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Electrical Conduction of Se_{85} Ge_{15-x} Bi_x Amorphous Thin Film

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Abstract: *Thin films of Se_{85} Ge_{15-x} Bi_x Chalcogenide glasses (where x – 0, 5, 10, and 15 at. %) were prepared by thermal evaporation technique. All samples were amorphous as checked by x-ray diffraction. The samples of as-deposited Se_{85} Ge_{15} and Se_{80} Ge_{10} Bi_5 thin films, as illustrative examples, were investigated using energy dispersive X-ray analysis (EDX); it indicates the absence of impurities in the studied alloys. The electrical properties of the thin films have been monitored by the DC conductivity measurements over a temperature range of 300 to 430 K. The electrical activation energy decreases from 1.08 to 0.054 eV with increasing Bi content. The results suggest that the addition of Bi leads to the formation of localized states near the conduction band edge so that the electric transport is due to the hopping of electrons after being excited into localized states at the conduction band edge. It shows that the activation energy decreases with annealing temperature.*

Keywords: *Thin films, DC conductivity; Electrical Properties.*

I. Introduction

The effects of impurities on the electronic properties of chalcogenides have been controversial since their discovery. Earlier it was believed that they are insensitive to the various added impurities as each impurity atom could satisfy its valence requirement by adjusting its nearest neighbor environment. According to the band model of semiconductors developed by Mott et al.[1-2]and Kastner et al. [3], this situation is explained by the pinning of the Fermi energy due to the equilibrium between negatively (D^-) and positively (D^+) charged dangling bonds. However, it has been shown that the effect of charged additives in a lone pair semiconductor depend on whether the charged additives equilibrate or not with valence alternation defects. Recent experiments revealed that the addition of impurity atoms (like Bi and Pb) to chalcogenide glasses produces a remarkable change(4).

Tohge et al. [5-8] prepared n-type chalocgenide glasses from low ratio of Bismuth into Ge-Se and Ge-Se-Te systems. The measured resistivity, thermoelectric power, and the optical absorption coefficient. They found that the resistivity (at 25°C) of Ge_{20} Bi_x Se_{80-x} ($x \leq 13$) glasses decreased by about four orders of magnitude between x = 9 and x = 10 and remained constant with $x \geq 10$. Accompanying this abrupt decrease, the conduction type changed from p to n in thermoelectric power measurements. They also found that the band gap decreased with the incorporation of a small amount of Bi while it remained nearly constant with a further increase in Bi content, indicating that the conduction type was controlled independently of the band gap change. They discussed their results on the basis of chemical bonds being present in the glasses, and a model for explaining the appearance of n-type conduction was proposed in relation to the charged dangling bond model. Thoge et al. [5-8] results were discussed later by Elliot and Steel[9] in terms of chemical modification. Also Alliot and Streel[10] studied the structural environment of Bi in Ge_{20} Bi_x Se_{80-x} for $3 \leq x \leq 10$ using extended X-ray absorption fine structure EXAFS microscopic information. However, for all $x \leq 6$ they found a large reduction in the amplitude of the radial distribution function P(r) compared to x = 3. These local softening correlates well the carrier-type reversal and the increase of conductivity found by previous workers [7, 11]. Using constraint theory, Philips [12] described a theoretical structural model explaining why carrier-type reversal occurs for Bi replacement. However, the change of the conductivity type has been observed in co-sputtered thin films of $Ge_{32}Te_{32}Se_{32}As_4$ modified by adding 11.4 at. % Ni [13], melt-quenched $Ge_{20}Bi_{10}Se_{70}$ glass [5] and Cd doped $As_2Se_1Te_2$ thin films [14]. Kumar et al. [15] studied the electrical, electronic and optical properties of both $Ge_{20}Se_{70}$ (unmodified) and $Ge_{20}Bi_{10}Se_{70}$ (modified) films. They observed that the incorporation of approximately 10 at. % Bi into p-type amorphous $Ge_{20}Se_{70}$ films increases the electrical conductivity (σ_{RT} at room temperature) by about six orders of magnitude. It also leads to transition from p to n-type conduction, a decrease in the optical gap from 1.85 to 1.15 eV and a large decrease in the electrical activation energy from 0.82 to 0.09 eV. They suggested that the addition of bismuth produce localized states near the conduction band edge, so that the electrical transport is due to the hopping of electrons after being excited into localized states at the conduction band edge.

This paper aims to study the conduction mechanism of the thin film system of samples $Se_{85}Ge_{15}$-xBi_x where (x= 0.5.10.15 at. %). Also the effect of Bi content on the conduction, mechanism will be investigated.

II. Experimental Techniques

The bulk glassy material of high purity (99.999%) Ge, Se and Bi of 5N purity were prepared by means of melt quenching technique. The necessary quantities of the elements were weighed using a sensitive balance with an accuracy of 0.1 mg. The weighed materials were placed in a clean sealed evacuated silica tube. The tubes were put in a furnace with a constant temperature 1100 °C for 24 h. During the course of heating, the tube was then quenched in an ice water bath. The prepared alloys, in powder form, were used as the source material for thin film deposition on a cleaned glass substrates using Edward E306 coating unit. The evaporation rates as well as the film thickness were controlled using quartz crystal monitor FTM5. The compositions of films were checked by energy dispersive X-ray analysis (EDX) technique and were found to be the same as those of the starting material. X-ray investigation of as-prepared films was performed using a Philips diffractometer type 1710 with Ni filtered CuKa source (h = 0.154 nm). Electrical measurements were carried out on the samples of film which were deposited onto cleaned glass substrates. The freshly prepared films were examined. The data of the resistance were obtained under a vacuum of 10^{-4} Pa in a temperature range 300- 425 K.

III. Results and Discussion

3.1. X-ray Diffraction Results

Fig.(1)shows the obtained X-ray diffraction patterns for the as prepared $Se_{85}Ge_{15}Bi_x$(x= 0.5.10.15 at. %) alloys in a powder form. The X-ray diffraction was recorded within a diffraction angle range 5°~ 70°. It was observed that they have amorphous structure due to the absence of sharp diffraction lines in these patterns.

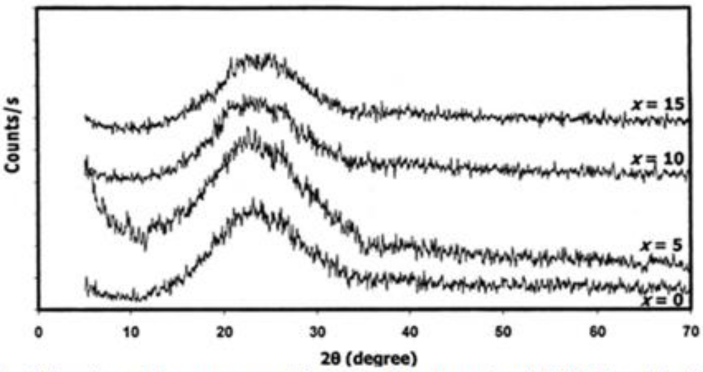

Fig. [1] X-Ray diffraction of the as prepared $Se_{85}Ge_{15}Bi_x$ where, (x= 0.5.10.15 at. %) alloys in a powder form

To investigate the structure of the obtained thin films. X-ray diffraction (XRD) studies were carried out. The X-ray diffractograms of the as-deposited $Se_{85}Ge_{15}$-xBi_x (x= 0. 5. 10. 15 at.%) thin films do not reveal any peak corresponding to Bragg's condition, as shown in Fig. (2).

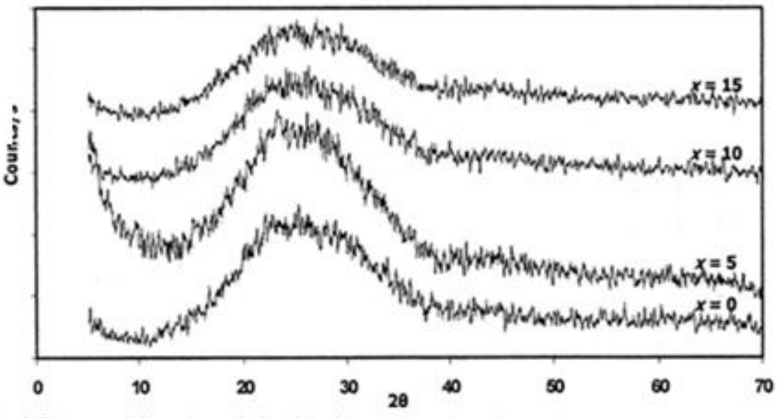

Fig. [2] X- Ray diffraction of The thin film system Se_{85} Ge_{15-x} Bi_x Where,(x = 0, 5, 10, 15 at%)

The absence of sharp peaks and appearance of humps in the X-ray diffraction (XRD) patterns of the bulk alloys and of as-deposited thin films confirms the amorphous nature of the samples.

The Energy dispersive X-ray analysis (EDX) of the prepared samples of the system $Se_{85}Ge_{15-x}Bi_x$ were investigated. The results, confirm, that, the Se, Ge, and Bi percentage of the elements are nearly the same, as the initial starting material percentage in both cases, bulk and thin film forms[17]

3.3. DC Electrical Conductivity

The DC electrical conductivity (σ) was expressed by the formula.

$$\sigma = \sigma_o e^{\frac{-\Delta E}{kT}}$$

Where ΔE is the activation energy for DC conduction, k is the Boltzmann constant and σ_o is the pre-exponential factor. The relation between the conductivity (σ) and the temperature (T) is shown in Fig (3).

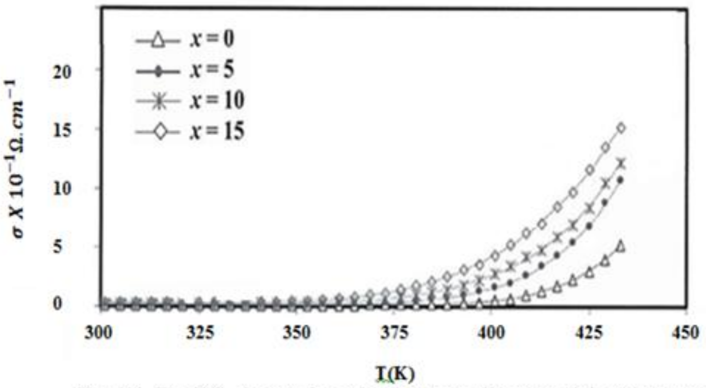

Fig. [3] The DC. electrical conductivity as a function of the temperature in the temperature range 300 – 450 K.

It is clear from this figure that the electrical conductivity (σ) increases with increasing the temperature (T), over all the temperature range.

The room temperature electrical conductivity was deduced and redrawn, as a function of Bi content as shown in fig. (4).

Fig (4),reveals that the room temperature conductivity increases as Bi content increases.

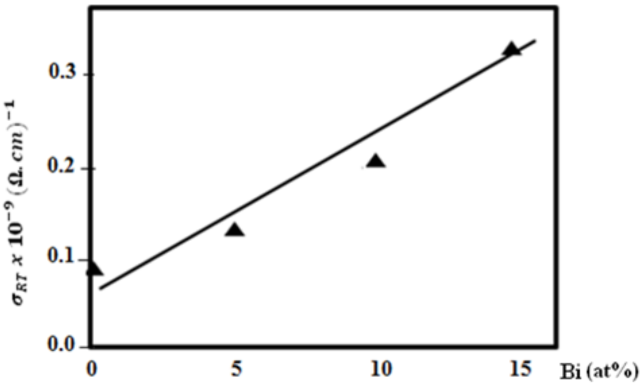

Fig. [4] The room temperature DC. conductivity as a function of the Bi content (at%)

Fig. (5) shows the plot of Ln (σ) versus 1000/T (°k^{-1}) in the temperature range 300 - 425 °k, for the $Se_{85}Ge_{15-x}Bi_x$ thin films. This Figure indicates that the conduction in these glasses takes place through an activated process having two conduction stages.

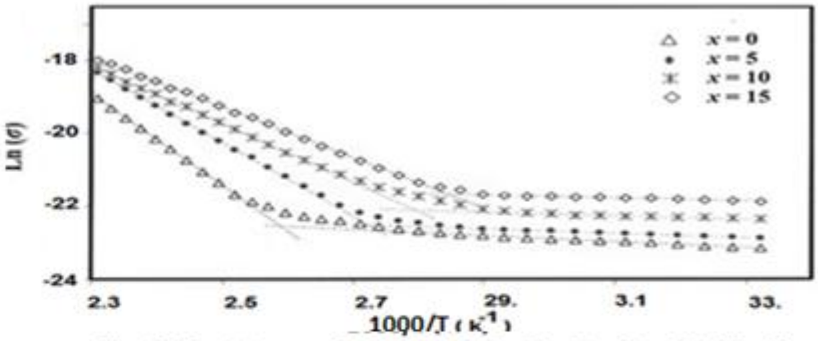

Fig. (5) Ln (σ) versus 1000/T (°k^{-1}) for the $Se_{85}Ge_{15-x}Bi_x$ thin films in the temperature range 300 °k- 425 °k.

Firstly, Ln (σ) shows linear dependence of conductivity on the temperature which reveals a semiconducting behavior.

Additionally, for each sample there are two distinct linear parts, one at the low temperature range and the other at the high temperature range.

The temperature separating the two straight lines for each sample (kink temperature) shifts towards the lower temperature, as Bi content increases, as shown in fig. [6]

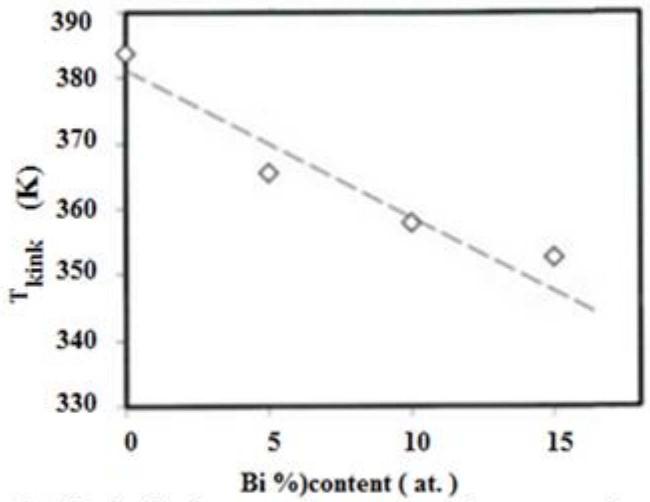

fig. [6] **The kink temperature as a function of Bi content**

In the same time, the conductivity corresponding to the kink temperature increases. This may be explained as the sample under the effect of low thermal energy, becomes electron rich as Bi content increases.

As, the sample becomes in the high temperature range after, the kink temperature the thermally activated mechanism is dominant. The role of increasing Bi content, appears as a shift to the lower temperature range and as well as increasing the electric condition due to the increase of the charge carriers, which been excited from valance to the conduction band**(16/17)**

The activation energies for both high and low temperature ranges were calculated and given in table (1) as $\Delta E_1$and ΔE_2 in addition to the kink temperature T_{kink} and the corresponding values of the electric conductivity $\sigma_{kink.}$

Table (1)

Bi content	ΔE_1	ΔE_2	T_{kink}	σ_{kink}
0	**1.0767**	**0.0703**	**376.0752**	**$8.72x10^{-11}$**
5	**0.8630**	**0.0503**	**366.8056**	**$1.16x10^{-10}$**
10	**0.6897**	**0.0446**	**357.9808**	**$1.93x10^{-10}$**
15	**0.5353**	**0.0366**	**351.7434**	**$3.16x10^{-10}$**

Where ΔE_1 is the low temperature activation energy, ΔE_2 – is the high temperature activation energy, T_{kink} is the absolute temperature at the kink point, σ_{kink} is the conductivity Ln σ at kink temperature.

Fig.[7], illustrates the effect of Bi content on the activation energies ΔE_1 and ΔE_2.

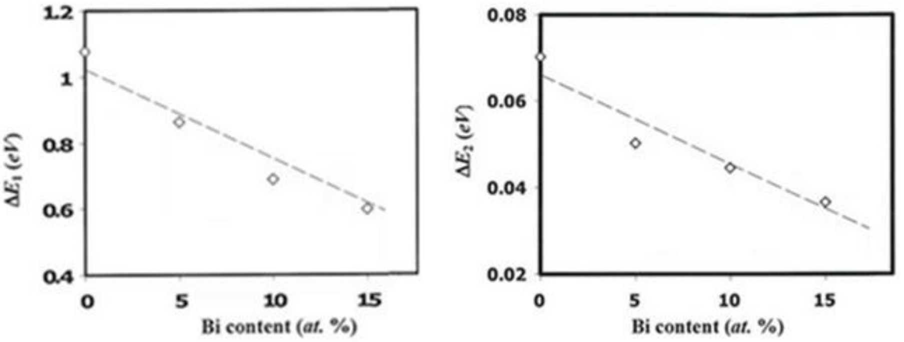

Fig. [7] The Bi content effect on the activation energy ΔE_1 and ΔE_2

From Fig. [7] it is clear that the activation energies decreases as the Bi content increases.

IV. Conclusion

The prepared samples of the system $Se_{85}Ge_{15-x}Bi_x$ show that:

- The samples structure for both bulk and thin film forms is amorphas as detected by X-ray diffraction.
- The electric conductivity increases as a function of temperature.
- The behavior of σ versus 1000/T shows semiconducting behavior with two straight lines separated by kink temperature.
- The kink temperature shifted to lower temperature as Bi content increases. In the sametime the electrical conductivity, at this kink temperature increases.
- The electrical conductivity of the samples increases during both temperature ranges.
- Although the activation energy during the high temperature ranges is much more than that of the low temperature ranges, the value of the obtained activation energies during the high temperature ranges decreases as the Bi content increases, while the corresponding electric conductivity increases.
- The effect of Bi content as it replaces Ge, illustrates, the best result, as it increases the electric current, and decreases the activation energy.

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