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Electrical conductivity and thermoelectric power of a-Ge_{20} $Se_{80-x}Bi_x$ thin films

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Abstract The dc electrical conductivity and thermoelectric power of a-$Ge_{20}Se_{80-x}Bi_x$ ($x = 0, 4, 6, 8, 10, 12$) thin films are reported in the present work. The thin films were deposited by flash evaporation at 10^{-5} Torr pressure and were well-characterized taking XRD, XRF, DSC and EPMA measurements of the system. The dc conductivity was measured over a temperature range 77 to 476 K. Conduction type and activation energies of electrical conductivity have been determined. The electrical transport takes place via two modes extended state conduction at higher temperatures and variable range hopping at lower temperatures. The conductivity was found to change by few orders of magnitude with Bi doping and the electrical activation energies (ΔE_σ) were found to decrease with increasing Bi content. The density of localized states and pre-exponential factor were determined. The thermopower measurements carried out using differential dc method in the temperature range 4.2 to 300 K and the activation energy (ΔE_s) for TEP determined. The change in band gap with increasing Bi content is due to increased band tailing and increase of Bi—Se bonds and decrease of Se—Se bonds thus leading to the modification of the network structure of $Ge_{20}Se_{80}$ system.

Keywords Electrical conductivity · Thermopower · Thin films · Chalcogenides · Band tails

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Introduction

Recent advances and trends in the field of chalcogenide semiconductors reveal applications in xerography, switching and memory devices, and reversible phase change optical recording [7–10, 12, 17]. Chalcogenides were considered for a long time to be insensitive to the added impurity as each impurity atom could satisfy its valence requirement by adjusting its nearest neighbour environment [13]. However, the effect of charged additives in lone pair semiconductor depend on whether the charged additives equilibrate or not with valence alternation defects [15]. The DC electrical conductivity measurements over a wide temperature range are needed to study the electronic structure of amorphous semiconductors. The dc electrical conductivity and thermoelectric power (TEP) of a-$Ge_{20}Se_{80-x}Bi_x$ ($x = 0, 4, 6, 8, 10, 12$) thin films as a function of composition are reported here.

Experimental

Bulk $Ge_{20}Se_{80-x}Bi_x$ ($x = 0, 4, 6, 8, 10, 12$) samples were prepared by the conventional melt quenching technique. Thin film samples were deposited on ultrasonically cleaned glass substrate using the flash evaporation technique at room temperature and vacuum of 10^{-5} Torr. Samples were well-characterized using XRD, XRF, DSC and EPMA data.

A Keithley model 617 electrometer was used for measuring resistance of the sample and the temperature was controlled to an accuracy of better than 10 mK 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 through an IEEE – 488 interface bus. The dc

Table 1 Various parameters calculated from dc conductivity for $Ge_{20}Se_{80-x}Bi_x$ thin films

Composition	σ_0 ($\Omega^{-1}cm^{-1}$)	ΔE_σ (eV)	σ_{h0} ($\Omega^{-1}cm^{-1}$)	T_0	$N(E_F)$ ($cm^{-3}eV^{-1}$)	R (cm)	W (eV)	n_σ (cm^{-3})
$Ge_{20}Se_{80}$	6.29×10^{-4}	0.858	2.68×10^{4}	1.24×10^{9}	1.498×10^{16}	1.29×10^{-6}	7.42	9.95×10^{10}
$Ge_{20}Se_{76}Bi_4$	1.01×10^{-3}	0.862	2.47×10^{-2}	2.95×10^{8}	6.30×10^{16}	9.01×10^{-7}	5.18	8.52×10^{10}
$Ge_{20}Se_{74}Bi_6$	2.98×10^{-5}	0.712	6.85×10^{-3}	1.86×10^{8}	9.98×10^{16}	8.03×10^{-7}	4.62	2.81×10^{13}
$Ge_{20}Se_{72}Bi_8$	3.24×10^{-5}	0.689	2.21×10^{-5}	1.06×10^{8}	1.76×10^{17}	6.97×10^{-7}	4.01	6.83×10^{13}
$Ge_{20}Se_{70}Bi_{10}$	6.99×10^{-6}	0.661	3.36×10^{-7}	2.96×10^{7}	6.27×10^{17}	5.07×10^{-7}	2.92	2.01×10^{14}
$Ge_{20}Se_{68}Bi_{12}$	1.09×10^{-5}	0.600	1.12×10^{-9}	1.66×10^{7}	1.12×10^{18}	4.39×10^{-7}	2.52	2.13×10^{15}

conductivity was measured over a temperature range 77 to 476 K.

The thermoelectric power (TEP) was measured using the differential dc method in the temperature range 4.2–300 K. Lakeshore temperature controller was used to maintain a controlled sample temperature (±30 mK) 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 min each, the TEP data recorded are estimated to have around 50 nV/K resolution. The dc conductivity and TEP measurements were carried out at UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore-452017, India.

Results and discussions

The X-ray diffraction patterns for the samples were found to contain no sharp peaks, indicating that all the samples were amorphous in nature. The compositions of the bulk alloy and thin films were confirmed using Electron Probe Micro Analysis and X-Ray Flouresence respectively. The crystallization and glass transition temperatures of each alloy determined using Differential Scanning Calorimetry.

The temperature dependence of the dc electrical conductivity σ gor amorphous $Ge_{20}Se_{80-x}Bi_x$ thin films was measured in the temperature range 77 to 476 K. It was found that σ increases with the increase of temperature for all compositions indicating that they have a semiconducting behaviour. Two types of conduction channels contributing to conductivity were found and the linearity in the high temperature region indicating that σ in this region exhibits activated behaviour [13] according to

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

where σ_0 is the pre-exponential factor and ΔE_σ is the conduction activation energy, which is a function of the electronic energy levels of the chemically interacting atoms in the glass and hence the emerging band gap. The conductivity data at high temperature is shown in Fig. 1. The values of σ_0, ΔE_σ and σ_{RT} as obtained from Fig. 1 are listed in Table 1.

With increasing Bi content, while the conductivity was found to increase, the activation energies (ΔE_σ) were found to decrease. The band energy gap is affected by the distribution of defect states within the band gap [15]. It is observed that conductivity increases by about an order of magnitude on Bi addition. Infact the existence of two different slopes in the temperature characteristic of the electrical conductivity indicates a competition between different conduction mechanisms.

In disordered semiconductors, low temperature electrical transport occurs via localized electronic states near a so-called 'transport level' (E_t) which depends on the DOS shape, fermi level position and temperature [1–3, 6, 11, 18]. As the temperature decreases, the activated Arrhenius behavior is replaced by a power law relationship between the logarithm of conductivity and temperature. The low temperature variable range hopping conductivity [14] is given as

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

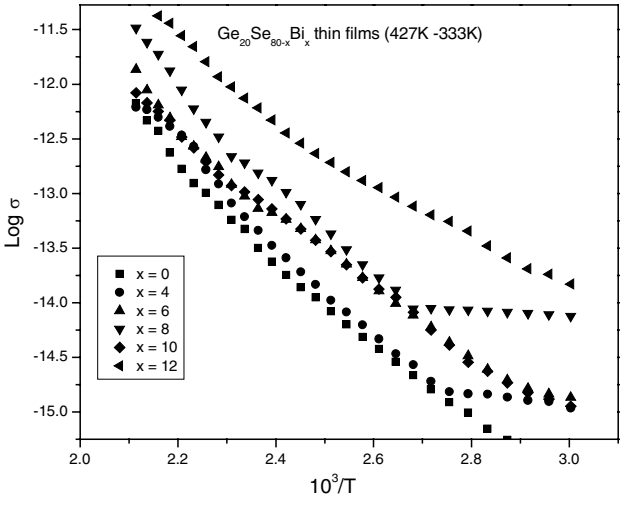

Fig. 1 log σ versus10^3/T for $Ge_{20}Se_{80-x}Bi_x$ thin films in high temperature region

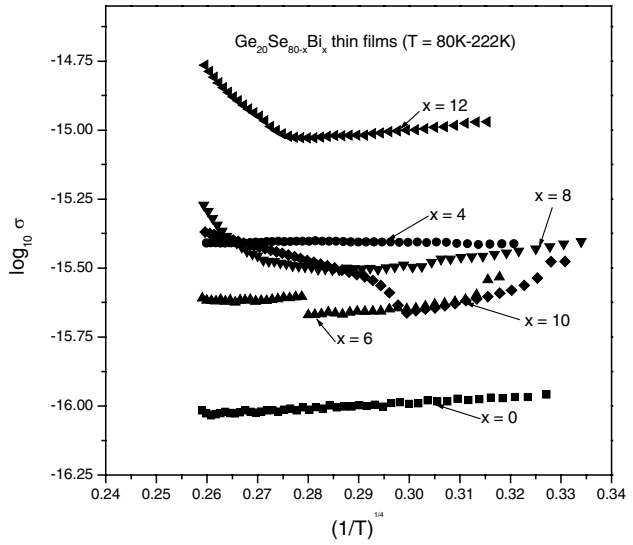

Fig. 2 log σ versus $(1/T)^{1/4}$ for $Ge_{20}Se_{80-x}Bi_x$ thin films in the low temperature region

where, T_0 is the hopping parameter which is given as

$$T_0 = \left(\frac{16\alpha^3}{kN(E_F)}\right) \tag{3}$$

and 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 which is taken as 10^{-9} m for electrons.

The $T^{-1/4}$ law does not result from any particular density of states distribution but rather from the dimensionality of the system. The log σ glotted linearly against $(1/T)^{1/4}$ is shown in Fig. 2, indicating that in this region, the transport is due to variable range hopping of charge carriers in the localized states near the Fermi level and is characterized by relation (2). Fitting low temperature data with Eq. (2) values of T_0 , σ_{h0} and density of states at the Fermi level $N(E_F)$ determined and are listed in Table 1. The other hopping parameters calculated using $N(E_F)$ includes the hopping distance R (cm), the average hopping energy W (eV) and the free charge carrier concentration, n [13, 16] are listed in Table 1. It is evident from this table that the free charge carrier concentration and density of states increases, while R and W decreases with increase in the Bismuth concentration. It is observed that in present case, the necessary conditions of Mott's Variable Range Hopping process, i.e., $W > kT$ and $\alpha R >> 1$ are satisfied. Thus the addition of Bi to $Ge_{20}Se_{80}$ glass produces a modified semiconductor by incorporating impurity induced structural modification in the host network of the vitreous semiconductor. When Bi added to Selenium rich glass $Ge_{20}Se_{80}$, it modifies the amorphous network to enter mostly into $(Se)_n$ chains [5] connecting the tetrahedral units and will thus make Bi—Se bonds.

The calculated values of activation energy and pre-exponential factor in the high temperature region (Table 1) suggest that the conduction is due to thermally assisted tunneling of charge carriers in the localized states present in band tails. The decrease in the activation energy with increasing Bi content entails an increase in conductivity. This decrease in activation energy can be attributed either to a decrease in the mobility gap, or to a increase in the width of the localized states region. On the other hand σ_0 gives an indication on the number of localized states in the gap. The decrease of σ_0 marks the increase of localized states in the gap. This result is further confirmed with the values of $N(E_F)$ which increases with increasing Bi content.

The valence band in Selenium rich systems is supposed to arise from the non-bonding lone pair $4p$ states and the conduction band from σ^* antibonding states of the chalcogen. In the Bi—Ge rich side, the valence band is expected to arise from the σ bonding states and the conduction band from the σ^* antibonding states. At the intermediate compositions, the valence band probably arises from the lone-pair p-band of the chalcogen and the conduction band from the resonating Bi—Bi p bond or sp^3 hybridized Ge—Se bonds [4]. As the concentration of Bi increases, the states will become delocalized and form the resonating p state character, first producing localized and then delocalized states as the bismuth content increases.

The general expression for thermoelectric power, S, is given by

$$S = \left(\frac{k}{e}\right)\left[\left(\frac{\Delta E_S}{kT}\right) + A\right] \tag{4}$$

where

$$\Delta E_S = (E_F - E_V) \text{ or } (E_C - E_F)$$

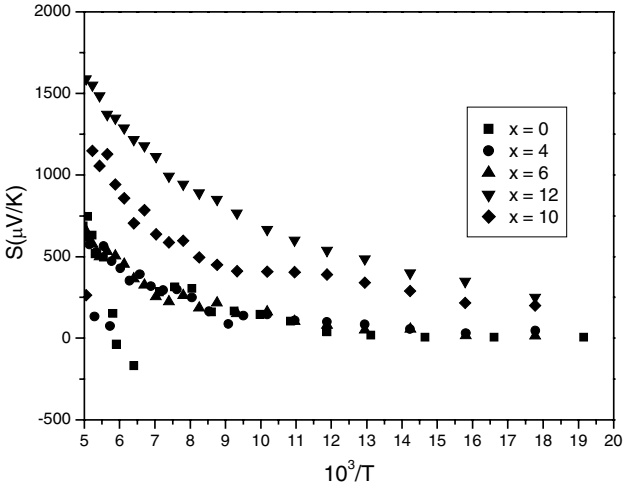

Fig. 3 Thermopower vs. $10^3/T$ for $Ge_{20}Se_{80-x}Bi_x$

Table 2 Parameters calculated from TEP measurements for $Ge_{20}Se_{80-x}Bi_x$

Composition	ΔE_S (eV)	n_S (cm^{-3})
$Ge_{20}Se_{80}$	0.358	2.42×10^{19}
$Ge_{20}Se_{76}Bi_4$	0.324	8.95×10^{19}
$Ge_{20}Se_{74}Bi_6$	0.306	1.85×10^{20}
$Ge_{20}Se_{72}Bi_8$	0.2845	4.10×10^{20}
$Ge_{20}Se_{70}Bi_{10}$	0.27	7.58×10^{20}
$Ge_{20}Se_{68}Bi_{12}$	0.25	1.57×10^{21}

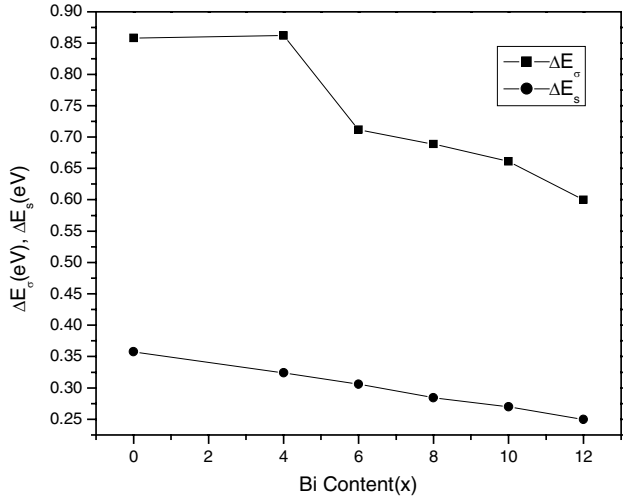

Fig. 4 Electrical activation energy ΔE_σ and TEP activation energy ΔE_s vs. Bi content for $Ge_{20}Se_{80-x}Bi_x$

and A is constant which depends on the nature of the scattering processes. Figure 3 shows the temperature dependence of the thermo-electric power (S) for $Ge_{20}Se_{80-x}Bi_x$ and the activation energy (ΔE_S) determined are reported in Table 2. The value of ΔE_S is found to decrease with the increase in Bi concentration. The difference ($\Delta E_\sigma - \Delta E_S$) decrease with the increase in Bi concentration in $Ge_{20}Se_{80-x}Bi_x$.

Conclusions

Critical analysis indicated two types of conduction mechanisms viz, extended state conduction (at higher temperatures) and variable range hopping (at lower temperatures). In the high temperature region conductivity exhibits thermally activated behaviour. Value of conduction activation energy was found to decrease with increasing Bi:Se ratio. The value of ΔE_σ is 0.858 for $Ge_{20}Se_{80}$ and it is decreased to 0.60 for $Ge_{20}Se_{68}Bi_{12}$. In the low temperature regime variable range hopping conduction dominates in which logarithm of conductivity varies as inverse of $T^{-1/4}$. The density of localized states increased from 1.498×10^{16} for $x = 0$ to 1.12×10^{18} for $x = 12$, while the hopping distance decreased from 1.29×10^{-6} cm for $x = 0$ to 4.39×10^{-7} and the hopping energy decreased from 7.42 eV for $x = 0$ to 2.52 eV for $x = 12$. The free charge carrier concentration values is found to increase from a value of 9.95×10^{10} cm^{-3} for $x = 0$ to 2.13×10^{15} cm^{-3} for $x = 12$. Both the necessary conditions for Mott's variable range hopping process are satisfied. The addition of Bi to $Ge_{20}Se_{80}$ glass produces modification in the host network, Bi will make bonds with Se. The decrease in band gap with increasing Bi amount is also related to the increase of Bi-Se bonds and the decrease of Se–Se bonds thus leading to the modification of the network structure of $Ge_{20}Se_{80}$ system. Positive sign of thermoelectric power suggest presence of p-type conduction in $Ge_{20}Se_{80-x}Bi_x$ samples. The thermoelectric power was found to increase with increasing temperature and with increasing Bi content. The values of activation energy for thermopower, ΔE_S is found to decrease with increasing value of "x" in $Ge_{20}Se_{80-x}Bi_x$ samples. The observed changes in thermopower could be due to increase in tailing of bands and the potential barrier at grain boundaries.

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