ELECTRICAL PROPERTIES OF GeSeTl THIN FILMS DEPOSITED BY E-BEAM EVAPORATION TECHNIQUE

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Five compositions of Ge$_{14}$Se$_{86-x}$Tl$_x$ (x=20,22,23.5,26.8 and 28%) are prepared using the melt quench technique. Thin films of thickness d = 15,30,60,90,120 and 180 nm were deposited using electron beam evaporation technique. All the films showed a non-Ohmic behavior. At higher range of ambient temperature, the activation energy $\Delta E_\sigma$ was studied as a function of the coordination number $r$, average number of constraints $N_{cos}$ and heat of atomization $H_s$. Mott's parameters of the system Ge$_{14}$Se$_{86-x}$Tl$_x$ were studied at lower range of temperature. The effect of annealing temperature $T_{ann}$ on the activation energy were taken in consideration.

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1. Introduction

The system Ge-Se-Tl considered to be one of the new generation of chalcogenide glasses. Therefore, a lot of work has been done on impurities effect on conductivity and optical properties [1-5]. The chemical bonds determine the structures and all properties of a body in any state of aggregation. The effect of the chemical ordering in determining the structure as compared to the influence of mechanical forces such as, strain associated with bond distortions, bond-stretching forces acting as mechanical constrains are present in Ge, Se and Tl, bond-bending constraints are also important in Ge, Se and Tl, this make Ge-Se-Tl a useful glass system to study. The change in transport properties of some chalcogenides is attributed to a corresponding change in thallium content [6-17]. Also, the addition of thallium to chalcogenide glasses causes a marked change in their structural properties [18-19]. The electrical conductivity found to increase with increasing thallium content [20]. Furthermore, it is reported that the activation energy decreases with increasing thallium content [21].

It is intended in this work to study the effect of the composition, the thicknesses and annealing temperature on the DC electrical properties of the films under test.

2. Experimental technique

99.999 purity Ge, Se and Tl were used with their appropriate mole percentage to prepare bulk samples of Ge$_{14}$Se$_{86-x}$Tl$_x$ (x = 20, 22, 23.5, 25, 26.5, and 28%) using the melt-quenching technique [5]. Thin films of the prepared compositions were deposited at room temperature by electron-beam evaporation at a pressure of $10^3$ torr using an Edwards high-vacuum coating unit model E306A. The rate of deposition was 1-2 nm s$^{-1}$. Ultrasonically cleaned Corning glass was used as a substrate. The film thickness was controlled by means of an Edwards TM200 Maxtek.
high vacuum film thickness monitor. The microstructure analysis was carried out using x-ray diffractometer type Philips model PW1710 which revealed that the prepared films under test were in amorphous state. The electrical measurements were carried out using two-terminal configuration by applying constant voltage to the sample and measuring the current through it using Keithley 614 electrometer. The electrical contacts were made by applying silver paste over the surface of the films with separation of 2 mm [22].

3. Results and discussions

The I - V characteristics for the thin films of the composition $\text{Ge}_{14}\text{Se}_{86-x}\text{Tl}_x$ (x=20,22,23.5,26.5 and 28%) of the same thickness 90 nm measured at the same ambient room temperature are shown in figure 1.

![Fig. 1. I-V characteristic curves of $\text{Ge}_{14}\text{Se}_{86-x}\text{Tl}_x$ thin films](image)

It is clear from figure 1 that the current $I$ increase with increasing thallium content. At low applied voltages, the current of the considered compositions approach to zero, the transition voltage $V_0$ at which the current increase abruptly depend on the composition as shown in figure 2.

![Fig. 2. Plots of $\ln I$-$\ln V$ of the compositions $\text{Ge}_{14}\text{Se}_{86-x}\text{Tl}_x$ thin films.](image)
Fig. 2 shows that the transition voltage $V_o$ decrease with increasing thallium content. Also, none of the slopes equal or approach to zero revealing non-Ohmic behavior.

The change of the current $I$ with changing the ambient temperature is demonstrated in figure 3.

It is clear from Fig. 3 that, for the same thicknesses (120 nm) of the composition $\text{Ge}_{14}\text{Se}_{86-x}\text{Tl}_x$ as an example to avoid repetition, as the measuring temperatures increase, the current $I$ increase too. In plotting the relations $\ln I$ – $\ln V$ for the thin films of the equal thicknesses at different measuring temperatures, the transition voltage $V_o$ found to decrease with increasing the measuring temperature. It was found also that, none of the slopes equal nor approach to unity revealing non-Ohmic behavior.

The thickness dependent of the $I – V$ characteristics is demonstrated in figure 4, where for the same composition ($x = 22\%$) and at fixed temperature (room temperature), the current $I$ found to decrease with increasing the thickness of the film.
The ln $\sigma - 1/T$ relations for the system Ge$_{14}$Se$_{86-x}$Tl$_x$ was found straight lines at higher range of T as shown in figure 5 which follow the equation;

$$
\sigma = \sigma_o e^{-\Delta E_{\sigma} / kT}
$$

(1)

Where $\sigma_o$ the pre-exponential factor, k is the Boltzmann constant, T is the absolute temperature and $\Delta E_{\sigma}$ is the activation energy for conduction which is a function of the energy gap. Both values of $\Delta E_{\sigma}$ and $\sigma_o$ are calculated from figure 5.

![Fig. 5. Plots of Ln $\sigma$ versus 1000/T for the compositions Ge$_{14}$Se$_{86-x}$Tl$_x$ thin films.](image)

The conduction activation energy $\Delta E_{\sigma}$ calculated from figure 5 found to decrease with increasing thallium content as recorded in table 1 which may owed to the decrease in the number of defected bonds in the selenium matrix [21]. For different thicknesses, the conduction activation energy $\Delta E_{\sigma}$ derived from figure 6 found to decrease slowly with increasing the film thickness, since it change from 0.667 to 0.604 as the thickness increase from 30 to 180 nm as seen in table 1.

![Fig. 6. Temperature dependence of the electrical conductivity for Ge$_{14}$Se$_{86}$Tl$_{20}$ thin films of different thickness.](image)
Table 1: Activation energy dependence on both composition and thickness.

<table>
<thead>
<tr>
<th>X%</th>
<th>$\Delta E_\sigma$ (eV)</th>
<th>$\sigma_\sigma$ ($\Omega m$)$^{-1}$</th>
<th>d nm</th>
<th>$\Delta E_\sigma$ (eV)</th>
<th>$\sigma_\sigma$ ($\Omega m$)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.915</td>
<td>499</td>
<td>30</td>
<td>0.667</td>
<td>824</td>
</tr>
<tr>
<td>22</td>
<td>0.844</td>
<td>219</td>
<td>60</td>
<td>0.646</td>
<td>692</td>
</tr>
<tr>
<td>23.5</td>
<td>0.781</td>
<td>103</td>
<td>90</td>
<td>0.625</td>
<td>639</td>
</tr>
<tr>
<td>26.5</td>
<td>0.716</td>
<td>48.6</td>
<td>120</td>
<td>0.619</td>
<td>503</td>
</tr>
<tr>
<td>28</td>
<td>0.646</td>
<td>21.2</td>
<td>180</td>
<td>0.604</td>
<td>389</td>
</tr>
</tbody>
</table>

It is obvious from table 1 that the pre-exponential factor $\sigma_\sigma$ decrease with increasing both thallium content and the thickness of the films which mean that the charge carrier mobility in the trap states decrease s with increasing thallium content.

The variation of the activation energy $\Delta E_\sigma$ with respect to the parameter which determine the deviation from stoichiometry $S$, coordination number $r$, average coordination number $\langle r_{\text{eff}} \rangle$, average number of constrain $N_{\text{con}}$ and average heat of atomization $H_s$ can be studied from table 2, whereas, these parameters were calculated from the following equations [23]:

$$r = 4XGe + 2XSe + 5XTl$$

$$N_{\text{con}} = N^\alpha + N^\beta$$

Where,

$$N^\alpha = \frac{r}{2}, \quad N^\beta = 2r - 3$$

$$\langle r_{\text{eff}} \rangle = \frac{2}{5}(N_{\text{con}} + 3)$$

$$H_s = (\alpha H_s^\alpha + \beta H_s^\beta + \gamma H_s^\gamma)/ (\alpha + \beta + \gamma)$$

$H_s^\alpha$ and $H_s^\beta$ are the average non-polar bond energy of the two atoms.

Table 2: $\Delta E_\sigma$, $r$, $S$, $\langle r_{\text{eff}} \rangle$, $N_{\text{con}}$, $H_s$ for the system Ge$_{14}$Se$_{86-x}$Tlx.

<table>
<thead>
<tr>
<th>x %</th>
<th>$S$</th>
<th>$r$</th>
<th>$\langle r_{\text{eff}} \rangle$</th>
<th>$N^\alpha$</th>
<th>$N^\beta$</th>
<th>$N_{\text{con}}$</th>
<th>$H_s$</th>
<th>$H_s/\langle r_{\text{eff}} \rangle$</th>
<th>$\Delta E_\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.532</td>
<td>2.880</td>
<td>2.880</td>
<td>1.440</td>
<td>2.76</td>
<td>4.200</td>
<td>53.87</td>
<td>18.71</td>
<td>0.915</td>
</tr>
<tr>
<td>22</td>
<td>0.598</td>
<td>2.940</td>
<td>2.940</td>
<td>1.470</td>
<td>2.88</td>
<td>4.320</td>
<td>53.74</td>
<td>18.28</td>
<td>0.844</td>
</tr>
<tr>
<td>23.5</td>
<td>0.649</td>
<td>2.985</td>
<td>2.985</td>
<td>1.493</td>
<td>2.97</td>
<td>4.463</td>
<td>53.64</td>
<td>17.97</td>
<td>0.781</td>
</tr>
<tr>
<td>26.5</td>
<td>0.757</td>
<td>3.074</td>
<td>3.073</td>
<td>1.533</td>
<td>3.15</td>
<td>4.63</td>
<td>53.44</td>
<td>17.39</td>
<td>0.716</td>
</tr>
<tr>
<td>28</td>
<td>0.814</td>
<td>3.120</td>
<td>3.13</td>
<td>1.560</td>
<td>3.24</td>
<td>4.800</td>
<td>53.35</td>
<td>17.04</td>
<td>0.646</td>
</tr>
</tbody>
</table>

It is seen from table 2 that, non of the compositions is a stoichiometric chalcogenide because non of the values of $S$ equals unity. The coordination number $r$ and the average coordination number $\langle r_{\text{eff}} \rangle$ increase with increasing thallium content, that is due to the larger coordination number of thallium with respect to that of selenium. The average number of constrain $N_{\text{con}}$ also increases with more enriching with thallium due to the larger value of the coordination number of thallium with respect to that of selenium. The average heat of atomization $H_s$ decrease with increasing thallium ratio which may owe to the larger value of the heat of atomization of selenium (49.4 k cal / gm .atom) with respect to that of thallium (43 k cal / gm .atom). Therefore, an increase in Tl leads to an increase in $N_{\text{con}}$ and $r$, on the other hand $\Delta E_\sigma$.  

\( \sigma_o \) and \( H_s \) decrease. Accordingly [24], the intercept \( \sigma_o \) is related to the density of localized states, as \( \sigma_o \) decreases the density of localized states increases. Replacing Tl instead of Se sites, leads to increasing the coordination number and corresponding modification in the chemical bond should directly affect the electrical properties of the Ge\(_{14}\)Se\(_{86-x}\)Tlx system. Besides, the observed changes in \( \Delta E_\sigma \) result from the local changes in the chemical bonding, therefore, the decrease in \( \Delta E_\sigma \), \( \sigma_o \) should be associated with a decrease in \( H_s \) and \( H_s / \langle r_{eff} \rangle \) where \( H_s \) represents the relative bond strength and \( H_s / \langle r_{eff} \rangle \) is the average single bond energy in the composition. Furthermore, It is suggested [24] that, the electrical conduction takes place in the extended states in the range of \( \sigma_o \) from \( 10^3 \) to \( 10^4 \ \Omega^{-1} \ m^{-1} \), and lower values of \( \sigma_o \) indicate greater participation of localizes states in the conduction process. The continuous decrease of \( \Delta E_\sigma \), \( \sigma_o \), \( H_s \) and \( H_s / \langle r_{eff} \rangle \) with increasing Tl content can be attributed to the presence of non-bridging selenium, which influenced the electron density around the bridging selenium that makes up the vitreous network [28].

At low temperature range, conduction take place through variable range hopping in localized states near the Fermi level. The plot of \( \text{Ln}[\sigma(T)T^{1/2}] \) vs \( T^{-1/4} \) found to be straight lines as shown in figure 7 which is in accordance with Mott’s variable range hopping process.

\[ \log(\sigma(T)) = kT^{-1/2} - \frac{1}{4} A^4 T^{-1/4} \]

Where
\[ A^4 = \frac{\lambda \alpha^3}{K g} \]

and \( \lambda \approx 16 \) is a dimensionless parameter, \( \alpha^{-1} \) the spatial extension of the wave function associated with the localized states and \( g \) is the number of localized state at the Fermi level. Also, the pre-exponential factor \( \sigma_o \) is given by:

\[ \sigma_o = 3e^2 v_{pb} (\frac{g}{8\pi aK})^{1/2} \]

**Fig. 7.** Plots of \( \text{Ln}(\sigma T^{1/2}) \) versus \( T^{-1/4} \) of the compositions Ge\(_{14}\)Se\(_{86-x}\)Tlx thin films.

Since, Mott assumes that, at very low temperatures, long hops from one site to the other become more likely than the sum of all other auxiliary hops so that the one-electron theory is applicable:

\[ \sigma(T) = \sigma_o T^{-1/2} e^{-A T^{-1/4}} \]
Since, \( \nu_{ph} \approx 10^{12} - 10^{13} \text{ Hz} \) is the characteristic phonon frequency in most amorphous materials. The average hopping distance \( R \) and the hopping energy \( W \) are given by:

\[
R = \left( \frac{9}{8 \pi \alpha kT g} \right)^{1/4}
\]

\[
W = \frac{3}{4 \pi R^3 g}
\]

The calculated Mott's parameters are recorded in table 2.

<table>
<thead>
<tr>
<th>Composition</th>
<th>( A(K^{1/4}) )</th>
<th>( \sigma_o(\Omega^{-1} \text{ cm}^{-1} K^{1/2}) )</th>
<th>( \alpha(\text{cm}^{-1}) )</th>
<th>( g(eV^{-1} \text{ cm}^{-1}) )</th>
<th>( R(\text{cm}) )</th>
<th>( W(eV) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=20%</td>
<td>19.77</td>
<td>16.666</td>
<td>4.64x10^4</td>
<td>1.21x10^20</td>
<td>2.65x10^{-7}</td>
<td>0.106</td>
</tr>
<tr>
<td>X=22%</td>
<td>21.454</td>
<td>16.622</td>
<td>5.45x10^4</td>
<td>1.42x10^20</td>
<td>2.45x10^{-7}</td>
<td>0.114</td>
</tr>
<tr>
<td>X=23.5%</td>
<td>24.983</td>
<td>15.979</td>
<td>7.10x10^4</td>
<td>1.70x10^20</td>
<td>2.19x10^{-7}</td>
<td>0.134</td>
</tr>
<tr>
<td>X=26.5%</td>
<td>25.535</td>
<td>16.039</td>
<td>7.47x10^4</td>
<td>1.80x10^20</td>
<td>2.13x10^{-7}</td>
<td>0.137</td>
</tr>
<tr>
<td>X=28%</td>
<td>27.823</td>
<td>15.573</td>
<td>8.58x10^4</td>
<td>1.96x10^20</td>
<td>2.02x10^{-7}</td>
<td>0.148</td>
</tr>
</tbody>
</table>

As it is seen in table 3 that, \( W/KT \) and \( \alpha R \) satisfy the necessary conditions for Mott's variable range hopping process, on the other side, \( g \) are unreasonably high which is observed for other materials [25-27], this may be owed to uncertainties involved in estimating \( \sigma_o \) in equation (8). This is because Mott's derivation of the variable range hopping relations implies a large number of simplifying assumption of which the most important are the energy independence of the density of localized states at the Fermi level, neglect of the correlation effect in tunneling processes and neglect of electron-phonon interaction. On the other hand, it is apparent from table 3 that the hopping distance \( R \) decrease with more enriching of thallium, whereas, the hopping energy \( W \) decrease with increasing thallium content. Further, the pre-exponential factor \( \sigma_o \) decreases very slightly with increasing thallium ratio ensuring that the charge carrier mobility and density of states increase.

In studying the effect of annealing temperature on the conduction activation energy, the variation of \( \ln \sigma \) vs \( 1/T \) has been drawn at different annealing temperatures (300, 328, 358, 390, 420, 450, 482, 510, 540, 570, and 598K) for thallium content 28%, and found to be straight lines verifying equation (1). From the slopes of the straight lines, the activation energies \( \Delta E_{\sigma} \) have been calculated and drawn vs annealing temperature as shown in figure 8. It is obvious that \( \Delta E_{\sigma} \) increase with increasing the annealing temperature which may be owed to the unsaturated defects are gradually annealed out producing a large number of saturated bond leading to a decrease in the density of localized states and consequently the energy gap increase.
4. Conclusion

It is concluded that: (1) All the films showed non-Ohmic behavior and the transition voltage becomes smaller with increasing thallium content, the thickness of the films and annealing temperature. (2) Both the activation energy $\Delta E_\sigma$ and the pre-exponential factor $\sigma_0$ decrease with increasing thallium content. (3) The activation energy $\Delta E_\sigma$ found to decrease with decreasing the heat of atomization $H_a$. (4) Increasing the numbers of constraints $N_{con}$ lead to decrease the value of $\Delta E_\sigma$. (5) Both the density of the localized states, hopping energy found to increase with increasing thallium concentration. (6) The hopping distance $R$ decreases with increasing thallium content. (7) The activation energy increases with increasing the annealing temperature.

References