Structural and Electrical Properties of Ge$_{12}$Bi$_x$Se$_{88-x}$ Films

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ABSTRACT

Ge$_{12}$Bi$_x$Se$_{88-x}$ system (x=3.5-17.5) was prepared by melt quenching technique using 99.999% purity of Ge, Se, and Bi. Thin films were deposited on cleaned glass substrate by the pulse laser deposition [PLD] technique using Nd:YAG laser operated at the wavelength of 532 nm. The thickness of the films [180-200 nm] was measured using a stylus profile. The energy dispersive analysis of X-ray [EDAX] attached by scanning electron microscope [SEM] is used to check the chemical composition of powders and films. The films were characterized by X-ray diffractometer [XRD], transmission [TEM] and scanning [SEM] electron microscopes. There aren't sharp diffraction peaks revealing the amorphous state of the prepared films. This was confirmed by TEM, however, the patterns of Ge$_{12}$Bi$_x$Se$_{88-x}$ powder with x = 3.5 – 17.5 indicate the polycrystalline nature of the compounds. The electrical conductivity was measured for the as-prepared films in the temperature range from 299 to 431K. The activation energy ΔE was estimated from the curve of “dc” electrical conductivity as a function of reciprocal of temperature. The results showed two regions with deferent values of ΔE which can be analyzed in the frame of Mott and Davis model.

Key words: Ge$_{12}$Bi$_x$Se$_{88-x}$, PLD technique, thin films, electrical properties

Introduction

Materials of amorphous nature have attracted much attention in the last decades because of the lack of understanding of many of its properties.

In recent years, significant amount of efforts have been exerted to understand the effect of bismuth on the electrical conduction in bulk semiconducting glasses. Unlike most other bulk semiconducting glasses, which are on the other hand p-type and insensitive to impurity doping, “Bi” doped Ge-X glasses [X = S or Se] show a carrier type reversal from p-type to n-type at a certain “Bi” doping level (Thomas and Philip, 1998).

Experimental on electrical resistivity and thermoelectric power were carried out on Ge$_{12}$Bi$_x$Se$_{88-x}$ glasses where x between 0 and 13 (Tohge et al., 1980). Between x = 9 and 10, the resistivity reduced by about four orders of magnitude followed by reduction in the activation energy and stayed constant for x ≥ 10. Measurement of the thermoelectric indicated that the conduction type is changed from “p” to “n” and is accompanied by reduction in resistivity. In n-type glasses, each of hopping conduction in the localized states tail and conduction in extended states were proposed in parallel. The optical band gap was estimated also and it was very slightly altered by adding Bi more than 2.5 at. %.

The same result is observed by A. El-Korashy et al. (El-Korashy et al., 2005) since they found that at x = 0, “Eg” is below the middle of the optical energy gap which indicated that the conduction is p-type. By incorporation of “Bi” with x = 5 at%, a shift of “Eg” nearer to the middle of the gap occurred and the value of conductivity increases while the conduction stays p-type. By adding more “Bi” to x = 10 at%, a shift of “Eg” slightly above the middle of the gap occurred and the value of conductivity increases suddenly while conduction turned from p- to n-type.

The aim of the present study is investigating the influence of “Bi” content on the structure and electrical properties of Ge$_{12}$Bi$_x$Se$_{88-x}$ thin films.

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Experimental details:

Bulk Ge\(_{12}\)Bi\(_x\)Se\(_{88-x}\) [\(x = 3.5, 7, 10.5, 14, 17.5\)] samples were prepared by the conventional melt quenching technique. An appropriate mixture of 99.999% purity of “Ge”, “Se”, and “Bi” was taken in chemically cleaned quartz ampoules. The ampoules were sealed under vacuum and held at 1000 °C for 24 h in a furnace in order to ensure a homogeneous melt and the melt is then quenched in ice water. Thin film samples were deposited on ultrasonically cleaned glass substrate using the pulse laser deposition (PLD) technique using Nd:YAG laser [the deposition is done in laser technology unit, national research center, Giza, Egypt] operated at the wavelength of 532 nm. The targets were put in a vacuum chamber at a background pressure of \(5 \times 10^{-4}\) torr with the laser power of 1.4 J. Ge\(_{12}\)Bi\(_x\)Se\(_{88-x}\) films were deposited at room temperature. The pulse repetition rate was set at 10 Hz and the incidence angle was 45°. The thickness of the films [180-200 nm] was measured using a stylus profile.

The structural properties of the films were determined using an X-ray diffractometer [XRD] [Type Philips X’Pert], high resolution transmission electron microscope (HRTEM) [Type JEOL-JEM 2100], field emission scanning electron microscope (FESEM) [type Philips-Quanta FEG 250]. The chemical composition of powder and films was checked by energy dispersive X-ray analysis which is attached to (FESEM) [type Philips-Quanta FEG 250].

The electrical conductivity measurements were carried out for the as-prepared films using a conventional circuit involving a keithley electrometer [Type Keithley 614] in the temperature range of 299–431 K. Metal electrodes “Ag” were pasted on the film surfaces.

Results and Discussion

Structure characterization:

X-ray diffraction:

Fig.1 Shows XRD patterns of Ge\(_{12}\)Bi\(_x\)Se\(_{88-x}\) powders with \(x = 3.5 – 17.5\). The presence of sharp peaks proves the polycrystalline nature of the prepared samples.

Analysis of x-ray shows that the prepared powder samples are mixed phases. The observed phases are Bi\(_2\)Se\(_3\) exhibits rhombohedral phase [JCPDA data cards No. 33-0214] and Ge-Se orthorhombic phase [JCPDA data cards No. 72-1468], GeSe\(_2\) [JCPDA data cards No. 71-0117] and Se [JCPDA data cards No. 75-1162] show monoclinic while as Bi\(_{0.38}\)Ge\(_{0.15}\)Se\(_{0.47}\) can't be identified which agree with JCPDA data cards No. 51-0985 (Rajagopalan and Reddy, 1998).

It is worth to mention that the dominant peaks are corresponding to the ternary composition Bi\(_{0.38}\)Ge\(_{0.15}\)Se\(_{0.47}\) while as less peaks are corresponding to the binary phases Bi\(_2\)Se\(_3\), GeSe\(_2\) and GeSe. In addition, the peaks for the “Se” element could also be identified.

The samples of compositions [\(x = 3.5, 7\)] exhibit predominant diffraction lines corresponding to \(2\theta = 29.39\). While the samples for [\(x = 10.5, 14\) and \(17.5\)] exhibit predominant diffraction lines corresponding to \(2\theta = 18.59\) and \(18.5\) of Bi\(_{0.38}\)Ge\(_{0.15}\)Se\(_{0.47}\). The shifting of peak positions of these prominent diffraction lines suggests the formation of solid solution corresponding to Ge\(_{12}\)Bi\(_x\)Se\(_{88-x}\) material from the basic starting compounds “Ge”, “Bi” and “Se” (Khairnar et al., 2011).

Fig.2 shows the X-ray diffraction patterns of the as-deposited Ge\(_{12}\)Bi\(_x\)Se\(_{88-x}\) films. As can be seen from the figure, there aren't sharp diffraction peaks indicating amorphous state of prepared films. This was confirmed by TEM.

Energy dispersive X-ray spectroscopy:

The elemental compositions of Ge\(_{12}\)Bi\(_x\)Se\(_{88-x}\) [\(x = 3.5, 7, 10.5, 14\) and \(17.5\)] for powders and thin films were investigated using EDAX. Fig.3 shows the spectral distribution of the constituent elements for the Ge\(_{12}\)Bi\(_{17.5}\)Se\(_{90.5}\) thin film as an example. The obtained results of EDAX for different compositions of Ge\(_{12}\)Bi\(_x\)Se\(_{88-x}\) powders and films are recorded in Table 1 which show that there is only small deviation in composition from the starting materials but for \(x = 3.5\) the atomic percentages of “Ge” and “Se” aren't as expected values. This can be attributed to the fact that “L-α” peaks [which arise from transition of electron from M-shell to L-shell] for “Ge” and “Se” are very close [1.188 and 1.379 keV]. The small deviation of atomic percentage is expected for these two elements. This can be attributed to the resolution limit of the instruments (Das and Ganesan, 1998).
Fig. 1: X-ray diffraction pattern of Ge-Bi-Se system in powder form (a) Ge$_{12}$Bi$_{3.5}$Se$_{84.5}$ (b) Ge$_{12}$Bi$_{7}$Se$_{81}$ (c) Ge$_{12}$Bi$_{10.5}$Se$_{77.5}$ (d) Ge$_{12}$Bi$_{14}$Se$_{74}$ (e) Ge$_{12}$Bi$_{17.5}$Se$_{70.5}$.

Fig. 2: X-ray diffraction patterns of as-deposited Ge-Bi-Se system thin films (a) Ge$_{12}$Bi$_{3.5}$Se$_{84.5}$ (b) Ge$_{12}$Bi$_{7}$Se$_{81}$ (c) Ge$_{12}$Bi$_{10.5}$Se$_{77.5}$ (d) Ge$_{12}$Bi$_{14}$Se$_{74}$ (e) Ge$_{12}$Bi$_{17.5}$Se$_{70.5}$.
**Fig. 3:** Energy dispersion X-ray spectrum of the Ge$_{12}$Bi$_{17.5}$Se$_{70.5}$ film.

**Table 1:** Energy dispersive spectral distribution of Ge$_{12}$Bi$_x$Se$_{88-x}$ powders and thin films.

<table>
<thead>
<tr>
<th>Target Compositions</th>
<th>Obtained Composition (at. %)</th>
<th>Bulk material</th>
<th>As-deposited film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$_{12}$Bi$<em>3$Se$</em>{84.5}$</td>
<td>Ge 10.48 Bi 3.74 Se 85.78</td>
<td>17.85</td>
<td>6.06</td>
</tr>
<tr>
<td>Ge$_{12}$Bi$<em>7$Se$</em>{81}$</td>
<td>Ge 12.16 Bi 6.54 Se 81.30</td>
<td>12.44</td>
<td>7.57</td>
</tr>
<tr>
<td>Ge$<em>{12}$Bi$</em>{10.5}$Se$_{87.5}$</td>
<td>Ge 10.32 Bi 8.73 Se 80.94</td>
<td>10.41</td>
<td>10.49</td>
</tr>
<tr>
<td>Ge$<em>{12}$Bi$</em>{14}$Se$_{74}$</td>
<td>Ge 13.11 Bi 14.64 Se 72.25</td>
<td>13.52</td>
<td>13.57</td>
</tr>
<tr>
<td>Ge$<em>{12}$Bi$</em>{17.5}$Se$_{70.5}$</td>
<td>Ge 12.17 Bi 18.54 Se 69.28</td>
<td>11.55</td>
<td>18.71</td>
</tr>
</tbody>
</table>

**Scanning Electron Microscope:**

Fig. 4 shows the SEM of as-deposited Ge$_{12}$Bi$_x$Se$_{88-x}$ films that indicate a smooth and uniform morphology throughout the films consisting of small grains of more or less equal size. We see also bright white spots all throughout the film. This may be due to the existence of “Bi” which is not fully networked in the Ge-Se matrix.

**Transmission Electron Microscope:**

Fig. 5 shows the TEM micrograph and the corresponding electron diffraction patterns of as-deposited Ge$_{12}$Bi$_x$Se$_{88-x}$ films of thickness < 100 nm. The electron diffraction patterns indicate that the films have a polycrystalline nature. It is interesting to observe that there are diffraction rings in the case of the as-deposited films compared to XRD as previously mentioned. This shows that the as-deposited films consist of the micro crystallites which were not detected in the x-ray diffraction study (Desai et al., 2001).

A representative TEM micrographs Fig. 5 (a) sample of $x = 3.5\%$ shows multiple reflections and steps due to overlapping of layers during growth while Fig. 5 (b, c, d, e) for $x = 7, 10.5, 14$ and $17.5\%$ show randomly distributed tiny crystals covering most of the film surface.

The corresponding selected area electron diffraction (SAED) pattern for samples $x = 3.5, 7$ and $14\%$ consists of diffraction discontinuous rings with spots of strong intensity which indicate that these films are made of bigger crystallites. For $x = 14\%$ we notice that the rings are sharper. The SAED pattern for samples $x = 10.5$ and $17.5\%$ shows that Stacking faults and twin boundaries were found as the main defect type within films.

Finally, from TEM micrographs it can be concluded that the formed films consist of fine micro crystallites with some orientation with increasing “Bi” content.
Fig. 4: SEM images for the as-synthesized Ge-Bi-Se system thin films (a) Ge$_{12}$Bi$_{3.5}$Se$_{84.3}$ (b) Ge$_{12}$Bi$_{7}$Se$_{81}$ (c) Ge$_{12}$Bi$_{10.5}$Se$_{77.5}$ (d) Ge$_{12}$Bi$_{14}$Se$_{74}$ (e) Ge$_{12}$Bi$_{17.5}$Se$_{70.5}$. 
Fig. 5: TEM images for the as-synthesized Ge-Bi-Se system thin films (a) Ge$_{12}$Bi$_{3.5}$Se$_{84.5}$ (b) Ge$_{12}$Bi$_{7}$Se$_{81}$ (c) Ge$_{12}$Bi$_{10.5}$Se$_{77.5}$ (d) Ge$_{12}$Bi$_{14}$Se$_{74}$ (e) Ge$_{12}$Bi$_{17.5}$Se$_{70.5}$

**DC Electrical conductivity:**

The effect of “Bi” content on the electrical conductivity “$\sigma$”, of the as-prepared Ge$_{12}$Bi$_x$Se$_{88-x}$ [3.5 < $x$ < 17.5 at.%] thin films of thickness 180-200 nm are studied. It is observed that conductivity at room temperature increases from $2.43 \times 10^{-7}$ ($\Omega^{-1} \text{cm}^{-1}$) to $6.54 \times 10^{-7}$ ($\Omega^{-1} \text{cm}^{-1}$), with “Bi” addition.

The electrical conductivity “$\sigma$” as a function of reciprocal temperature for as-prepared films is shown in Fig. 6 according to the well known Arrhenius equation (Balboul et al., 2013; Mott and Davis, 1979):

$$\sigma = \sigma_0 \exp \left( -\frac{\Delta E}{kT} \right),$$

(1)
Where “σ₀” is the pre-exponential factor [Ω cm⁻¹], “ΔE” is the activation energy [eV] and “k” is the Boltzmann’s constant. From the slope and intercept on the y-axis, the activation energy, “ΔE”, and pre-exponential factor, “σ₀”, can be calculated.

From Fig. 6, it was found that “σ” increases by increasing temperature for all samples which indicates that they have a semiconducting behavior. Detailed analysis of Fig. 6 reveals that the plot consists of two regions [I] a high temperature band conduction region and [II] a low temperature tail region with two quite different slopes, indicating two different transport mechanisms prevail in a different temperature range. The values of the conductivity at room temperature, σ_RT, pre-exponential factor and activation energy for two regions are listed in Table 2.

![Fig. 6: Plot of ln conductivity versus reciprocal temperature for the as-deposited Ge_12Bi_xSe_88-x thin films](image)

### Table 2: Conductivity at room temperature and activation energy calculated from dc conductivity for Ge_12Bi_xSe_88-x thin films

<table>
<thead>
<tr>
<th>Composition</th>
<th>σ_RT (Ω cm⁻¹)</th>
<th>high temperature region</th>
<th>low temperature region</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge_12Bi_3Se_84.5</td>
<td>2.43×10⁻⁷</td>
<td>700.931</td>
<td>0.621</td>
</tr>
<tr>
<td>Ge_12Bi_5Se_82</td>
<td>3.06×10⁻⁷</td>
<td>246.103</td>
<td>0.575</td>
</tr>
<tr>
<td>Ge_12Bi_7Se_80</td>
<td>3.63×10⁻⁷</td>
<td>185.203</td>
<td>0.558</td>
</tr>
<tr>
<td>Ge_12Bi_9Se_78</td>
<td>4.75×10⁻⁷</td>
<td>98.405</td>
<td>0.527</td>
</tr>
<tr>
<td>Ge_12Bi_11.5Se_76.5</td>
<td>6.54×10⁻⁷</td>
<td>71.746</td>
<td>0.509</td>
</tr>
</tbody>
</table>

The measured conductivity is the sum of two components:

\[
σ = σ_{hop} + σ_{ext}
\]

Where σ_{hop} and σ_{ext} are the conduction contribution due to hopping between the nearest localized states and the conduction contribution between the extended states respectively.

In the high temperature region, the linearity denoted that “σ” is thermal activated process (Hassanien, A.S., A.A. Akl, 2016. Effect of Se addition on optical and electrical properties of chalcogenide CdSSe thin films. Superlattices and Microstructures, 89: 153.) according to equation [1].

Fig. 7 shows the variation of the activation energy for two regions with different compositions of Ge_12Bi_xSe_88-x. By increasing “Bi” content, the conductivity increased while the activation energies “ΔE” decreased. This means that at high concentrations of “Bi”, the Fermi-level may shift towards the conduction band (Bhatia, 1985). Also, the reduction of “ΔE” is due to the reduction of average binding
energy by addition of Bi (Amer et al., 2013; Hassanien and Akl, 2016; Fayek et al., 1995). As it is clear from SEM, spots of Bi appear at the surface of the samples. This can affect the conductivity of the films.

Similar results have been observed for glassy Ge$_{40}$Te$_{60-x}$Sb$_x$ alloys (Shukla and Kumar, 2010). The authors reported that the reduction in “$\Delta E$” because of the addition of “Sb” may alter the energy band diagram of Ge-Te by generating new charged centers in the mobility gap. This may lead to unpinning the Fermi level which in the undoped chalcogenides glasses is found in the middle between the deep line levels of the charged centers. When “Sb” is added to the Ge-Te system, it stimulates structural changes in the host network Ge-Te, leading to a readjustment in the local environment. This perhaps upset the balance of characteristic charged defects in a chalcogenide semiconductor, which can alter the electronic conduction. In such a case, the distribution and the localized states density are adjusted, and some new trap states can appear in the gap of semiconductor. Thus, we suppose that after addition of “Sb”, the Fermi energy level is shifted owing to changes in the energy states in the mobility gap. The value of ‘$\sigma_0$’ also increases by increasing “Sb”, which shows that the localized states density may be influenced by addition of “Sb”.

![Fig. 7: Plot the dependance of activation energy“$\Delta E$, on Bi concentration.](image)

In fact, the existence of two different slopes in the investigated temperature range suggests that there is a competition between different conduction mechanisms (Sharma et al., 2006). The activated Arrhenius behavior is substituted by a power law relationship between ln $\sigma$ vs. $(1/T)^{1/4}$ at low temperature.

The low temperature variable range hopping conductivity is characterized by Mott’s variable-range hopping relation (Mott and Davis, 1979; Sharma et al., 2006)

$$
\sigma_h = \sigma_{ho} \exp\left[-\left(T_o/T\right)^{1/4}\right]
$$

(3)

where $T_o$ is the hopping parameter given by:

$$
T_o = \left(\frac{16\alpha^3}{\kappa N(E_F)}\right)
$$

(4)

where $\sigma_{ho}$ is the pre-exponential factor for hopping conduction, “$\alpha$” is the decay length of a localized wave function at the Fermi level which is taken as $10^{-9}$ m for electrons, “$\kappa$” is Boltzmann’s constant and $N(E_F)$ is the density of states at Fermi level. The linear dependent of ln $\sigma$ against $(1/T)^{1/4}$ is shown in Fig. 8, showing 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 [3]. Fitting low temperature data with Eq. [3] values of $T_o$, $\sigma_{ho}$ and $N(E_F)$ are calculated and recorded in Table 3.
Fig. 8: ln $\sigma$ versus $(1/T)^{1/4}$ for Ge$_{12}$Bi$_x$Se$_{88-x}$ thin films in the low temperature region (a) Ge$_{12}$Bi$_{3.5}$Se$_{84.5}$ (b) Ge$_{12}$Bi$_3$Se$_{81}$ (c) Ge$_{12}$Bi$_{10.5}$Se$_{77.5}$ (d) Ge$_{12}$Bi$_{14}$Se$_{74}$ (e) Ge$_{12}$Bi$_{17.5}$Se$_{70.5}$

According to Mott (Mott, 1969), there are two hopping parameters which are hopping distance $R$ (cm) and the average hopping energy $W$ (eV). These parameters can be calculated by (Abdel-Rahim et al., 2012)

$$R = \left[ \frac{9}{8\pi\alpha N(E_F)K} \right]^{1/4}$$

and

$$W = \frac{3}{4\pi R^3 N(E_F)}$$

The calculated values of “$R$” and “$W$” for investigated films are recorded in Table 3.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\sigma_{ho}$ ($\Omega^{-1}cm^{-1}$)</th>
<th>$T_o$</th>
<th>$N(E_F)$ (cm$^{-3}$eV$^{-1}$)</th>
<th>$R$ (cm) At 299 K</th>
<th>$W$ (eV) At 299 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$<em>{12}$Bi$</em>{3.5}$Se$_{84.5}$</td>
<td>$5.33\times10^3$</td>
<td>1.97$\times10^6$</td>
<td>9.43$\times10^{11}$</td>
<td>1.10$\times10^{-5}$</td>
<td>0.189</td>
</tr>
<tr>
<td>Ge$_{12}$Bi$<em>3$Se$</em>{81}$</td>
<td>$4.43\times10^3$</td>
<td>1.85$\times10^6$</td>
<td>1.01$\times10^{18}$</td>
<td>1.084$\times10^{-6}$</td>
<td>0.186</td>
</tr>
<tr>
<td>Ge$<em>{12}$Bi$</em>{10.5}$Se$_{77.5}$</td>
<td>$2.87\times10^3$</td>
<td>1.69$\times10^6$</td>
<td>1.10$\times10^{18}$</td>
<td>1.061$\times10^{-6}$</td>
<td>0.182</td>
</tr>
<tr>
<td>Ge$<em>{12}$Bi$</em>{14}$Se$_{74}$</td>
<td>$2.61\times10^3$</td>
<td>7.53$\times10^6$</td>
<td>2.46$\times10^{18}$</td>
<td>8.665$\times10^{-7}$</td>
<td>0.149</td>
</tr>
<tr>
<td>Ge$<em>{12}$Bi$</em>{17.5}$Se$_{70.5}$</td>
<td>7.8</td>
<td>2.12$\times10^7$</td>
<td>8.75$\times10^{18}$</td>
<td>6.312$\times10^{-7}$</td>
<td>0.108</td>
</tr>
</tbody>
</table>

Conclusion

The structure and electrical conductivity of Ge$_{12}$Bi$_x$Se$_{88-x}$ are studied in the present work and the results can be summarized as the following:

1. XRD pattern of Ge$_{12}$Bi$_x$Se$_{88-x}$ powders with $x = 3.5 – 17.5$ indicates the polycrystalline nature of the compounds.
2. XRD pattern indicates the amorphous nature of films while TEM reveals that the films are polycrystalline materials.
3. There is a small deviation in the chemical composition of films from the powder which is detected by EDAX.
4. The electrical conductivity ($\sigma$) was measured in the temperature range from 299 to 431K for the as-prepared films compositions.
5. From the dc measurements, all compositions have a semiconducting behavior since the conductivity ($\sigma$) increases with the increase of temperature.
6. The two slopes in the temperature dependence of the electrical conductivity show that there are two different conduction mechanisms. The activation energy decrease from 0.621 to 0.509 by increasing Bi content.

References

Das, V.D., P.G. Ganesan, 1998. Thickness and temperature effects on thermoelectric power and electrical resistivity of (Bi0.25Sb0.75)2Te3 thin films. Materials Chemistry and Physics, 57: 57.