Electrical Properties of Amorphous Pb-Ge-Se Thin Films

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Abstract: Amorphous thin films of \( \text{Pb}_x\text{Ge}_{1-x}\text{Se}_{15} \) (\( 3 \leq x \leq 15 \)) and \( \text{Pb}_x\text{Ge}_{1-x}\text{Se}_{70} \) (\( 17 \leq x \leq 24 \)) have been prepared by thermal evaporation of bulk glasses of the same composition on glass substrates. Thermoelectric power measurements showed that p-type to n-type transition occurred in \( \text{Pb}_x\text{Ge}_{1-x}\text{Se}_{15} \) at \( x = 9 \) at. wt. \% Pb and in \( \text{Pb}_x\text{Ge}_{1-x}\text{Se}_{70} \) at \( x = 21 \) at. wt. \% Ge. The dc electrical resistivity of these samples was measured in the temperature range of 340 to 400 K. The sheet resistance \( (\rho_s) \) and the activation energy for electrical conduction \( (E_a) \) of the films decreased with increasing Pb content in the \( \text{Pb}_x\text{Ge}_{1-x}\text{Se}_{15} \) series, whereas \( \rho_s \) and \( E_a \) exhibited a maximum at 21 at. wt. \% of Ge in the \( \text{Pb}_x\text{Ge}_{1-x}\text{Se}_{70} \) series. The electronic conduction in the Pb-Ge-Se films in the measured temperature range has been attributed to the band transport mechanism.

Key words: Amorphous thin films, thermal evaporation, thermolectric power, optical band gap, dc electrical resistivity

INTRODUCTION

The pioneering work has demonstrated that majority charge carrier reversal (MCCR) could be realized in bulk (p-type) amorphous germanium chalcogenides with the addition of sufficient amount of Bi\(^{10}\) or Pb\(^{11}\). Several attempts have been made to understand this electronic transition. An overview of these models can be found elsewhere\(^8,9\). Extensive literature is available on bulk Pb modified germanium chalcogenide glasses\(^{12-14}\). These amorphous semiconductors with tailored properties have a potential for thermoelectric and photovoltaic device applications. To explore the possibility of such applications, it is necessary to obtain these materials in thin film form and to understand their physical properties. Some attempts have been made to prepare and study the properties of Bi-Ge-Se\(^{15}\) and Bi-Ge-Se-Te\(^{16-18}\) thin films. Rahman et al.\(^{19}\) have prepared amorphous \( \text{Pb}_x\text{Ge}_{1-x}\text{Se}_{15} \) (\( 7 \leq x \leq 9 \)) films by thermal evaporation technique and reported their activation energy of electrical conduction as a function of electrical field strength. The lack of a systematic study of amorphous Pb-Ge-Se thin films motivated us to prepare amorphous Pb-Ge-Se films from two series of bulk glasses and to study their electrical and optical properties. The compositions \( \text{Pb}_x\text{Ge}_{1-x}\text{Se}_{15} \) (\( 3 \leq x \leq 15 \)) and \( \text{Pb}_x\text{Ge}_{1-x}\text{Se}_{70} \) (\( 17 \leq x \leq 24 \)) were specifically chosen since the p-type to n-type transition has been reported to occur in these two series of bulk glasses. The objective was to understand the variation in the electrical properties of Pb-Ge-Se thin films as a function of composition.

MATERIALS AND METHODS

Thin films with composition of \( \text{Pb}_x\text{Ge}_{1-x}\text{Se}_{15} \) (\( 3 \leq x \leq 15 \)) and \( \text{Pb}_x\text{Ge}_{1-x}\text{Se}_{70} \) (\( 17 \leq x \leq 24 \)) were prepared by thermal evaporation of the respective bulk glasses on glass substrates under a low pressure of \( 10^{-4} \) Torr. The substrates were cleaned with neutral soap solution, rinsed with doubled distilled water, sonicated in an ultrasonic bath and dried in a hot air oven. Bulk glasses were evaporated from molybdenum boats. The substrates were rotated at the rate of 30 rpm in order to minimize variation in the thickness of the film. Films deposited has a mirror finish and showed good adherence to the substrate. The amorphous nature of the as-deposited samples was confirmed by the absence of any sharp peaks in the x-ray diffraction pattern obtained using a grazing incidence device (GID) attached to a powder X-ray diffractometer (Seifert 3003 T/T). Thermo electric power (TEP) measurement on the as-deposited films was carried out using an indigenously fabricated set-up. The TEP set-up consisted of a low-pressure chamber with a Teflon (PTFE) sample holder fitted with PT100 temperature sensors and a resistance heater. With this arrangement, a temperature gradient of 5 to \( 10^\circ \)C could be maintained across the ends of the thin film sample. The thermo EMF developed across the sample was measured with an electrometer (Keithley 6512) under a low pressure of \( 10^{-4} \) Torr. As a convention, the hot end of the film was connected to the positive \( Q \), which is characteristic of a p-type semiconductor. On the other hand, a positive potential difference gives a negative \( Q \), which is characteristic of

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n-type semiconductor. With this set-up, Q values within ±2% error could be obtained in the temperature range of 300 to 500 K. Composition analysis of the films was done using a Scanning electron microscope (Jeol 5800) equipped with EDAX facility. The film thickness was measured using a commercial ellipsometer (Gaertner LXUV910). The thickness of the samples was in range of 140 to 180 nm with an overall error of 2%. dc electrical resistivity of the thin films was measured by the four probe method. These measurements were performed over a temperature range of 340 to 400 K under a low pressure of 10⁻⁴ Torr. A constant current source (Keithley 220) and an electrometer (Keithley 6512) were employed in the measurements.

Table 1: Seebeck coefficient (Q) at 3.8 K, activation energy for thermo electric power (Eₐ), sheet resistance (ρₛ) at 3.8 K, activation energy for electrical conduction (Eₐ), and optical band gap of (E₀) Pb-Ge-Se thin films. The errors in the values of Q is ±2%, Eₐ is ±2%, Eₐ is ±2%, ρₛ is ±2% and E₀ is ±2%

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Q (mV K⁻¹)</th>
<th>Eₐ (eV)</th>
<th>ρₛ (10⁻⁴ Ω m)</th>
<th>E₀ (eV)</th>
<th>Sample composition</th>
<th>Q (mV K⁻¹)</th>
<th>Eₐ (eV)</th>
<th>ρₛ (10⁻⁴ Ω m)</th>
<th>E₀ (eV)</th>
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</thead>
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<tr>
<td>PbₓGeₙSeₙₓ</td>
<td>1.34</td>
<td>1.02</td>
<td>9.17</td>
<td>1.33</td>
<td>PbₓGeₙSeₙₓ</td>
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<tr>
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<td>4.18</td>
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<tr>
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<td>0.76</td>
<td>4.64</td>
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<td>0.89</td>
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<tr>
<td>PbₓGeₙSeₙₓ</td>
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<td>0.87</td>
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<td>0.95</td>
<td>PbₓGeₙSeₙₓ</td>
<td>-1.71</td>
<td>1.14</td>
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<tr>
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<td>1.09</td>
<td>0.81</td>
<td>0.77</td>
<td>PbₓGeₙSeₙₓ</td>
<td>-1.99</td>
<td>1.27</td>
<td>0.56</td>
<td>1.43</td>
</tr>
</tbody>
</table>

Fig. 1: Temperature dependence of the seebeck coefficient of amorphous, a) PbₓGe₁₋ₓSeₓ and b) PbₓGe₁₋ₓSeₓ thin films

Fig. 2: ln(σ) versus 1000/T plots for amorphous, a) PbₓGe₁₋ₓSeₓ and b) PbₓGe₁₋ₓSeₓ thin film
least squares fit to the $Q$ versus 1000/T plots, the activation energy ($E_a$) of each film composition was calculated and the same are given in Table 1.

The sheet resistance ($\rho_s$) of the as-deposited thin films measured at 348 K is tabulated in Table 1. It can be seen from the data that $\rho_s$ decreases with the addition of Pb in Pb$_{x}$Ge$_{1-x}$Se$_{y}$ films, whereas $\rho_s$ exhibits a maximum near the composition with 21 at. wt.% Pb$_{2}$Ge$_{3}$Se$_{16}$ films. The ln ($\sigma$) versus 1000/T plots for all the films are shown in Fig. 2. The activation energy for electrical conduction ($E_a$) calculated from the slope of the ln ($\sigma$) versus 1000/T curves is tabulated in Table 1.

**DISCUSSION**

The carrier sign reversal phenomenon observed in amorphous Pb-Ge-Se thin films could be interpreted in terms of KOLOBOV’s proposals of modifications in defect states with the addition of Pb. In the case of Selenium, the triply and singly coordinated defect states are Se$_{3}^{+}$ and Se$_{3}^{-}$, respectively. One can consider as a hole-bearing atom. X-ray studies have confirmed that Pb exists as Pb$^{2+}$ in lead chalcogenide glasses. With the addition of Pb to a-Ge-Se, Pb$^{2+}$ converts some into, whereas, the number of defect states remains unaffected. As the number of defects, the number of holes generated during thermal excitation also decreases. Simultaneously, the number of negative charge defect states increases. This results in the reduction of hole generating (triplly coordinated and positively charged) defect states and at the same time increases the number of electron generating (singly coordinated and negatively charged) defect states. This disturbance in the concentration of the VAPs culminates in the unpinning of the Fermi level and shifts it towards the conduction band.

In the case of Pb$_{x}$Ge$_{1-x}$Se$_{y}$, samples, the concentration of Pb remains constant, whereas Ge atoms gradually replace Se atom as we increase x. The effect of Pb in suppressing Se$_{3}^{+}$ defect states has already been discussed. When Ge replaces Se, Ge$_{3}^{-}$ states increase in number, gradually depleting Se$_{3}^{+}$. Effectively, the positively charged defect state responsible for the generation of holes reduces in number, resulting in the alternation of charge defect states. This unpins the Fermi level and shifts it towards the conduction band. Electron microscope studies on Pb-Ge-Se glasses do not show any noticeable inhomogeneities even at sub-micron scales. This observation rules out the percolation of microcrystalline clusters as a plausible mechanism for the carrier type change in these glasses.

The sheet resistance of the Pb$_{x}$Ge$_{1-x}$Se$_{y}$ monotonously decreased with increasing Pb concentration, whereas, in the case of Pb$_{2}$Ge$_{3}$Se$_{16}$ films, the sheet resistance showed a maximum near 21 at. wt.%.

The linearity of the ln ($\sigma$) versus 1000/T plots over the temperature range of study confirms that the electronic conduction is due to a single conduction mechanism, namely, band transport, in which the electron in the extended state behaves as a conduction electron.

A comparison of the above results obtained for amorphous thin films of Pb$_{x}$Ge$_{1-x}$Se$_{y}$ (3<x<15) and Pb$_{2}$Ge$_{3}$Se$_{16}$ (17<x<24) with the bulk glasses of appropriate composition reveals the following interesting feature. Amorphous Pb$_{x}$Ge$_{1-x}$Se$_{y}$ thin film exhibited p-type conduction, whereas the corresponding bulk composition showed n-type conduction. This observation suggests that a large number of dangling bonds (VAPs) are present in the thin film as compared to the bulk glass, demanding more Pb$^{2+}$ concentration for suppressing the Se$_{3}^{-}$ defects present in the thin films. However, no such difference was observed in the case of Pb$_{x}$Ge$_{3}$Se$_{16}$ films and bulk glasses. The thin films show a higher Q value in comparison with the corresponding bulk compositions, which may be due to the lower dimensionality of the thin films.

Amorphous Pb-Ge-Se thin films belonging to two series have been prepared by thermal evaporation of the respective bulk glasses. The Pb-Ge-Se thin films show a p to n-type conduction type change as a function of composition. Seebeck coefficient (Q) at 348 K, activation energy for thermo electric power ($E_a$), sheet resistance ($\rho_s$) at 348 K, activation energy for electrical conduction ($E_a$) Pb-Ge-Se thin films were determined by experimental measurement of the relevant physical entities. The dc conduction mechanism has been attributed to band transport mechanism. Composition dependence of Q and $E_a$ have been interpreted in terms of KOLOBOV’s model and variation in average bond energy, respectively. The high seebeck coefficient of these films and its variation with composition could be exploited in the fabrication of thermoelectric devices.

**REFERENCES**


