhramout University for Science and Technology, Yemen.

Abstract

The optical energy gap (E_g^{opt}) and energy band tailing (ΔE_t) for Ge33Se67_XBix (x=0, 5, 10, 15, 20) vacuum deposited amorphous thin films of about (300±5)nm thickness are studied in the photon energy range (hv = I to 5.4) eV.

The optical study showed that the optical energy gap decreases rapidly with increasing Bi concentration from (0-10)%, then it decreased slowly with increasing x. The width of tails of localized states at the band edges showed an increase with increasing Bi concentration.
Depending on these optical and related thermoelectric properties for these Films, a tentative energy band diagram is being suggested.

Key words: Vacuum deposition , Thin films , Germanium Selenium Bismuth , Optical energy gap , Energy band tailing , a tentative energy band diagram.

Introduction

It has been observed that vitreous germanium chalcogenides can be doped n-type with the addition of Bi in a large concentration (>7 at %) [[11, [3]. This insensitivity is ascribed to the presence of charged dangling bonds. An equal number of positively and negatively charged dangling bonds pin the Fermi level around the mid band gap slightly closer to the valence band. If the added impurity can alter the value of the charged dangling bonds considerably, the conductivity may be increased by many orders of magnitudes and conduction type reversal may even occur [5, 4]. Further, EXAFS study has recently been conducted [12] on Ge SBi glass with 6, 8, and 16 Bi (at %)

The optical absorption coefficient (α) for many amorphous and glassy materials in the high absorption region is found to obey the relation [7]

$\alpha h\nu = B(h\nu - E_g^{opt})^r$ ..... (1).

Where B is a constant, r is a number between 1 and 3 ,^{or} and (E_g^{opt}) is the optical energy gap of the material.

The width of the tails of localized states at the band edges (ΔE_t)can be estimated, using the Urbach relation [9]:

$\alpha(w) = a_o \exp(h\nu / \Delta E_t)$.....(2)

Where a_o is a constant, and ΔE_t is a measure of extent of the band tailing in the band gap of the material and determined from the reciprocal of the slope of $\ln\alpha$ against photon energy hv.

This paper will give results of a systematic study of the optical absorption edge of the $Ge_{33}Se_{67-x}Bi_x$. (x=0,5,10,15,20) amorphous thin films.

Experimental

The purity of the material are (99.999% pure). They were weighted in proportion to their atomic percentages, then sealed in an evacuated quartz tube to ~ 10^{-2} torr and kept in a furnace

whose temperature was raised to 950°C. The ampoules were rocked frequently for (8)h in order to ensure a homogeneous melt, then the melt is quenched in water.

Thin films of the alloys were prepared at room temperature by vacuum evaporation in a base pressure ~ 10 torr. The thicknesses of films were measured using crystal monitor and Tolansky method.

The glassy nature of the samples were investigated using X-ray diffraction (XRD). Absorbance measurement (A) in the wavelength range (λ=200-1100)nm was measured using UV/VIS recording spectrophotometer (UV-160 Schmatizu).

The optical band gap is calculated using equation (1) in the form (αhν)1/2 plotted versus the photon energy.

Results and discussions

The film samples were amorphous as revealed by X-ray diffraction technique. Figure(1) shows the plots of absorption coefficient (α) versus photon energy (hν) for $Ge_{33}Se_{67-x}Bi_x$ thin films with (x=0,5,10,15,20). As evident from figure (1), (α) varies exponentially with (h ν) in the measured range of (α), and increased with increasing the valueof x. This result is in agreement with results on Ge20Se8o-x Bix(x=0-13)[10].

Figure (2) shows plots of (αh ν) 1/2) against photon energy of $Ge_{33}Se_{67-x}Bi_x$ films deposited at room temperature in accordance with eqn(1) and r=2. The extrapolated values of the non-direct energy gap were (1.93,1.55,1.21,1.13,1.1)eV at x=0,5,10,15, 20 respectively, as shown in figure (3). The incorporation of 5% Bi into $Ge_{33}Se_{67}$ results in a decrease of (Eg opt) by about (0.38) eV, and the addition of another Bi into $Ge_{33}Se_{67}Bi_5$ results in a decrease of (E_g^{opt}) to about 0.34 eV. Further addition of Bi, howevere causes very small very change in (E_g^{opt}). Thus, the effect of adding Bi in the composition range (10-20) has low effect on the electronic structure that becomes nearly constant. Our interpretation for this is the effect of Bi, when the localized states approach saturation or when its effect on the electronic structure becomes very low. The value of energy gap at x=0 is in a good agreement with Kumar etal [6] who found that the addition of 11 at% Bi to amorphous $Ge_{20}Se_{80}$ films results in a decrease of the optical gap from 1.85 to 1.15 eV.

Figure (4) shows the plot of ln α against photon energy of $Ge_{33}Se_{67-X}Bi_X$ films deposited at room temperature in accordance with eqn(2). The reciprocal of the slopes of the linear parts of the curves give the values of corresponding ΔE_t (0.0858, 0.105, 0.119, 0.121, 0.125)eV at the value of x=(0,5,10,15,20) respectively as shown in figure.(5). The optical data suggest that the addition of bismuth produces localized states near the valance band edge for p-type and near the conduction band edge for n-type so that the electrical transport is due to hopping of electrons after being excited into localized states [1].

Table I shows the values of (E_g^{opt}), ΔE_t and the constant B (in equation (1)) which is found from the slope of figure (2) for all values of x. [2]

Table 1: Values of (Eg^{opt}),ΔE_t and the constant B at different percentage of x.

x%	(E_g^{opt}) (eV)	ΔE_t (e V)	B(cm-1eV-1)
0	1.93	0.0858	0.94X105
5	1.55	0.105	1.11X105
10	1.21	0.119	1.322X105
15	1.13	0.121	1.6X105
20	1.10	0.125	2.02X105

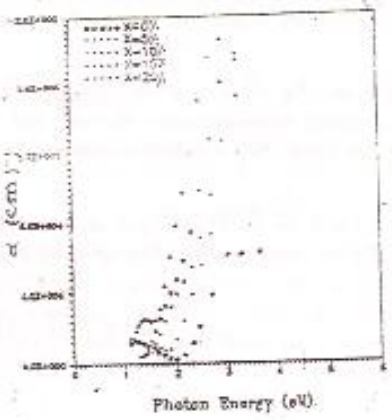
The observed decrease in the optical gap can be explained by the increased tailing of the conduction band edge into the gap, due to the addition of bismuth. The constant B in equation (I) has been calculated and also listed in Table I. These values are within the range of reported data for non-crystalline materials [7].

A model has been suggested for $Ge_{33}Se_{67-X}Bi_x$ thin films (fig.(6) with x=(0,5,10,15,20% to fit our optoelectronic data. The Hall effect and thermoelectric measurements showed that the electrical conductivity at room temperature was p-type for x=(0,5%), while it becomes n-type for x= (10,15,20%) [1].

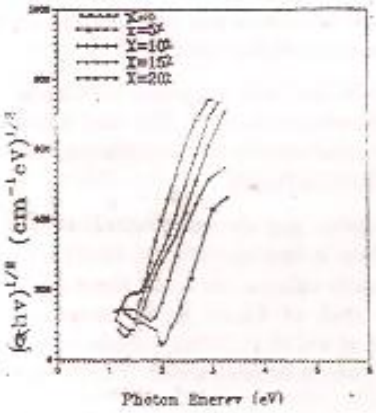
The optical gap showed a reduction from 1.93eV to 1.55eV for Ge33Se67 and doped with 5 % Bi, while it becomes (1.21,1.13,1.1)eV at x=(10,15,20%), respectively. The shift of Fermi level towards valance band was about 0.0278eV and 0.0745eV at x=0,5% (p-type), while for n-type the shift of Fermi level toward conduction band was about 0.234eV, 0.276eV and 0.2415eV at x=(10,15,20%), respectively. The width of tail is the same near E_C and E_V, i.e, E_C-E_A=E_B-E_V which increases with increasing x, as shown in Table (I).

Conclusions

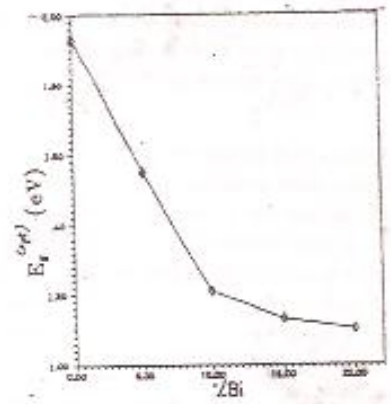
The optical transmission and absorption of $Ge_{33}Se_{67-X}Bi_x$, (x=0,5,10,15,20) films of thickness (300±5)nm have been measured in order to derive data on the absorption edge and band tailing. The (E_g^{opt}) for $Ge_{33}Se_{67-X}Bi_x$ films showed a decrease from a value of (1.93)eV at x=0 to (1.55)eV and (1.21)eV at x=5 and 10 respectively. while ΔE_t showed an increase with increasing the value of x. The optical data suggest that the addition of bismuth produces localized states near the valance band edge or near the conduction band edge.



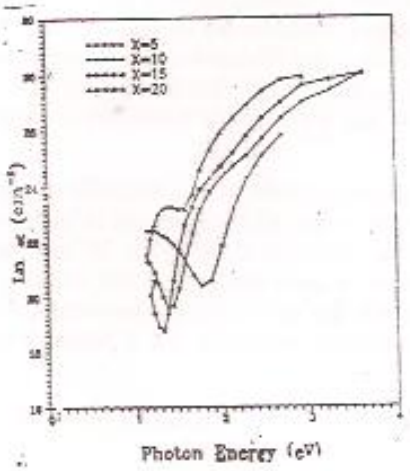
Fig(1) : Optical absorption coefficient α versus photon energy hv for $Ge_{20}Se_{80-x}Bi_x$ thin films.



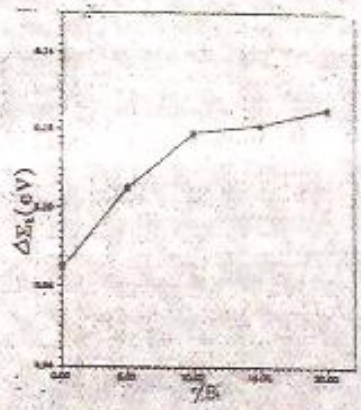
Fig(2) : The variation of $(\alpha h\nu)^{1/2}$ with photon energy for $Ge_{20}Se_{80-x}Bi_x$ thin films.



Fig(3) : Composition dependence of optical band gap E_g^{opt} for $Ge_{20}Se_{80-x}Bi_x$ thin films.



Fig(4) : The variation of (ln α) versus photon energy for $Ge_{20}Se_{80-x}Bi_x$ thin films .



Fig(5) : Composition dependence of ΔE_g for Ge_xSe_{1-x} thin films .

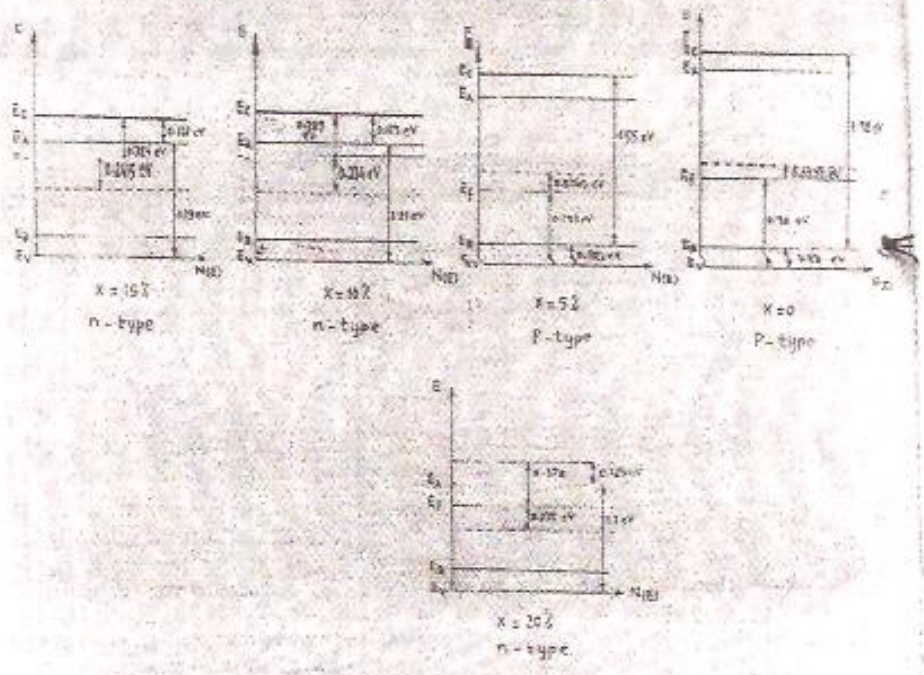


Figure (6) : proposed density of states model for the $Ge_{30}Se_{70-x}Bi_x$ thin films

References

1- Al-Ani.S.K.S.Makadsi, S.S.Al-Rawi and N.K.Abass (2001): "Electron transport properties of Bismuth – doped Germanium Selenide semiconductor", presented to The 7th Arab International Solar Energy Conference & Regional world Renewable Energy Congress, Sharjah, U.A.E, 123-SMOA.

2- Al-Ani S.K.J. (1993), (Determination of the Optical Gap of Amorphous Materials) Int. J.Electronics, 75, PP.(1 153-1163).

3- Bhatia K.L., (1983). "Electrical transport in Bi doped n-type amorphous semiconductors $(GeSe_{3.5})_{100-x}Bi_x$ at high pressure", J.Non-Cryst. Solids. 50 & 60, 1019-1022.

4- Bhatia, K.L., (1986), "Optical constants of doped n-type vitreous semiconductors $(GeSe_{3.5})_{100-x}Bi_x$ ", J. of Non. Cryst. Solids, 61: 285-291.

5- Elliott, S.R., (1986), "Mechanism for doping in Bi chalcogenide glass" Phys. Review letters, v.57, 11.

6- Kumar, S., C. Kumar,S.,C. Kashyap and K.L. Chopra,(1986) "Electron transport properties of n – type.

7- Bismuth modified a-$Ge_{20}Se_{70}$ films), J. Non-Cryst. Solids, 85 (100-104).

8- Mott,.N.F. and E. A. Davis, (1971), "Electronic processes in Non-Crystalline materials ", Clarendon press, Oxford.

9- Pankov, J.I.(1971), "Optical Processes in Semiconductor ",Prentic -Hall, Inc. Englewood, Cliffis, N.J..

10- Tohge. N., T. Minami, Y.Yamamoto, and M.Tanka (1980), "Electrical and optical properties of n-type semiconducting chalcogenideglasses in the system Ge-Bi-Se J.Appl.Phys. 51(2).

11- Vikhrov S.P.. G.Yashka, and V.N.A. Ampilogov, (1984), (Nature of inversion of the type of conduction in Ge-Se –Bi and Ge-S-Bi glass chalcogenide semiconductors ", Sov. Phys. Semicond, 181(2).

12- Zumaillan, A. and J.M. Saiter (2001) " Extended X- ray absorption fine structure study on Bi modified Ge S bulk glasses ", J. Optoelectronics and Advance Materials, 3, No.2,PP 485 – 490.

الخواص البصرية لأغشية الجرمانيوم السلينيوم المطعمة بالبزموث شبه الموصلة

سلوان كمال جميل العاني ، متي ناصر مقادسي ، صبحي سعيد الراوي ، ندى خضير عباس
قسم الفيزياء - كلية العلوم - جامعة بغداد - بغداد - العراق

الملخص

تمت دراسة كل من فجوة الطاقة البصرية (E_g^{opt}) وعرض الذيول الموضعية في فجوة الطاقة (ΔE_x) لأغشية الجرمانيوم السلينيوم المطعمة بالبزموث بالتراكيز (x).

$$(x = 0,5,10,15,20)Ge_{33}\ Se_{67-x}\ Bi_x$$

الرقيقة عشوائية التركيب المرسبة بالفراغ ذات السمك (300 ±s nm) في مدى طاقة الفوتون (1-5.4 الكترون فولت). لقد بينت الدراسة البصرية بأن فجوة الطاقة البصرية تقل بشكل سريع مع زيادة تركيز البزموت (x) للمدى (صفر – 10) % ثم تبدأ تقل ببطئ مع زيادة التركيز (x).

أما عرض الذيول للحالات الموضعية في حافات الحزمة فقد زادت مع زيادة تركيز البزموث تم اقتراح نموذج حزمة الطاقة بالاعتماد على الخواص البصرية والكهروحرارية لهذه الأغشية.

الكلمات المفتاحية: الترسيب بالفراغ ، أغشية رقيقة ، الجرمانيوم السلينيوم المطعم بالبزموث ، فجوة الطاقة البصرية ، عرض الذيول للحالات الموضعية ، مقترح نموذج لحزمة الطاقة.