Study of transport properties of Ni ion irradiated $Ge_{20}Se_{74}Bi_6$ for different ion fluences

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Amorphous semiconductors in the system $Ge_{20}Se_{80-x}Bi_x$ exhibit p-n transition in the electronic transport. This makes them an interesting class of amorphous semiconductors. Amorphous thin films of $Ge_{20}Se_{74}Bi_6$ prepared by flash evaporation in a vacuum of 10^{-5} Torr were characterized using XRD, XRF, DSC, EPMA. Samples were irradiated with 75 MeV Ni ions at fluences varying from $5x10^{12}$ to 10^{14} ions/cm^2. The ion induced effects on the properties of the unirradiated and irradiated films studied by measuring dc electrical conductivity, optical band gap and thermoelectric power. Dc electrical conductivity measured from 77K to 476K, optical spectra were recorded in the range 200nm to 800nm while the thermoelectric power measurements carried out using differential dc method in the temperature range 4.2K to 300K. Both the electrical activation energy and the optical band gap decreases with increasing ion fluence. The results thus obtained suggest increase in band tailing.

(Received May 28, 2007; accepted June 27, 2007)

Keywords: Chalcogenide, fluence, ion irradiation, electrical conductivity, thermoelectric power

1. Introduction

Chalcogenide glasses have received a lot of attention because of their potential use in various solid state devices. The common feature of these glasses is the presence of localized states in the mobility gap as the result of the absence of long range order as well as various inherent defects[1]. Chalcogenide glasses comprise one of the major categories of amorphous semiconductors because of the importance of their physical properties such as the switching and memory effects [2, 3] and are well known for their IR transmittance [4]. The effect of impurities on the electronic properties of chalcogen based amorphous semiconductors has been controversial issue ever since their discovery [5]. In the last 2-3 decades, KeV energy ion-implantation has emerged as a versatile technique for modifying the properties of amorphous semiconductors. It has been shown that Ni ions with KeV energies implanted in thin films of a-As_2Se_3 can induce doping effects [6]. Swift heavy ions(SHI), ions with energy which produce large electronic energy loss are being used for modification of the properties of the materials through electron phonon coupling. Electronic energy loss in the materials can be varied from eV/A^o to 10 keV/A^o by choosing appropriate ions and their energies [7]. At MeV energies the major source of ion-energy loss is the electronic excitations. Transition metal ions having incomplete electronic d-shell, should affect the ion-solid interaction to a greater extent than the non-transition metal ions [8]. Infact, Ni has shown its promising effects of doping when it is co-sputtered with or added in the host solid[6, 8]. In the present work we have irradiated the ternary chalcogenide $Ge_{20}Se_{74}Bi_6$ thin films with Ni ions of 75 MeV energy and studied the ion induced effects on the electrical, optical and thermo electrical properties as a function of incident ion fluence.

2. Experimental

Bulk materials of $Ge_{20}Se_{74}Bi_6$ were prepared by the conventional melt quenching technique. Thin films of the bulk alloys were deposited at room temperature under a vacuum of 10^{-5} Torr inside a high vacuum coating unit using the flash evaporation technique on to a ultrasonically cleaned glass substrate. The bulk and thin film samples were checked for amorphicity by taking X ray diffraction patterns. The compositions of bulk materials prepared were confirmed by taking EPMA and that of thin films by taking XRF. The film thickness was kept around 2000A^o. The crystallisation and glass transition temperatures were determined using Differential Scanning Calorimetry . For irradiation of samples, a 75MeV ^{58}Ni ion beam from NEC 16MV Tandem Van de Graaff type Electrostatic Accelerator (Pelletron) of the Nuclear Science Centre, New Delhi, India was used. The beam current was kept at 5pnA and the fluence was varied from $5x10^{12}$ to $1x10^{14}$ ions/cm^2. All the irradiation work was carried out at room temperature [9].

A Keithley model 617 electrometer was used for measuring the resistance of the sample and the temperature was controlled to an accuracy of better than 10mK using a Lakeshore DRC 93CA temperature controller. The resistance measurement was automated and controlled by an IBM compatible personal computer PC 286- AT / PC 386 – AT using a PCL 238 card (available from M/s Dynalog Micro computer Systems, Mumbai) through an IEEE – 488 interface bus. The electrical resistance of thin films deposited on to the glass substrate of dimension 1cmx1.5cm was measured in the temperature range of 77K to 476K. These where kept on a copper ladder inside a specially prepared sample holders so as to avoid leakages and get appropriate shielding. Dc electrical conductivity was carried out at a vacuum of the order of 10^{-5} Torr at UGC-DAE, Consortium for Scientific Research, Indore.

The spectral transmittance T(λ) and reflectance R(λ) measurements were taken at normal incidence in the wavelength range 200nm - 840nm by means of a Hitachi double monochromator spectrophotometer model 330.

The thermoelectric power (TEP) was measured using the differential dc method in the temperature range 4.2K – 300K. Lakeshore temperature controller was used to maintain a controlled sample temperature (±30mK) and SI7071 Solartron nanovoltmeter measured ΔV, and a thermocouple, was connected to the SI7071 Minat scanner. With the temperature stabilization time of more than 6 minutes each, the TEP data recorded are estimated to have around 50nV/K resolution. TEP measurements of the thin film samples were carried out at UGC-DAE, Indore.

3. Results and discussion

The temperature dependence of dc conductivity of the $Ge_{20}Se_{74}Bi_6$ thin films irradiated with 75 MeV Ni ion of ion fluences ranging from 5 × 10^{12} ions/cm^2 to 10^{14} ions/cm^2 is presented in the Fig. 1. The corresponding data for virgin (unbombarded) sample are also presented in the figure for comparision. It was found that σ increases with the increase of temperature for all compositions indicating that they have a semiconducting behavior. As is evident from figure the plot consists of two regions (A) a high temperature band conduction region and (B) a low temperature tail region. The data of conductivity in the high temperature range of Fig. 1 were fitted using the following equation

$$\sigma = \sigma_0 \exp\left(\frac{-\Delta E_\sigma}{kT}\right) \qquad (1)$$

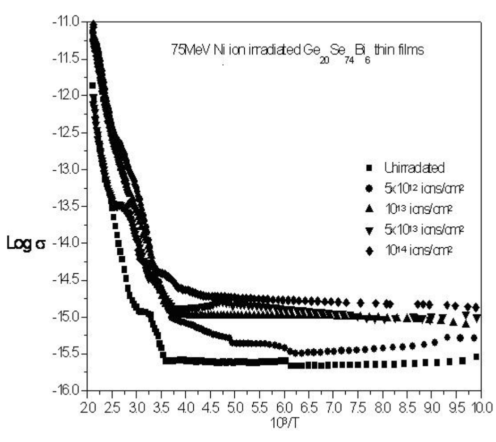

Fig. 1 Log of conductivity versus incident energy for unirradiated and Ni ion irradiated $Ge_{20}Se_{74}Bi_6$ thin films for fluences 5 × 10^{12}, 10^{13}, 5 × 10^{13}, 10^{14} ions/cm^2.

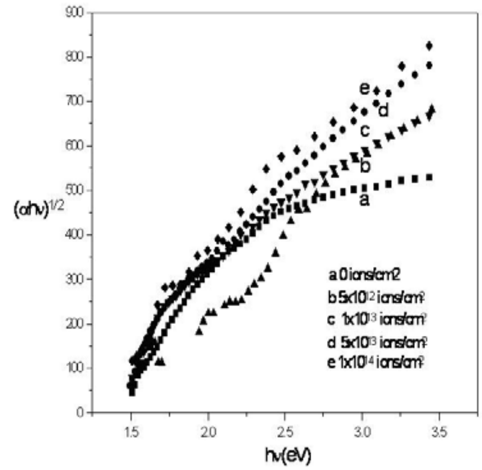

Fig. 2. Stopping power vs. depth for $Ge_{20}Se_{74}Bi_6$.

Here ΔE_σ is the thermal activation energy for band conduction and σ_0 is the pre-exponential factor. The estimated fitting parameters σ_0 and ΔE_σ are presented in Table.1. The linearity in the high temperature region indicates that σ in this region exhibits activated behavior. Infact the existence of two different slopes in the temperature characteristic of the electrical conductivity indicates a competition between different conduction mechanisms.

The conductivity data in the low temperature was fitted using the relation

$$\sigma = \sigma_{h0} \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right] \qquad (2)$$

where, $T_0 = 16\alpha^3/kN(E_F)$ is a hopping parameter, σ_{h0} is the pre-exponential factor for hopping conduction, $N(E_F)$ is the density of states at the Fermi level, α^{-1} is the decay length of a localized wave function at the Fermi level. The data were fitted with equation (2) and from the fitting , the density of localized states at the Fermi level $N(E_F)$ taking part in the variable range hopping process has been estimated for the Ni irradiated samples and the values are given in Table.1. Irradiation of the thin film samples with Ni ions results in increase in conductivity with increasing ion fluence however, it is found that Ni ion introduces larger changes in conductivity in low temperature conduction and this is due to increased hopping conduction. When a Ni ion passes through the film it experiences many violent atomic collisions and a large number of atoms will be displaced by primary and secondary collisions forming an ion track. Around each ion track there is an area of displaced atoms; these areas increase in number with increasing ion fluence. In the present case the concept of theoretical transport of ions in materials (TRIM)[10] calculations have been used to estimate the projected range R_p, the nuclear and electronic energy loses and straggling ΔR_p etc for 75MeV energy Ni ion in $Ge_{20}Se_{80-x}Bi_x$ samples. The value of R_p is about 11μm from the surface which is much larger compared to the thickness of the samples so the ion will not get implanted rather the present work is an irradiation work. The modifications induced in these cases are not due to implantation of ion as ion passes through the film. Rather changes observed are due to energy of SHI, as ion passes through the thin film it produces a hot ion track i.e a high energy zone and finally leading to (1) surface morphology changes including sputtering, reorganization etc. (2) structural changes like hollow track formation, piling up of material around track etc. As the ion passes through the film it produces a zone of high energy with high mobility of atoms inside the path and with time the energy finally annihilates resulting in modifications of various properties of the thin films. It may even cause the amorphous matrix to move towards more disordered state or cause re-crystallization induced inside the structure. Typical results of TRIM calculations for the depth dependence of the electronic and nuclear energy losses for the 75MeV Ni ion in $Ge_{20}Se_{74}Bi_6$ glasses is presented in Fig. 2.

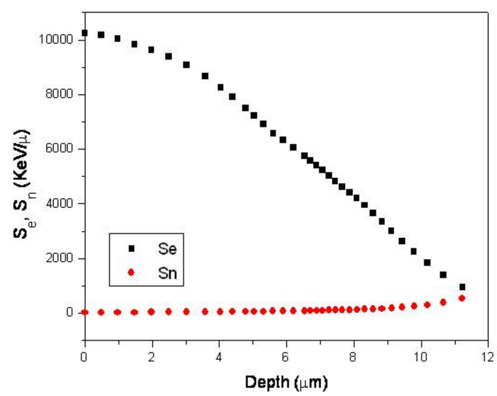

Fig. 3. $(\alpha h\nu)^{1/2}$ versus $h\nu$ for unirradiated and Ni ion irradiated $Ge_{20}Se_{74}Bi_6$ thin films for fluences 5 x 10^{12}, 10^{13}, 5 × 10^{13}, 10^{14} ions/cm^2.

The irradiation with increasing dose decreases the value of ΔE_σ from 0.712eV in virgin sample to 0.453eV in sample irradiated with a fluence of 10^{14} ions/cm^2. Following the argument of Street and Mott, lower value of σ_0 (10^{-2} or 10^{-4} or lower) suggests presence of wide distribution of localized states in the band gap. In the present case the irradiation process induces wide distribution of localized states in the band gap. Thus the decrease in the value of ΔE_σ is associated with the increased tailing of band edges and production of localized defect states near Fermi level [11].

From the density of states values the average hopping distance R and hopping energy W was found [12 - 14]. It is observed that the necessary conditions for Mott's VRH process i.e. W > kT and αR >>1 are satisfied in the present case. The values of density of states $N(E_F)$, hopping distance R, and hopping energy W, as found in the present case are reported in Table1. The density of states was found to increase both on irradiation as compared to the unirradiated samples as well as increasing ion fluence for $Ge_{20}Se_{74}Bi_6$ thin films. While the hopping distance R(cm) and the hopping energy were found to decrease and both on irradiation and also with increasing ion fluence. The free charge carrier concentration was found to increase with irradiation and ion fluence.

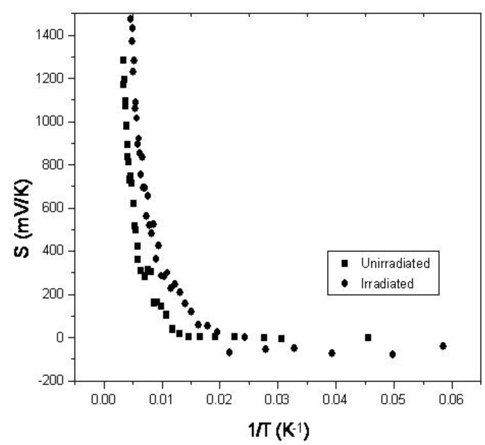

Fig. 4 Thermopower S versus 1/T for unirradiated and Ni ion irradiated $Ge_{20}Se_{74}Bi_6$ thin films for the fluence 5 × 10^{13} ions/cm^2.

Table 1. Data on $Ge_{20}Se_{74}Bi_6$ irradiated at various Ni ion fluencies.

Ni ion (s/cm^2)	$\sigma_0(\Omega^{-1}cm^{-1})$	ΔE_σ(eV)	σ_{10} (($\Omega^{-1}cm^{-1}$)	T_0	$N(E_F)(cm^{-3}eV^{-1})$	R(cm)	W(eV)	$n_\sigma(cm^{-3})$
0	2.98×10^{-5}	0.712	6.85×10^{-3}	1.86×10^{8}	9.985×10^{16}	8.03×10^{-7}	4.62	2.81×10^{8}
5×10^{12}	1.07×10^{-6}	0.494	1.78×10^{-2}	4.28×10^{7}	4.33×10^{17}	5.56×10^{-7}	3.20	1.28×10^{7}
10^{13}	3.87×10^{-7}	0.472	3.36×10^{-7}	3.43×10^{7}	5.41×10^{17}	5.26×10^{-7}	3.03	2.99×10^{7}
5×10^{13}	7.167×10^{-10}	0.318	3.8×10^{-10}	7.79×10^{6}	2.38×10^{18}	3.63×10^{-7}	2.09	1.15×10^{6}
10^{14}	3.11×10^{-6}	0.453	6.3×10^{-11}	2.63×10^{6}	7.05×10^{18}	2.77×10^{-7}	1.59	6.24×10^{6}

The transmission and reflection spectra for $Ge_{20}Se_{74}Bi_6$ thin films were recorded in the wavelength range 200 nm to 840 nm from these data absorption coefficient was calculated. The absorption edge could be divided into two regions depending on the value of absorption coefficient α. (I) For $\alpha < 10^4$ cm^{-1}, there is usually an Urbach tail [15] in which α depends exponentially on photon energy, hν as

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_e}\right) \quad (3)$$

where α_o is a constant and E_e is the width of the band tail of the localized states in the band gap also called Urbach slope. From the slope of lnα versus hν plot E_e was determined. Variations in the width of the exponential region E_e, provide information about the relative changes of the structural disorder induced by an additive. It arises from electronic transitions between localized states in the band edge tails; the density of which is assumed to fall off exponentially with energy.

(II) For $10^4 \le \alpha \le 10^6$ cm^{-1} in the high absorption region (where absorption is associated with interband transitions) for $Ge_{20}Se_{74}Bi_6$ thin films. Tauc[16] and Davis and Mott [17] independently derived an expression relating the absorption coefficient α to the photon energy hν

$$\alpha h\nu = \beta\left[h\nu - E_{gopt}\right]^n \quad (4)$$

where, β is the band tailing parameter and $E_{g\,opt}$ is the optical band gap. In equation (4) the integer takes value n = ½ for a direct transition and n = 2 for an indirect transition. Thus $(\alpha h\nu)^2$ vs. hν and $(\alpha h\nu)^{1/2}$ vs. hν plots provides β, direct band gap E_g^d and the indirect band gap E_g^i resp which are tabulated in Table 2. Fig. 3 shows the $(\alpha h\nu)^{1/2}$ vs. hν plots for unirradiated and irradiated $Ge_{20}Se_{74}Bi_6$ samples for all fluences. The transmission was found to decrease while the optical absorption increases with increasing fluence, the variation is however, less. This feature is associated with Ni ion induced defects producing localized states near the band edges and in the gap of the target. The decrease in the both direct and indirect optical band gaps with increasing ion fluence is related to the increase in the localized state density within the band gap as suggested by Davis and Mott i.e. deeper band tails in the gap are introduced. The defects produced along ion tracks could be one of the contributing factor to the production of localized tail states. This leads to decrease in the energy difference between the bonding and antibonding orbitals, and thus to a decrease in both the direct and indirect optical band gaps. The values of the parameters obtained after fitting i.e. E_e, β, E_g^i, E_g^d are reported in Table.2. The slope parameter β is a measure of structural randomness and it is found to increase with increasing ion fluence indicating increase in the rigidity of the network and thus resulting in the modification in the network structure of the $Ge_{20}Se_{74}Bi_6$ thin film systems. The method provides a tool for custom tailoring of the spectral characteristics of the glass [18]. Variations in the width of the exponential region E_e, provide information about the relative changes of the structural disorder induced by an additive. The value of E_e is found to increase on irradiation and with increasing ion fluence. Thus the observed effects are due to Ni ion induced structural modifications of the $Ge_{20}Se_{74}Bi_6$ thin film samples.

Table 2. The band gaps in $Ge_{20}Se_{74}Bi_6$ irraiated various Ni ion fluences.

Ni ion (s/cm^2)	E_g^d (eV)	E_g^i (eV)	β × 10^5($cm^{-3}eV^{-1}$)	E_e (meV)	ΔE_s(eV)	n_s
0	1.95	1.4625	1.94	34.4	0.306	1.85×10^{20}
5×10^{12}	1.89	1.461	2.43	57.64		
10^{13}	1.51	1.442	2.54	75.96		
5×10^{13}	1.27	1.43	2.48	89.23	0.233	3.05×10^{21}
10^{14}	1.26	1.41	3.62	96.44		

The observed positive sign of thermopower for both unirradiated and irradiated $Ge_{20}Se_{74}Bi_6$ thin film samples at a fluence of 5 x 10^{13} ions/cm^2 indicates that the hole conduction is predominant even after irradiation. The temperature dependence of S corresponds to the energy difference between the Fermi level and the energy level where charge transport occurs. The expression for S is given by

$$S = \left(\frac{k}{e}\right)\left[\left(\frac{\Delta E_s}{kT}\right) + A\right] \quad (5)$$

where

$$\Delta E_s = (E_F - E_V) or (E_C - E_F)$$

and A is the small constant between 1 and 4, dependent on the nature of the scattering processes. Fig. 4 shows the temperature dependence of the thermo-electric power (S) for unirradiated and irradiated $Ge_{20}Se_{74}Bi_6$ thin films. The linear portion of the TEP data were fitted using the equation (5) and the corresponding values of the activation energy (ΔE_S) has been calculated. The values ΔE_S of $Ge_{20}Se_{74}Bi_6$ decreases with the increase in fluence. ΔE_S

may be, in general, lower than ΔE_σ and this difference is considered as equal to the mobility activation energy or to the polaron-hopping barrier if the conduction is by small polarons.

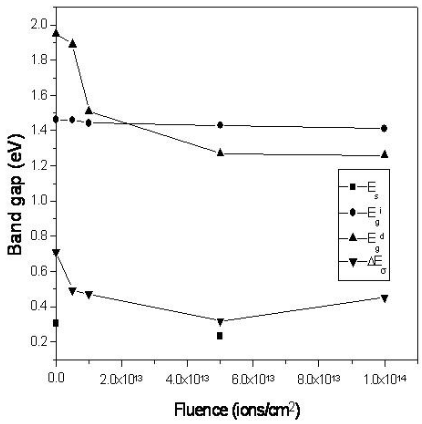

Fig. 5. Direct (E_g^d) and indirect optical gaps (E_g^i), electrical activation energy ΔE_σ, and thermoelectric activation energies ΔE_S versus fluence for $Ge_{20}Se_{74}Bi_6$ thin films .

From the thermoelectric measurements, the free-charge carrier concentration was calculated using the equation

$$n_S = 2M^{3/2}\exp\left(\frac{-\Delta E_S}{kT}\right) \qquad (6)$$

where M = ($2\pi mkT/h^2$), k is the Boltzmann constant. From the values of the thermal activation energy (ΔE_σ), the free charge carrier concentration for different samples can be calculated using the equation

$$n_\sigma = 2M^{3/2}\exp\left(\frac{-\Delta E_\sigma}{kT}\right) \qquad (7)$$

where M = ($2\pi mkT/h^2$), k is the Boltzmann constant. The calculated values of the free charge carriers are given in Table 1.

It is evident from this table that the free charge carrier concentration increases with the increase in Ni ion fluence. Fig. 4 compares the values of activation energy obtained from dc conductivity and thermopower measurements, band gaps obtained from optical measurements for unirradiated and irradiated $Ge_{20}Se_{74}Bi_6$ thin films for different ion fluences. In general it is found that activation energies and band gap decrease with increasing ion fluence.

4. Conclusions

In the present case the irradiation process induces wide distribution of localized states in the band gap. Thus the decrease in the value of ΔE_σ is associated with the increased tailing of band edges and production of localized states. The analysis of the results of conductivity, optical absorption and thermoelectric power data revealed that ion irradiation induces states near the Fermi level which contribute to the electronic conduction process by a variable range hopping mechanism. The band tailing parameter β increases with the increase in ion fluence indicating that there is an increase in the rigidity of the network and an increase in structural randomness. The carrier transport remains p-type in both unirradiated and irradiated samples.

Acknowledgement

Author is thankful to SSPL New Delhi India for EPMA and Prof. Nirmal Singh of Physics Department Panjab University Chandigarh India for XRF. The author thank the director NSC for providing the Pelletron facility, director UGC-DAE, Consortium for Scientific Research, Indore for electrical and thermoelectric measurements. The author is grateful to Dr. V. Ganesan UGC-DAE, Consortium for Scientific Research, Indore and Dr.Y.K.Vijay of University of Rajasthan, Jaipur, India for providing the experimental facility.

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