The change and variations in electrical properties of the $\text{Se}_{85}\text{Ge}_{15-x}\text{In}_x$ amorphous thin film system before and after thermal annealing

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Abstract:
This paper studies the electronic properties of Theas prepared amorphous thin film system that constitutes $\text{Se}_{85}\text{Ge}_{15-x}\text{In}_x$, with $x = 0, 5, 10, 15$ at %, where ($x = 0, 5, 10, 15$ at %). Besides, the same study was done on the similar system of samples after hardening them thermally at 380 K, and 490 K for an hour each. According to the results, there is a decrease in the activation energy of the samples that were annealed, the IN content, and the temperature of annealing increases and as a result, there is an increase in the electrical conductivity.

I. Introduction
Any material containing S, Se, or Te, is called chalcogenide material. These materials have many applications in the scientific and technological fields. [1]. In the recent days the chalcogenide materials' researches focus on photonics and x-ray imaging, [2]. Amorphous Se chalcogenide shows unique semiconducting properties, [3–5]. It was found that the addition of some elements like Ge, In, and Sb, improve the Se optical sensitivity and its electrical conduction. [6–11]. As example (Se-Ge), (Se-In), and (Se-Ge-In) alloys confirm this idea. [12–19]. The structure of such alloys were studied using XRD, IR absorption, and other techniques [20–29], while DTA and DSC are good suitable tool to specify the fixed temperatures which affect the structure, [30]. Davis and Mott gave a model, which gives a good explanation for the DC conductivity of the amorphous semiconductors. [30–34].

The aim of this work is to study the effect of the thermal annealing temperature on the electrical properties of the thin film system having the composition, $\text{Se}_{85}\text{Ge}_{15-x}\text{In}_x$, where ($x = 0, 5, 10, 15$ at %).

II. Experimental technique:
The amorphous thin films of the system $\text{Se}_{85}\text{Ge}_{15-x}\text{In}_x$, with ($x = 0, 5, 10, 15$ at%), were prepared in two steps using two different techniques of preparations. First preparing the samples in solid bulk glassy ingots, and then preparing the amorphous thinfilms.

a- Preparation of the system $\text{Se}_{85}\text{Ge}_{15-x}\text{In}_x$, samples in glassy ingots.

The alloys of the system ingots were prepared using the well-known melt quenching technique, [4, 45]. This was done using the adequate molar amounts and ratios of each element contributing in the composition of the alloys of this system in a powder form having 5n purity from Aldrich. The powderson each sample were thoroughly mixed to ensure its stoichiometric composition, then were contained in an evacuated silica tube, sealed and then well shaken for half an hour using an electric shaker. Before starting the melting process, differential scanning calorimetry tests (DSC), were performed for the different samples composition powders, Fig. [1]. The data obtained from these tests were used to design the melting plan. After melting, the molten were quenched in ice water, the solid ingot samples, were grinded into fine powders and checked for amorphous structure using XRD Fig. [2].
B- Preparation of the system, Se$_{85}$Ge$_{15-x}$In$_x$ thin films, where, (x = 0, 5, 10, 15 at.%).

The thin films samples of the Se$_{85}$Ge$_{15-x}$In$_x$ system were prepared using the well-known CVD technique, under vacuum condition of $10^{-5}$ Torr. The vapor of the materials powder were deposited on clean quartz glass substrates, the films thickness were controlled using a quartz thickness monitor, and confirmed by an interferometric technique. Then were checked for amorphous structure using XRD, Fig. [3].

c- Measurement of the Se$_{85}$Ge$_{15-x}$In$_x$ system DC conductivity.

The system Se$_{85}$Ge$_{15-x}$In$_x$, thin films DC conductivity was measured using a two probe method through the evaporation of gold probe electrodes.

III. Results and discussion

The I-V characteristics for the as prepared samples and for the thermally annealed samples at 380 K and 490 K, for one hour each, were performed, and the collected data was plotted as illustrated in Figures, [4, 5, 6].
The linear behavior of these relations reveal ohmic contact and no diffusion from the gold electrode atoms into the samples’ core. This probable zero diffusion length, proves that the thin layers of such material keep themselves pure with respect to the electrode material. Also as the purity of this system is still unaffected by the gold electrode atoms, this confirms that the contact resistance could be neglected in the electrical measurements.

Also it is noticed that the increase of In content on the expenses of Ge in this system from 0% up to 15%, leads to very slight variation in the I-V characteristic curves.

This behavior was detected for both the as prepared and the thermally annealed samples, as per the previously mentioned Figures. The temperature dependence of the DC conductivity fits with the well-known Arrhenius formula, \( \sigma = \sigma_0 e^{\frac{-E_a}{kT}} \).

The relation \( \ln \sigma vs \frac{1000}{T} \) displayed two straight lines with different slopes for both the as prepared, and the thermally annealed samples, as shown in figure [7] for the as prepared samples, and figures [8, 9] for the thermally annealed ones.
From these figures we notice that the slope of the relation \( \ln o vs \frac{1000}{T} \) in the low temperature range is small, while the slope becomes high in the high temperature range.

From the figures too, it could be noticed that the kink temperature between the two straight lines for each sample in both the as prepared and the thermally annealed films was a function in the indium content.

The values of the activation energy of each straight line, for each sample was calculated and found to be different. The smaller ones characterized the low temperature range, while the higher ones characterized the high temperature range, and are denoted as \( \Delta E_1 \) and \( \Delta E_2 \) for each sample and tabulated in tables [1], [2], [3].

### Table [1] The Activation Energies of the as prepared samples of the system Se-Ge-In thin films

<table>
<thead>
<tr>
<th>X%</th>
<th>( T_e ) [K]</th>
<th>( \Delta E_1 ) [eV]</th>
<th>( \Delta E_2 ) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>361</td>
<td>1.023</td>
<td>0.075</td>
</tr>
<tr>
<td>5</td>
<td>368</td>
<td>0.956</td>
<td>0.068</td>
</tr>
<tr>
<td>10</td>
<td>352</td>
<td>0.900</td>
<td>0.089</td>
</tr>
<tr>
<td>15</td>
<td>342</td>
<td>0.845</td>
<td>0.087</td>
</tr>
</tbody>
</table>

### Table [2] The Activation Energies of the thermally annealed samples at 380 K

<table>
<thead>
<tr>
<th>X%</th>
<th>( T_e ) [K]</th>
<th>( \Delta E_1 ) [eV]</th>
<th>( \Delta E_2 ) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>370</td>
<td>1.026</td>
<td>0.084</td>
</tr>
<tr>
<td>5</td>
<td>376</td>
<td>1.063</td>
<td>0.019</td>
</tr>
<tr>
<td>10</td>
<td>380</td>
<td>0.96</td>
<td>0.062</td>
</tr>
<tr>
<td>15</td>
<td>366</td>
<td>0.87</td>
<td>0.12</td>
</tr>
</tbody>
</table>

### Table [3] The Activation Energies of the thermally annealed samples at 490 K

<table>
<thead>
<tr>
<th>X%</th>
<th>( T_e ) [K]</th>
<th>( \Delta E_1 ) [eV]</th>
<th>( \Delta E_2 ) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>357</td>
<td>0.94</td>
<td>0.08</td>
</tr>
<tr>
<td>5</td>
<td>377</td>
<td>0.90</td>
<td>0.13</td>
</tr>
<tr>
<td>10</td>
<td>373</td>
<td>0.84</td>
<td>0.057</td>
</tr>
<tr>
<td>15</td>
<td>368</td>
<td>0.87</td>
<td>0.056</td>
</tr>
</tbody>
</table>

From these tables we may notice that the values of \( \Delta E_1 \) and \( \Delta E_2 \) for the thermally annealed samples at 380 K for one hour, table[2], were, less than those of the green thin film samples table [1]. As the samples were thermally treated again at higher temperature (490 K), the values of \( \Delta E_1 \) and\( \Delta E_2 \), table [3], were decreased more. These data fits well with previous work. [35].
Figures [10, 11] show the XRD patterns of the system thermally annealed films at 380 K, and 490 K, from which one can notice distinct peaks in the samples thermally annealed at 490 K, this may be attributed to the transition from a disordered state into an ordered one. This is revealed from the detected crystalline phase which is In$_2$Se$_3$ in the hexagonal structure.

**IV. Conclusion**

The study of the electrical conductivity of the as prepared, and the thermally annealed amorphous chalcogenide thin film system Se$_{85}$Ge$_{15-x}$In$_x$, where (x = 0, 5, 10, 15 at%) at different annealing temperatures showed that this system of material could be recommended as a good candidaterawmaterial for the manufacturing of solar cells with high efficiency.

**References**


[31]. N. F. Mott, Phil. Mag. 26 (1972) 505.