Composition Dependence of Photoconductivity in Chalcoginide Glasses

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Abstract : In the present paper our aim is to investigate the composition dependence of photoconductivity and carrier lifetime in $Ge_{2o}Bi_xSe_{80-x}$ glasses with x varying 2 to 12 at. % the average coordination number (Z) of this system varies from 2.4 to 2.52 corresponding to the above variation in x. and also to test whether any special feature is reflected around the critical composition of Ge-Bi-Se glasses at which $p \rightarrow n$ transition has been reported.

Key Words : *photoconductivity, chalcogenide, FRPC measurements*

1. Introduction

The effect of incorporation of Bi as an impurity in chalcogenide glasses has been a topic of great interest ever since the synthesis of such glassy systems. A great deal of effort has been expended to understand the role of Bi in controlling the mechanism of electrical conduction in chalcogenide glasses. Chalcogenide glasses are generally p-type semiconductors and are expected to be insensitive to the addition of impurities^[1]. For them Fermi level is considered to be pinned due to the equilibrium between the positively and negatively charged dangling bonds which make them insensitive to impurity doping. But there are experimental results which are against this argument^[2-5]. In the case of the Ge-Bi-Se system the addition of a critical quantity of Bi brings about a carrier type reversal from p-type to n -type in the basic Ge-Se system^[6-8]. The Ge-Se system, which is a p-type semiconductor, changes to n-type with the addition of 7 atomic percent of Bi, which corresponds to an average coordination number Z = 2.47 for the system. Carrier type reversal has been observed in certain Pb doped germanium chalcogenides also^[9]. Appreciable variations in different physical properties have been found around the composition with this critical Bi concentration, which occurs in the vicinity of $x_{1} = 7$ at. % (Coordination number Z = 2.47) in Ge-Bi-Se glasses with the general formula $Ge_{20}Bi_xSe_{80-x}$. Composition dependence of various physical properties such as thermoelectric power, electrical resistivity and IR absorption exhibit anomalies near the critical composition corresponding to x = 7 at. %. Measurements by Tohge et.al^[7] have shown a gradual decrease in resistivity with increasing Bi content up to 9 at. % and then decreases by about four orders of magnitude between x = 9 and la at. % but remains almost constant for x > 10 at %. Composition dependence of Seebeck coefficient shows that glass containing 7 at. % of Bi is p-type, similar to other melt quenched chalcogenide glasses but incorporation of 9 at. % of Bi changes it into n-type. In the case of optical band gap (E_g), a decrease by 0.65 e V was reported by incorporation of 2.5 at. % of Bi into Ge₂₀Se₈₀ glass. Further addition of Bi causes only very small change in E_g and it remained constant for glasses containing more than 7.5 at. % of Bi. Heat capacity measurements at 323 K show a drastic change in the value of C_p between x=6 and 8 at. %. The carrier type reversal observed in Bi containing chalcogenide glasses has been accounted for by several authors. Studies of electrical, thermoelectric and optical properties as a function of composition led Tohge et.al^[7-8] to explain the transport mechanism on the basis of chemical bonds. Based on EXAFs data, Elliot and Steel^[10] have discussed the reasons for this mechanism as due to the

formation of partially ionic Bi chalcogen bonds and subsequent unpinning of the Fermi level. Storiopoulous and Fuhs^[11] have put forwarded the explanation that a drastic decrease in band gap induces an Increase of conductivity and a reversal in the type of the carriers. Analysis based on network modeling led Phillips^[8] and Nagels to conclude that carrier type reversal occurs in the vicinity of the percolation threshold and is the result of transport anomalies in the system.

2. Experimental Method

Bulk semiconducting glasses with the general formula $Ge_{2o}Bi_xSe_{80_x}$ (0<x<12) have been prepared by the conventional melt quenching technique starting with 5N purity constituents. The cooling rate is approximately 500°C/Sec. The amorphous nature of the samples has been checked by X-ray powder diffraction method. Two compositions have been analyzed by XPS. The largest region of glass formation with bismuth was obtained for alloys with 20 to 30 at. % of Ge and 70 to 80 at. % of Se^[7]. It is seen that for 20 at. % of Ge, the maximum Bi content that can be incorporated into the glass matrix is 13 at. %, the remaining being selenium. If bismuth content is increased further, the glasses formed may be partially crystallized. Bulk samples having rectangular shape with surface area 3 x 4 mm2 and thickness 0.5 mm have been prepared for the present measurements. The samples have been sandwiched between two SnO₂ coated conducting transparent glass plates for the measurements. The contacts have been found to be Ohmic from V -I characteristic study. The sample has been illuminated by light from a Xe arc lamp. The intensity of light falling on the sample is 25 mWcm⁻² during photoconductivity and carrier lifetime measurements.

3. Results and Discussion

3.1. Temperature, Intensity and Spectral Dependence

Temperature dependence of dark conductivity for Ge₂₀Se₈₀. Ge₂₀Bi₂Se₇₈ and Ge₂₀Bi₁₀Se₇₀ are shown in Fig.1. The behavior is almost identical to earlier reports^[7-12]. Temperature dependence of ac photoconductivity and dc photoconductivity for the same compositions are shown in figures 2 and 3 respectively. In both these cases photoconductivity initially increases gradually with inverse temperature and then decreases. The same behavior is exhibited by other compositions of the Ge-Bi-Se system. Photoconductivity increases by nearly two orders of magnitude with the addition of bismuth, as is clear from figures 2 and 3. The increase is reflected more or less identically in both ac (pulsed excitation) and d.e (steady state) measurements. The enhancement in photoconductivity can be attributed to the increase in the density of charged defect states formed in the energy gap with the addition of bismuth^[13]. There may be hopping conduction through the defect states. Another reason may be the change in band gap with the addition of bismuth. From Fig 4. it can be seen that the band gap decreases appreciably by the incorporation of 2 at. % and 4 at. % of bismuth. Further addition of bismuth does not alter the band gap appreciably. Therefore it can be concluded that the observed general increase in photoconductivity of Ge-Bi-Se system compared to Ge-Se is also related to the shrinkage of the band gap^[4]. The variation of optical band gap together with that of activation energy for conduction is plotted in Fig 4. The activation energy does not change significantly for lower concentrations of bismuth. Similar results have been obtained by Tohge et.al.^[7]. At low Bi concentrations the optical band gap decreases appreciably with increase of Bi content. At higher Bi concentrations optical band gap remains unaltered whereas activation energy decreases. This occurs as a result of the shift of the Fermi level towards the conduction band^[14]. Fig.5 shows the variation of photoconductivity with intensity of incident light for the sample $Ge_{20}Bi_{10}Se_{70}$. Other compositions show similar variation. Photoconductivity exhibits almost a linear variation at lower intensities of illumination and become almost constant at higher intensities of

illumination. The results shown in Fig.5 indicate that photoconductivity saturates at higher intensities of illumination the results on photoconductivity of Ge-Bi-Se system have been analyzed in terms of the ABFH model and the results are shown in Fig.6. In the frame work of ABFH model the material exhibits characteristics of a type I photoconductor. A plot of E_g vs Tm.ln((σ_{max}) is shown in Fig.6. The points obtained can be fitted to a straight line. Referring to the description of the ABFH model based analysis for our photoconductivity data on these glasses fit very well with that of a type I photoconductor. The spectral dependence of photoconductivity for Ge₂₀Se₈₀ and Ge₂₀Bi₂Se₇₈ have been measured and are plotted in Fig.7. The photocurrent is normalized for the intensity variation of the source and normalized photoconductivity gives actually quantum efficiency of the sample. Though the normalized photocurrent peaks around the absorption edge, a correct determination of the band gap is not possible from the data obtained. In general, the quantum efficiency of Ge-Bi-Se system is found to be less than that of Ge-In-Se by nearly two orders of magnitude.

3.2. Frequency Resolved Photoconductivity (FRPC) Measurements

FRPC measurements have been carried out on different compositions of Ge₂₀Bi_xSe_{80-x} system and the plots for four compositions are shown in Fig.8. Also FRPC measurements have been carried out on various compositions at different temperatures and intensities of illumination. Each curve is normalized with respect to its maximum value. The peak position shifts to higher frequencies with increase of temperature or intensity for all the compositions. The frequency (f_{max)} corresponding to the peak in photoconductivity, is noted from the figures and the carrier lifetime(r) is determined. The carrier life time is calculated from the formula $\tau = 1/2\pi r f max$. It is found to possess an almost linear variation with temperature as shown in Fig.9. Since the carrier lifetime exhibits a linear decrease with temperature we can assume that the number of traps in the band gap increases with temperature. Similar results have been reported for other chalcogenides by earlier workers^[15]. The carrier lifetime measured by FRPC method is found to decrease almost exponentially with intensity. At high intensities there is no appreciable decrease and the carrier lifetime almost constant. The plot of carrier lifetime vs. intensity for the composition Ge₂₀Bi₂Se₇₈ obtained by FRPC measurement is shown in Fig.10. Carrier lifetime (τ) and generation rate G are related as $\tau = AG^{v}$ from in G vs. In ' τ plot the value of the exponent can be obtained. Generation rate, G is directly proportional to the intensity of illumination. From The plot shown in Fig.11 the value of the exponent v have been calculated for Ge₂₀Bi₂Se₇₈ and Ge₂₀Bi _{IO}Se₇₀. The value of v for these is 0.62 and 0.867. For other compositions also similar calculations have been done and for all of them the value of the exponent v lies between me and 0.5 which is an indication for the presence of localized states in the band gap of the material as explained with the results of Ge-In-Se^[16-20]. Composition dependent variation of carrier lifetime is shown in Fig.12. In general carrier lifetime decrease with increase in Bi Content. It exhibits a clear slope change corresponding to the critical composition where p-m transition has been reported by earlier workers. A discussion of composition dependent behavior of Ge-Bi-Se system is given in the next section where the explanations by different workers are outlined.

3.3. Composition Dependence of Photoconductivity

The composition dependence of photoconductivity (σ'_{ph}) is shown in Fig.13 and that of photodetectivity, the ratio of photoconductivity to dark conductivity ($\sigma'_{ph} / \sigma'_{d}$) is shown in Fig.14. Both σ'_{ph} and ($\sigma'_{ph} / \sigma'_{d}$) have sharp variations around the critical composition x=7 corresponding to Z=2.47 where the p~ \rightarrow n transition occurs. In general, photoconductivity increases up to x=6 and then decreases to a minimum and thereafter remain more or less constant. But photodetectivity, in general, decreases with increase in x and it remains almost

constant beyond x=7. Photodetectivity (or photosensitivity) of the material is a factor which detentions the quality of a photoconductor in using it as a photo detector. Although $p \rightarrow n$ transition and anomalous change of many physical properties have been analyzed and explained by various authors before^[6-8, 20-22], the mechanism of this phenomenon is not yet fully understood. More experimentation and modeling seem to be necessary to get a clear picture of the mechanisms involved in the process. Studies of electrical, thermoelectric and optical properties as a function of composition led Tohge et.al^[6] to explain the transport mechanism in Ge-Bi-Se glasses on the basis of chemical bonds. Based on EXAFs data Elliot and Steel^[9] have attributed the mechanism to the formation of partially ionic Bi- chalcogen bonds and the subsequent unpinning of the Fermi level. They suggested that the $p \rightarrow n$ transition in these glasses is accompanied by a significant change in the local structural order surrounding the Bi impurity atoms. At low Bi concentrations, the Bi-Se bonds remain covalent in character and at higher Bi concentrations; it becomes partially ionic with a slight increase in bond length^[9]. It has further been proposed that the process of the dissolution of the Bi impurity in the selenium rich regions at lower concentrations produce Se- centers making the Bi impurities positively charged. Further additions of Bi in larger concentrations don't produce appreciable additional defects as it enters a modified network. Consequently the absorption edges are not appreciably affected. Phillips^[8] and Thorpe^[23] predicted the critical composition of the binary glass system of the type IV_x -VI_{IOO-x} to be around x= 20 at. % which corresponds to average coordination number Z= 2.4, IV and VI indicating the corresponding group of elements in the periodic table. According to this we can expect a critical composition for the $Ge_{20}Bi_xSe_{80 x}$ system to be around x=7 at. %. However, for $Ge_x Se_{IOO-x}$ glasses, this value is found to be slightly higher, at x =23 at. %, which is attributed to the fact that not all bond bending constraints are effective in hindering inter cluster motions^[24]. There are reports that Bi_2Se_3 is an n-type semiconductor and in Ge-Bi-Se glasses the Bi_2Se_3 clusters are embedded in the Ge-Se glass matrix^[8, 25]. The $Ge_{20}Bi_xSe_{80-x}$ glasses can be represented as $Ge_{20}Se_{80-Sz}$ + Bi_{2z} -Se_{3z}. According to Phillips, when Bi content is appreciably low localized unconstrained Se- defects are present in the Bi₂Se₃ tetradymite surfaces which are dispersed uniformly in the rest of GeSe₂ and Se flexible chains making them p-type semiconductors. At 6 at. % of Bi, the Bi_2Se_3 clusters retain in the melt. Also x=6 corresponds to $Ge_{20}Se_{65}$ -Bi₆Se₉ and $Ge_{20}Se_{6}$ -Se₂₀Se_{100,v} with y = 24, which agrees with the elastic stiffness threshold composition Ye= 23 of the binary glasses found in other Experiments^[24]. At x>6 at.% the Bi₂Se₃ tetradymite clusters find themselves in a matrix of increased mechanical rigidity and the mechanical misfit between the clusters become high which lead to a plastic deformation of these clusters? This gives rise to an increase in Se-defects which evolve in a percolative manner at the mechanical threshold and produce n-type conduction in these glasses. In terms of chemical bond formation the carrier type reversal is related to the formation of fairly large number of Bi-Se bonds and the disappearance of Se-Se bonds a this critical composition. According to charge dangling bond model, the equilibrium, between the positively and negatively charged dangling bonds which pin the Fermi level is affected maximum at this critical composition by charged impurities^[7]. Bhatia et.al^[21] have reported that, at lower Bi concentrations there is little change in the activation energy E_{ea} whereas at higher concentrations a considerable decrease in E_{av}, is observed which is explained as due to the shift in the Fermi level towards the conduction band. According to Tohge eLal^[7], in Ge₂₀Se₈₀ glasses, only Ge-Se and Se-Se bonds are supposed to be present. When Bi is incorporated in to this glass, Bi is expected to combine freely with Se, followed by the decrease in the concentration of Se -Se bonds, because the bond energy of the Bi-Se bond is larger than that of a Bi-Ge bond (40.7 and 31 k cal/mole respectively)^[26]. The concentration of Ge-Se bonds remain the same over the whole composition range whereas that of Bi-Se bond increases and that of Se-Se bond decreases monotonically with increasing Bi content up to 10 at.% after which the Se-Se bond vanishes. A further increase of the Bi content results in the formation of Bi-Bi or Bi-Ge

Bonds provided Bi is still six fold coordinated with Se. Coordination numbers four and two are assumed for Ge and Se respectively and the number of covalent bonds per Bi atom mis reported to be six in these glasses^[27]. Investigations on electrical properties on these glasses show an abrupt decrease in resistivity which may be related to the formation of fairly large number of Bi-Se bonds and the disappearance of Se-Se bonds. For six fold coordinated Bi in crystalline Bi₂Se₃, the occurrence of p^3d3 or sp^3d2 hybridization have been suggested. If this is the situation with Bi in chalcogenide glasses, the Bi-Se bond becomes electron deficient and Bi atoms get negatively charged which is compensated by the positive charge on the Se atoms. Thus the equilibrium between the positively and negatively charged bonds which pins the Fermi level are affected by the charged impurities. This is described in the charged dangling model. Sunil Kumar et.al^[28]. based on XPS measurements of Ge-Bi-Se thin films have suggested that Bi atoms are positively charged. According to their results the charged Bi atoms perturb the equilibrium between Positively and negatively charged defect centers, thereby causing a shift of the Fermi level towards the conduction band. Vaidyanathan et.al^[29] has considered the Bi based glasses as a pseudo binary system with Bi acting as network modifiers to the basic Ge₂₀Se₈₀ network. The modification of the host network makes the Fermi level move towards the conduction band edge and alters the conduction mechanism from p-type .to n-type. They have also proposed a structural model to explain the carrier type reversal in Pb incorporated germanium chalcogenides. Spectroscopic investigations such as diffuse reflectance spectra and variation of optical energy gap obtained from peak maximum energies in diffuse reflectance spectra as a function of Pb concentration also show similar behavior. FTIR and Raman spectra together confirm that Ge and Pb or Bi in this type of glass system are present only in tetrahedral and octahedral coordination's using the above spectroscopic features. The Pb is assumed to be in a $sp^{3}d^{2}$ state of hybridization. The Se atoms are in spn (n= 1,2, and 3) hybridization. Germanium utilizes its Sp³ hybridized orbitals for bond formation. The lowest energy levels result from the overlap of the bonding orbitals. The Ge-Se and Ge-Ge bonds constitute the lowest energy levels. The next higher energy level is constituted by spin lone pair originating from Se. The sp^3d^2 orbitals of Pb ions are likely to occupy a slightly higher level and just above Se lone pair levels. Similarly increase in Bi concentration in Ge-Bi-Se glasses leads to a rapid growth of sp³d² band which results in the rapid increase of electron contribution to conductivity which exceeds contribution from holes. As consequence $p \rightarrow n$ transition occurs as a function of Bi concentration. Only Pb and Bi containing Ge-Se glasses are known to exhibit such a $p \rightarrow n$ transition. Bi and Pb have a unique tendency towards octahedral coordination and more importantly the energetic disposition of their d-bands, which can overlap in energy with those of lone pair bonds of Se, in particular, may be the reasons for this $p \rightarrow n$ transition. Based on the we can draw the following general conclusions regarding various explanations, photoconductivity of Ge-Bi-se glasses. The Ge-Bi-Se system is a pseudo binary system with Bi atoms acting as an impurity. The Bi atoms modify the structure of the host Ge-Se network and it results in the shifting of the Fermi level towards the conduction band. The decrease in photoconductivity beyond x=6 (Z=2.46) at.% can be explained as due to the formation of Bi^2Se^3 ionic bonds and the corresponding disappearance of Se-Se bonds. In the interpretation given by Vaidyanathan et.al^[29], the disappearance of Se-Se bonds with increase in Bi content is outlined as due to the overlap of d-orbitals of Bi or Pb with those of lone pair bonds in Se. The increase in defect concentration due to the addition of bismuth may be the reason for the decrease in carrier lifetime with increase in Bi content. Carrier lifetime decreases in general with increase of Bi content and exhibits a clear slope change around the critical composition with x=7 as shown in Fig.4.12. At the same time photoconductivity slightly increases with increase in Bi content and around the critical composition it exhibits a rise and a clear decrease as shown in Fig.4.13. It is interesting to note that the average coordination (Z) of this composition is 2.47 close to which the system has a mechanical threshold according to Phillips-Thorpe model.

4. XPS analysis of Ge-Bi-Se glasses

Two compositions from the $Ge_{20}Bi_xSe_{80-X}$ system, namely with x=2 and x= 10 have been analyzed by x-ray photoelectron spectroscopy the composition with x=2 is p-type while that with x= 1 0 is n-type. The binding energy values of the characteristic levels of pure Ge.Ei and Se as well as their values in the two compositions obtained from XPS spectra are show in Table 4.1. The corresponding spectra are given in figures 15, 16 and 17. As is clear from the figures, Bi suffers a positive shift in its 4f level for the two compositions compared to that of the pure element. Germanium also undergoes positive shift when the compound is formed. But the b.e values of selenium are found to decrease in the compounds compared to that of pure selenium. The shifts can be attributed to the bonds formed and variation in number of structural units in the two compositions. The differences in electronegativity values could also be responsible for the observed shifts.

Conclusions

Our investigations indicate that a photoconducting property of Ge-Se system in general improves by the incorporation of Bi. The increase is nearly of the order of two. Photoconductivity exhibits a clear change corresponding to the critical composition of the Ge-Bi-Se system at which the material undergoes a $p \rightarrow n$ transition. At the same time photodetectivity ($\sigma_{ph}/(\sigma_d)$, In general, decreases with the incorporation of bismuth. Photodetectivity also exhibits a clear change at the critical composition. Carrier lifetime measured by FRPC method, decreases in general with the incorporation of bismuth. Carrier lifetime has a sharp slope change around the critical composition. These results are analyzed in the light of various models and explanations proposed by different research workers. Analysis of the material in terms of ABFH model reveals that the Ge-Bi-Se system is a typeI photoconductor. One n-type and one p-type compositions have been analyzed by XPS and the results are discussed.

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Fig. 6 Plot of E_g against the product $T_m \cdot ln \sigma_{max}$ for the $Ge_{20}Bi_x Se_{80-x}$ system. The points can be fitted to a straight line.



Fig. 7 Spectral dependence of photoconductivity in $Ge_{20}Se_{80}$ and $Ge_{20}Bi_2Se_{78}$



Fig. 8 FRPC measurements in four compositions of the $Ge_{20}Bi_xSe_{80-x}$ system.($\blacksquare\blacksquare....x=2$, ++++....x=6, ** **....x = 8, $\Box\Box\Box\Box\Box...x=12$)



Fig. 9 Temperature dependent variation of carrier lifetime measured by FRPC method for $Ge_{20}Bi_2Se_{73}$ (...===) and $Ge_{20}Bi_{10}Se_{20}(..._{10}mm)samples$



Fig .10 Variation of carrier lifetime with intensity for $Ge_{20}Bi_2Se_{78}$ and $Ge_{20}Bi_{10}Se_{70}$



Fig 11 Plot of $\ln G$ vs $\ln \tau$ for $Ge_{20}Bi_2Se_{78}$ and $Ge_{20}Bi_{10}Se_{70}$



Fig. 12 Variation of carrier lifetime with Bi content. The measurements have been carried out at 298 K. Intensity of light 25 mWcm⁻²



Fig 13 Variation of photoconductivity with increase in Bi content in the Ge-Bi-Se system.



Fig 14 Variation of photodetectivity with increase in Bi content.



Fig 15 XPS of $3p_{3/2}$ levels of pure germanium(A) , germanium in $Ge_{20}Bi_2Se_{78}~(B)$ and in $Ge_{20}Bi_{10}Se_{70}.~(C)$



Fig 16 XPS of $4f_{7/2}$ levels of pure Bi (A), Bi in $Ge_{20}Bi_2Se_{78}$ (B) and in $Ge_{20}Bi_{10}Se_{70}$.(C)



Fig 17 XPS of $3p_{3/2}$ levels of pure selenium.(A) selenium in $Ge_{20}Bi_2Se_{78}$ (B) and in $Ge_{20}Bi_{10}Se_{70}$.(C)

Та	ble	1
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Sample	Ge	Bi	Se
	3p _{3/2}	4f _{7/2}	3P _{3/2}
Pure element	120.8	157.4	161.9
Ge ₂₀ Bi ₂ Se ₇₈	121.7	158.5	161.2
(Z=2.42)	(+0.9)	(+1.1)	(-0.7)
Ge ₂₀ Bi ₁₀ Se ₇₀	121.3	158.6	160.8
(Z=2.5)	(+0.5)	(+1.2)	(-1.1)

Binding energy values from XPS measurements eV