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Electrical properties and phase transition of $Ge_{1-x}Sn_xSe_{2.5}$ thin films

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The $Ge_{1-x}Sn_xSe_{2.5}$ system was prepared by melting the correct ratio of high purity elements in quartz evacuated ampoules followed by quenching in ice. It was found that, within the $Ge_{1-x}Sn_xSe_{2.5}$ system, a glassy state can be formed when $0 \leqslant x \leqslant 0.4$. On increasing x to 0.6 a glassy state could not be obtained, as is confirmed by X-ray diffraction. Differential thermal analysis (DTA) was carried out to study the effect of composition on the stability of amorphous phase. $Ge_{1-x}Sn_xSe_{2.5}$ (where $0 \leqslant x \leqslant 0.6$) thin films have been prepared by the thermal evaporation technique. The electrical conductivity of the thin films have been studied as a function of composition and film thickness.

1. Introduction

Evidence for layer-like clusters as the dominant feature in the structure of melt-quenched $GeSe_2$ glass is well established [1–8]. When this material was alloyed with a second group IV element (e.g. Sn), the substitution of some Ge atoms by Sn atoms will cause variations in the physical properties and stability of the primary amorphous compound. Therefore, $Ge_{1-x}Sn_xSe_2$ system ($0 < x < 0.7$) has been studied with emphasis on the effect of tin on the tendency for the system to phase separate into the constituent $GeSe_2$ and $SnSe_2$ binary components using Raman scattering and Mossbauer spectroscopy [8–10]. Authors studying this system reported that there is nonmonotonic behaviour with increasing Sn concentration in several measured quantities [11–14].

The problem with using $Ge_{1-x}Sn_xSe_2$ is the natural tendency for glasses with this stoichiometric pseudo binary composition to undergo phase separation during quenching. As a result, it is difficult to prepare completely homogeneous samples. Moreover, during Raman scattering measurements, the excitation light promotes phase separation and crystallization of the glass samples.

In the present study $Ge_{1-x}Sn_xSe_{2.5}$ ($0 \leqslant x \leqslant 0.6$) were selected to minimize the effects mentioned above. By setting the composition on the selenium rich side of the stoichiometric compound $GeSe_2$, the tendency to crystallize is strongly reduced [15]. Griffiths and Espinosa [16] studied this system using Raman scattering to probe the effect of tin atom substitution for germanium in $GeSe_{2.5}$ homogeneous glasses. To the best of the authors' knowledge, there are no detailed studies on the electrical and optical properties and X-ray diffraction (XRD) of this system. Detailed studies on the physical properties of such system will increase our understanding of its behaviour. We aim to study the electrical, optical properties and the XRD for this system as a part of detailed studies. The present work deals with the electrical properties of $Ge_{1-x}Sn_xSe_{2.5}$ thin films where $0 \leqslant x \leqslant 0.6$.

Mott and Davis [17] showed that the plot of $\log \sigma$ against T^{-1} in amorphous solids is found to consist of three distinct regions, and the conductivity σ of the chalcogenide glasses can be written as

$$\sigma = \sigma_0 \exp(-\Delta E_\sigma/KT) + \sigma_1 \exp(-E_{\sigma 1}/KT) + \sigma_2 \exp(-E_{\sigma 2}/KT) \quad (1)$$

The three terms arise from three different conduction processes.

1.1. Band conduction in extended states

In this mode of conduction, the first term on the right-hand side of Equation 1 dominates. The constant σ_0 for the chalcogenide glasses varies from 10^2 to $5 \times 10^3 \ \Omega^{-1} cm^{-1}$ and is found to depend on composition. ΔE_σ is the activation energy.

1.2. Hopping conduction in localized states

This contribution to the conductivity arises from tunnelling to unoccupied levels of nearest-neighbour centres. In this case the conductivity is given by the second term on the right-hand side of Equation 1. Here σ_1 is approximately 10^2–10^4 times less than σ_0, partly because of the smaller density of states and mainly because the charge carriers have a much lower mobility.

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1.3. Hopping conduction near the Fermi level

This third contribution to conductivity in an amorphous semiconductor is analogous to impurity conduction in heavily doped semiconductors. In this case the conductivity is given by the third term on the right-hand side of Equation 1.

2. Experimental procedure

Glass samples with composition x between zero and 0.6 were synthesized by the conventional method of heating the constituents (all of 99.999% purity) in evacuated sealed-off silica ampoules (8 mm inner diameter) to high temperatures (above the highest melting point of any of the constituents). The sealed ampoules were kept in a furnace at 470 K for 1 h and the temperature was raised gradually to 650 K for 1 h, then it was raised to 1025 K for 6 h followed by quenching in ice. During heating, the ampoules were shaken several times to ensure a thorough mixing of the constituents. These compositions were examined by X-ray powder diffraction (XRPD) Philips PW 1400/90 attached to PW1050/70 vertical goniometer. The homogeneity and the transition temperatures of these compositions were identified by differential thermal analysis (DTA) Shimadzu 30.

We succeeded in obtaining glass samples in the range $0 \leqslant x \leqslant 0.4$ by preparing small samples (2 g). This small melt size was selected because Fukunaga *et al.* [18] could not obtain completely glassy samples of $Ge_{1-x}Sn_xSe_2$ for $x > 0$ working with a 10-g sample. Stevens *et al.* [9, 19] were working with a melt size of 0.25 g and they explained that if the melt size is increased to 0.40 g, water quenching of samples invariably leads to partially crystalline ingots.

$Ge_{1-x}Sn_xSe_{2.5}$ ($0 \leqslant x \leqslant 0.6$) were deposited by the thermal evaporation technique. A vacuum of the order of 10^{-6} Torr was maintained during evaporation using an Edward 306 E evaporation unit. Thoroughly cleaned glass slides were used as substrates. $Ge_{1-x}Sn_xSe_{2.5}$ ($0 \leqslant x \leqslant 0.6$) thin films employed for d.c. conductivity measurements were deposited onto glass substrates previously equipped with coplanar gold electrodes separated by a gap of width about 0.2 cm. The d.c. conductivity was measured using Keithley 616 digital electrometer for resistance measurements and Philips PM 2441 digital voltameter for measuring millivolts across the thermocouple. The electrical conductivity was measured in the temperature range from 113 to 400 K. In order to study the effect of film thickness on the electrical properties, films having different thickness in the range 80–400 nm were grown at room temperature. The thickness of the films were determined by the weight method.

3. Results and discussion

The $Ge_{1-x}Sn_xSe_{2.5}$ systems were prepared with different compositions in the range $0 \leqslant x \leqslant 0.6$. Fig. 1 shows the XRPD patterns for the ingots. The figure shows that the compositions $x = 0$, 0.2 and 0.4 are amorphous, while the composition $x = 0.6$ is partially crystalline. It is clear that this system exhibits a large glass-forming region in the range $0 \leqslant x \leqslant 0.4$. X-ray data reveal that tin has an important role in forming crystalline compositions. Increasing tin content enhances the crystallization process. Hence, at $x = 0.6$ the ingot is partially crystalline.

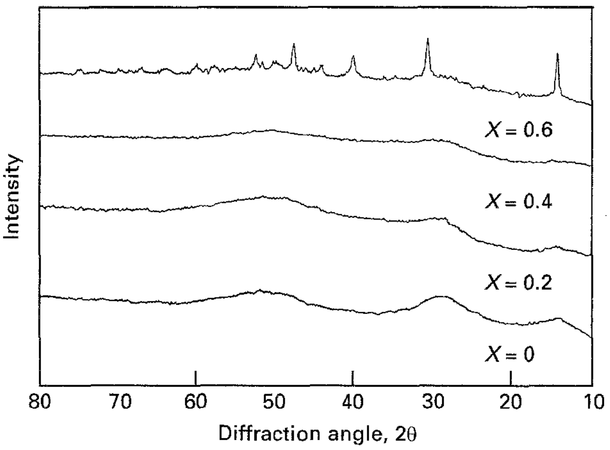

Figure 1 X-ray powder diffraction patterns for $Ge_{1-x}Sn_xSe_{2.5}$ ingots with different compositions, $x = 0$, 0.2, 0.4 and 0.6.

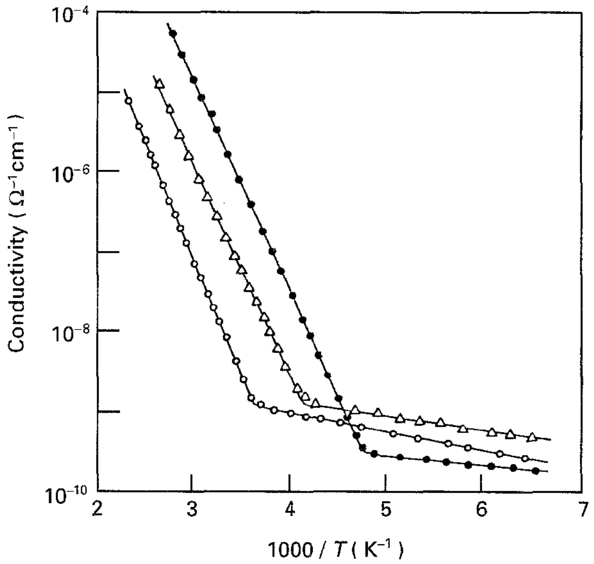

Figure 2 Variation of the electrical conductivity versus reciprocal of the absolute temperature for $GeSe_{2.5}$ thin films. ○ 94 nm; △ 282 nm; ● 376 nm.

$Ge_{1-x}Sn_xSe_{2.5}$ thin films were deposited with different compositions to study the electrical properties as a function of composition and film thickness. XRD of $Ge_{1-x}Sn_xSe_{2.5}$ thin films at different compositions in the range $0 \leqslant x \leqslant 0.6$ have the same behaviour as that of Fig. 1.

Figs 2–5 show that variation of the electrical conductivity versus reciprocal of absolute temperature for $Ge_{1-x}Sn_xSe_{2.5}$ thin films deposited with different thickness and with compositions $x = 0$, 0.2, 0.4 and 0.6 respectively. For all these films the electrical conductivity was found to be a negative exponential function of the absolute temperature expressed by the first term

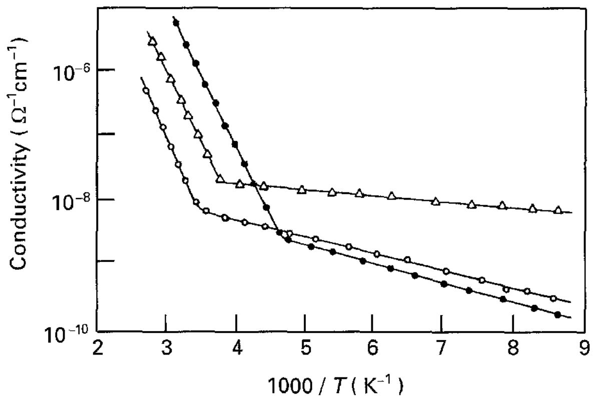

Figure 3 Variation of the electrical conductivity versus reciprocal of the absolute temperature for $Ge_{1-x}Sn_xSe_{2.5}$ thin films, where $x = 0.2$. ○ 89 nm; △ 267 nm; ● 364 nm.

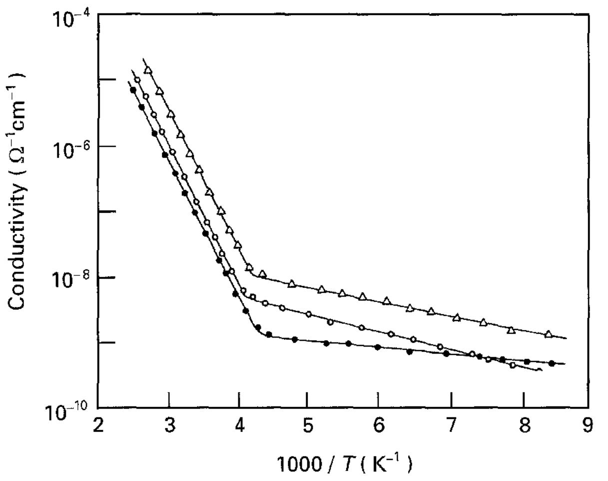

Figure 4 Variation of the electrical conductivity versus reciprocal of the absolute temperature for $Ge_{1-x}Sn_xSe_{2.5}$ thin films, where $x = 0.4$. ○ 88 nm; △ 263 nm; ● 350 nm.

of the right-hand side of Equation 1 up to a given temperature, depending on the film thickness and the glass composition. At a given temperature a deviation of the linear dependence is observed for all investigated samples. The presence of two linear regions in the $\log \sigma$ versus T^{-1} plots is most likely due to the appearance of another conduction mechanism. Such behaviour allows the conclusion that at low temperature the dominant conduction mechanism is due to hopping conduction. On the other hand, at higher temperature it may be due to the band conduction in extended states.

The values of the thermal activation energy (ΔE_{σ}) were calculated for different compositions and different thickness and are listed in Table I. The logarithm of the conductivity at room temperature ($\log \sigma_{20}$), the logarithm of the pre-exponential factor ($\log \sigma_0$), $E_{\sigma 1}$ and $\log \sigma_1$ are also listed. It is found that $\Delta E_{\sigma} > E_{\sigma 1}$. Such results agrees well with Mott and Davis' prediction [17].

3.1. Effect of film thickness

Comparing the results of Table I for films deposited at different thickness and at same composition we can conclude that, for each composition, the values of the thermal activation energy (ΔE_{σ}) decrease slightly with increase in the film thickness. This behaviour may be explained by the Neugebauer theory [20, 21] for electrical conduction in ultra-thin films which in a modified form could be applied to semiconductor continuous films. Table I also shows that the electrical conductivity at room temperature ($\log \sigma_{20}$) increases with an increase in film thickness. This is due to the fact that in thinner films the resistivity includes contributions from both lattice and surface scattering. As the thickness increases, the surface scattering component decreases and the resistivity is mainly due to lattice scattering. Moreover, at higher thicknesses there is also the possibility of formation of larger grain sizes. This results in an increase in the conductivity.

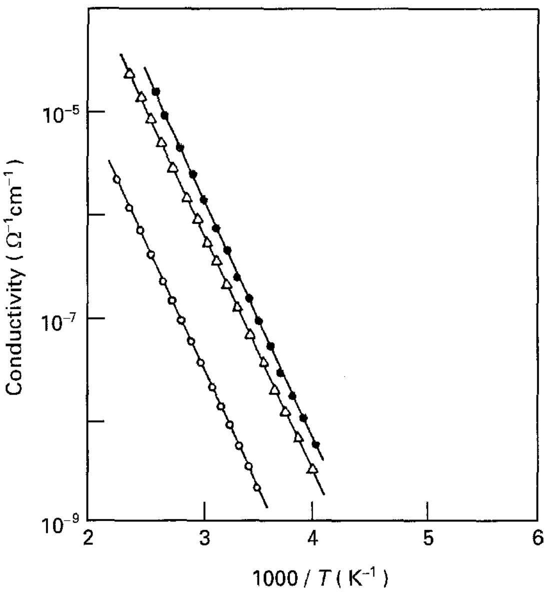

Figure 5 Variation of the electrical conductivity versus reciprocal of the absolute temperature for $Ge_{1-x}Sn_xSe_{2.5}$ thin films, where $x = 0.6$. ○ 86 nm; △ 258 nm; ● 344 nm.

3.2. Effect of composition

To study the effect of composition on the electrical properties of $Ge_{1-x}Sn_xSe_{2.5}$ thin films we should compare (ΔE_{σ}) and ($\log \sigma_{20}$) for films of nearly the same thickness but with different composition. Obtained data reveal that in the composition range $0 \leqslant x \leqslant 0.4$ the activation energy decreases with increasing tin content (Fig. 6(a)), while the conductivity at room temperature is found to increase. At composition $x = 0.6$, the activation energy increases. This is due to the formation of partially crystalline ingot.

The study of the ternary $Ge_{1-x}Sn_xSe_{2.5}$ is particularly important because of the structural changes which have been observed to occur as Ge is replaced by Sn [13, 22]. The structure of $GeSe_2$ in both its crystalline [23] and glassy [1] states is built up of $Ge(Se_4)_{1/2}$ tetrahedra which form corner-sharing chains cross-linked by edge-sharing bitetrahedra. In the crystal this structure forms layers which are then stacked in the out-of-plane direction to form an anisotropic three-dimensional structure. The glassy form

TABLE I The dependence of the thermal activation energy (ΔE_{σ}), the conductivity at room temperature ($\log \sigma_{20}$), the pre-exponential factor ($\log \sigma_0$), $E_{\sigma 1}$ and $\log \sigma_1$ on thickness and composition of $Ge_{1-x}Sn_xSe_{2.5}$ thin films

Composition (x)	Thickness (nm)	ΔE_{σ} (eV)	$\log \sigma_{20}$ (Ω^{-1} cm^{-1})	$\log \sigma_0$ (Ω^{-1} cm^{-1})	$E_{\sigma 1}$ (eV)	$\log \sigma_1$ (Ω^{-1} cm^{-1})
0	94	1.097	− 8.337	1.096	0.089	− 8.108
	282	1.005	− 7.081	1.561	0.068	− 8.201
	376	0.997	− 6.027	2.546	0.045	− 8.967
0.2	89	0.934	− 8.060	− 0.029	0.096	− 7.347
	267	0.869	− 6.939	0.533	0.029	− 7.468
	364	0.854	− 5.914	1.430	0.108	− 7.337
0.4	88	0.880	− 6.896	0.671	0.105	− 7.200
	263	0.857	− 6.372	0.998	0.084	− 7.092
	350	0.841	− 7.060	0.171	0.038	− 8.488
0.6	86	0.978	− 8.432	0.022		
	258	0.945	− 7.081	1.045		
	344	0.934	− 6.721	1.310		

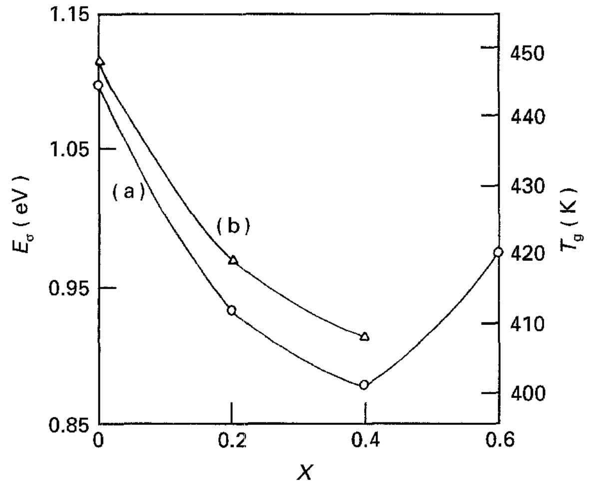

Figure 6 Effect of composition on (a) the thermal activation energy (○) and (b) the glass transition temperatures (△) for $Ge_{1-x}Sn_xSe_{2.5}$ thin films.

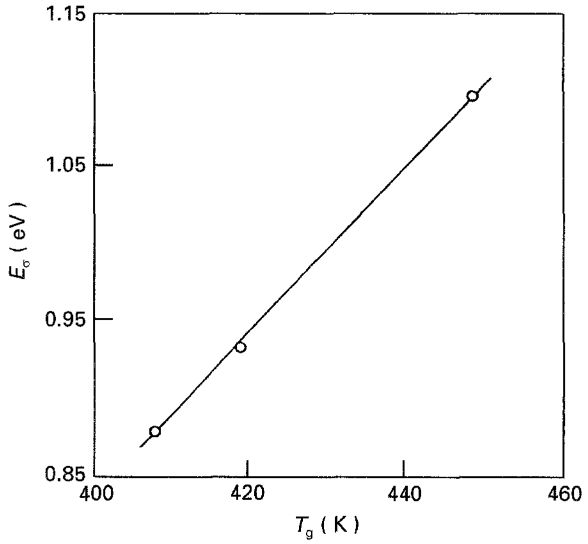

Figure 7 The dependence of the thermal activation energy on the glass transition temperatures.

is made up of fragments of these layers which form randomly-oriented clusters terminated in the direction of the cross-linking by Se–Se bonds. The widths of these clusters vary from an average of ten chains in $GeSe_2$ to only two chains in $Ge_{1-x}Sn_xSe_2$ with $x > 0.3$ [22]. These clusters are slightly Se-rich, so that the stoichiometry must be maintained by additional units in which Ge–Ge bonds occur. These have been postulated to form ethane-like chains [5]. In the ternary compounds Sn goes substitutionally into Ge sites in both the crystal [24] and the glass [5, 21], preferentially occupying the sites at the edges of the clusters. As the number of Sn atoms is increased and more edge sites are required to accommodate them, the average size of the clusters within the glass decreases. This leads to a decrease in the vibrational mode frequencies and in the glass-transition temperature. Fig. 6(b) shows the decrease of the glass-transition temperature with increase in Sn content.

The decrease of the activation energy with increase in Sn content can be explained as reported earlier by Mikrut and McNeil [11]. They reported that the Sn atoms bind their valence electrons more loosely than do the Ge atoms. As the number of Sn atoms increases, the difference in energy between the bonding and antibonding states at the band edge decreases. This is responsible for the decrease in ΔE_{σ}. The observed results suggest that the increase of conductivity arises from a decrease in the activation energy. The decrease of the glass transition temperature (T_g) may indicate weaker average bond strength and hence less stability in Sn-rich glasses. Similar effects have been reported by Stevens *et al.* [9, 19] for the effect of increasing tin content on the glass transition temperature of $Ge_{1-x}Sn_xSe_2$ bulk glasses. Islam and Cappelletti [14] showed a decrease of the optical band gap in $(GeSe_2)_{1-x}(SnSe_2)_x$ thin films with increasing Sn content which supports our results.

Fig. 7 shows the dependence of the activation energy (for the highest values) with the glass transition temperatures. The obtained linear plot suggests that there is a close relationship between carrier generation and bond breaking.

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