

CONDUCTION STUDIES ON AMORPHOUS InSbX₃ (X = Te or Se) THIN FILMS

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ABSTRACT

Amorphous InSbX₃ (X = Te or Se) thin films were obtained by thermal evaporation technique of bulk material on to well cleaned glass substrates. The current-voltage characteristics have been measured in the temperature range (303-393 K) and thickness range (230-490 nm). The obtained I-V curves revealed two types of conduction. The first region is ohmic type in the lower field followed by non-ohmic type of conduction in the high filed region. In the high-filed region, the field lowering coefficient β is evaluated, and has been analyzed by the anomalous Poole-Frenkel effect. The temperature dependence of ohmic current is that of thermally activated process. The variation of dielectric constant with temperature for the two compounds has been studied.

Key words: Conduction, Amorphous, InSbX₃, Thin film.

INTRODUCTION

In the recent years, investigations of thin film systems of metal-dielectric-metal type led to the establishment of thin film microelectronics as a promising new branch of modern electronics. Thin film microelectronics deals with processes taking place in thin metal, dielectrics and semiconductor films as well as with the properties of the interface between two phases. The knowledge of some physical properties of semiconductor films is necessary. Chalcogenide films are new kind of materials with immense qualities of use in many practical applications. These materials exhibit unique infrared transmission and electrical properties, which makes them potentially useful for applications such as threshold and memory switching¹. Since a high – speed switching and the memory effect of an amorphous semiconductor were reported^{2,3}, its properties have been studied very actively. There have

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been many discussions on the mechanism of high-speed switching and of electric conduction in amorphous semiconductors.

The study of the pre-switching current-voltage characteristics is necessary to identify the electrical conduction mechanism occurring in the off state of chalcogenide glass switches. One possible conduction mechanism is the space charge limited current⁴, hopping conduction⁵, small polaron conduction⁶ and the Poole-Frenkel conduction⁷.

The system In_2Se_3 -Sb₂Se₃ is a semiconducting compound with very interesting electrical and optical properties, which has not been sufficiently investigated^{8,9}. Few authors studied the optical¹⁰ and electrical^{11,12} properties of InSbSe₃ single crystal; however, little attention is devoted to study the physical properties of InSbSe₃ thin films. In₂Te₃-Sb₂Te₃ system (Sb_{2-x}, In_x Te₃ solid solution) belongs to the family of layered compounds having the structure of space group. Physical properties of Sb_{2-x}, In_x Te₃ single crystal were described in a number of papers^{13,18}; however, little attention is devoted to study the physical properties of InSbTe₃ thin films.

This paper aimed to investigate the voltage and temperature dependence of current in amorphous InSbSe₃ and InSbTe₃ films produced by vacuum deposition to identify the dominating conduction mechanism of charge transport.

EXPERIMENTAL

InSbSe₃ and InSbTe₃ compositions were prepared in bulk form by melting together the stoichiometric amount of the constituent elements of each compositions of purity 99.999% using a specially designed oscillation furnace to insure the homogeneity of the samples. The furnace temperature was raised at a rate of 50 K h⁻¹ to 1223 K for InSbSe₃ composition¹⁹ and to 1003 K for InSbTe₃ composition²⁰. At this temperature the melt was held for 2 days. Then the ampoules were cooled slowly at a rate of 1 K min⁻¹ and 3 K min⁻¹ for InSbSe₃ and InSbTe₃ compositions to room temperature. Thin films of the obtained compositions were then prepared by thermal evaporation technique using a high vacuum coating unit (Edwards type E306A), onto the well cleaned glass substrates of suitable dimensions with the desired mask, and provided with A1 electrodes in sandwich configuration for I-V measurements. Thin films with different thicknesses (230-490 nm) were deposited at constant rate under vacuum of L3 mPa (10⁻⁵ torr). The substrate temperature was held at room temperature ~ 300 K. The film thickness was measured by Tolanskys interferometric method.

The X-ray diffractometer of the type Philips (PM 8203) was used to investigate the structure of the obtained samples in bulk and thin film forms. The chemical composition of

the obtained samples in bulk and thin films was checked by energy dispersive x-ray analysis (EDX) in the scanning electron microscope (JEOL 5400).

The current-voltage (I-V) characteristics were measured through the temperature range 303-393 K using electrometer (Keithley type 616A) for the potential drop measurements and a rnicrodigit multimeter (TE 924) for the current measurements. The temperature of the sample was monitored using a chromel-alumel thermocouple.

RESULTS AND DISCUSSION

X-ray diffraction pattern obtained for the two systems under investigations the bulk form has a polycrystalline nature, while their thin film form has an amorphous nature²¹.

EDX analysis indicated that the compositions of the prepared materials under test in powder and thin film forms are closed to the initial compositions with an experimental error $\pm 2\%^{21}$.

I-V characteristics

Fig. 1 (a & b) shows the current-voltage (I-V) characteristics for InSbSe₃ and InSbTe₃ films at different temperatures in the temperature range (303-393 K). It is observed that the curves show two different regions; first the linear part for lower voltage, indicating ohmic conduction due to the presence of thermally generated carriers (electrons and holes) followed by non-linear part at higher voltage.



Fig. 1: (a) Current- voltage characteristics for InSbSe₃ film of thickness 250 nm at various temperatures (b) Current- voltage characteristics for InSbTe₃ film of thickness 230 nm at various temperatures.

It was found that at higher temperature the linear regions, extend to higher values of the applied filed. The ohmic region is believed to be controlled by electron hopping. Similar results have been obtained previously for other amorphous semiconductor materials²²⁻²⁵. The I-V characteristics exhibited an ohmic region at low applied voltage with low filed followed by a transition to supra linear at higher field up to the breakdown voltage value.

In order to analyze the basis of this behavior, the effect of sample thickness and electrode material such as gold and silver on the conductivity of the samples under investigation was examined. Fig. 2 (a & b) shows the thickness dependence of current for thin film samples of systems under investigations, which reveals that the current is independent of film thickness at constant voltage through the studied range of thickness. Thus, we can conclude that the current is independent of these factors. This suggests that space charge limited conduction and Schottky emission do not specify the conduction mechanism and consequently, the field dependence was a property of the bulk material.



Fig. 2: (a) Thickness dependence of room temperature current for InSbSe₃ film of different voltage. (b) Thickness dependence of room temperature current for InSbTe₃ film of different voltage.

Fig. 3 (a & b) represents the plot of I (in logarithmic scale) against $E^{1/2}$ for the data of Fig. 1 (a & b) for two compositions. It is clear from this figure that there is a dependence of type I $\propto E^{1/2}$ for both lnSbSe₃ and InSbTe₃ films over at least two order of magnitude of current. This field dependence of current indicates that the conduction mechanism may be either the Schottky²⁶, or Poole-Frenkel²⁷ type. The following evidence allows us to eliminate Schottky conduction: (a) log IT⁻² should vary linearly with T⁻¹ at different fixed voltage. This is not found to be the case in any of the two compounds under test, (b) The activation energy for Schottky emission should generally be greater than 0.8 eV. In the present case, it

is lower than this value. These results together with other features mentioned above, clearly suggest that the conduction is a bulk effect. Moreover the different parameters estimated from graphs found to lie in an acceptable range only if the Poole-Frenkel effect is assumed to be operative.



Fig. 3: (a) I (in logarithmic scale) vs $E^{1/2}$ plots for the InSbSe₃ film at different temperatures. (b) I (in logarithmic scale) vs $E^{1/2}$ plots for the InSbTe₃ film at different temperatures.

According to Poole-Frenkel effect, the electric field interacts with the coulombic potential barrier of a donor center or trap and the height of barrier is lowered. In the presence of an electric filed, the electrons are thermally emitted from the randomly distributed traps to the conduction band by the lowering of the coulombic potential barrier by the external electric field. At higher fields in excess of 10^4 V/m for many dielectric films containing shallow traps exhibits current density (J). Voltage characteristics is of the form is given by the following equation²⁸:

$$J = J_0 \exp(\beta E^{1/2} / kT) \qquad ...(1)$$

Where J_0 is the low field current density, E the applied electric field, k the Boltzmann constant, T the absolute temperature and β the Poole-Frenkel field lowering coefficient which is given by:

$$\beta = (e^3 / a\pi\varepsilon\varepsilon_0)^{1/2} \qquad \dots (2)$$

Where a equal to 1 for Poole-Frenkel emission and equal to 4 for Schottky emission²⁸, is the electronic charge, ε is the dielectric constant of the material and ε_0 the permittivity of the free space.

Now, β_{PF} can be calculated theoretically according to Eq. (2) (where the dielectric constant a has been determined) and calculated experimentally from the slope of the linear part in the non-ohmic region of Fig. 3 (a & b).

The experimental values of β_{PF} calculated from the slope of the graphs in Fig. 3 (a & b) for the two systems under investigation are listed in Tables 1 and 2. Values of the dielectric constant ε can be calculated according to Eq. (2) and are also given in Tables 1 and 2. The obtained value of β_{PF} at room temperature (303 K) is about $2.77 \times 10^{-5} \text{ eVm}^{1/2} \text{V}^{1/2}$ for InSbSe₃ films, but if using the estimated value of $\varepsilon = 8.8^{29}$, the theoretical values of β_{PF} calculated from Eq. (2) is $2.6 \times 10^{-5} \text{ eV m}^{1/2} \text{ V}^{-1/2}$ and the Schottky coefficient $\beta_2 = 1/2 \beta_{PF} = 1.38 \times 10^{-5} \text{ eVm}^{1/2} \text{V}^{-1/2}$. Similarly, the experimental value of β_{PF} at room temperature (303 K) is about $1.86 \times 10^{-5} \text{ eVm}^{1/2} \text{V}^{-1/2}$ for InSbTe₃ films, but if using the estimated value of $\varepsilon = 35$ obtained from ac measurements (using a PM 6404 programmable automatic RCL meter bridge) the theoretical value of β_{PF} is $1.65 \times 10^{-5} \text{ eVm}^{1/2} \text{V}^{-1/2}$ and the Schottky coefficient $\beta_z = 8.25 \times 10^{-5} \text{ eVm}^{1/2} \text{V}^{-1/2}$. These calculations suggested that the experimental values of β_{PF} is in agreement with the Poole-Frankel mechanism rather that the Schottky mechanism. However, this agreement between the experimental and theoretical values of β_{PF} can not be taken for suggesting the conduction mechanism, which will be operated.

Element	$\beta [evm^{1/2}v^{-1/2}]$	3	T (K)
In-Te	1.86 x 10 ⁻⁵	8.8 ²⁹	303
	1.93 x 10 ⁻⁵	8.8 ²⁹	323
	1.96 x 10 ⁻⁵	8.8 ²⁹	343
	2.15 x 10 ⁻⁵	8.8 ²⁹	363
Sb-Te	1.65 x 10 ⁻⁵	35	303
	1.78 x 10 ⁻⁵	35	323
	1.83 x 10 ⁻⁵	35	343
	2.06 x 10 ⁻⁵	35	363

Table 1: Variation of β and ϵ with temperature for InSbTe₃ film of thickness 230 nm

Element	$\beta [evm^{1/2}v^{-1/2}]$	3	T (K)
In-Se	2.77 x 10 ⁻⁵	8.8 ²⁹	303
	2.95 x 10 ⁻⁵	8.8 ²⁹	323
	3.06 x 10 ⁻⁵	8.8 ²⁹	343
	3.24 x 10 ⁻⁵	8.8 ²⁹	363
Sb-Se	2.6 x 10 ⁻⁵	8.8 ²⁹	303
	2.8 x 10 ⁻⁵	8.8 ²⁹	323
	2.95 x 10 ⁻⁵	8.8 ²⁹	343
	3.08 x 10 ⁻⁵	8.8 ²⁹	363

Table 2: Variation of β and ε with temperature for InSbSe₃ film of thickness 250 nm

It is clear also from Table 1 and 2 that the experimental values of β_{PF} for both InSbSe₃ and InSbTe₃ films show an apparent dependence on temperature, which increases with increasing temperature through the investigated range.

Various models are put forward to explain the anomalous values of β . The first one³⁰ is based on the presence of shallow neutral traps at energy E_t and a deep donor level at energy E_d , with the Fermi level lying centrally between them. E_t and E_d were measured from the bottom of the conduction band. The second model³¹ is based on donor composition and the presence of acceptor; such that the relative densities of donor and acceptor sites control the slope of log I versus $E^{1/2}$ graph.

Hill⁷ proposed that donors and traps co-exist and the density of ionized donor is only a small fraction of the total density of ionized donor. If this is the case, then ionization of donor by Poole-Frenkel emission can stimulate further ionization by other processes. The initial ionized donor acts as a capture center for the electron released from the second donor, giving rise to an effective mobile donor and anomalous values of β .

The variation of I (in logarithmic scale) vs $E^{1/2}$ at room temperature (303 K) for both InSbSe₃ and InSbTe₃ films are shown in Fig. 4. It is clear from this figure that for a constant value of the applied voltage, a decrease in electrical conductivity for InSbSe₃ than for InSbTe₃ films is observed. The presence of a high concentration of localized states in the band structure is responsible for the larger value electrical conductivity the case of InSbTe₃ films³⁶.



Fig. 4: I (in logarithmic scale) vs E^{1/2} plots for the InSbSe₃ and InSbTe₃ films of thickness 250 and 230 nm, respectively at room temperature.

Using the values of β_{PF} (listed in Tables 1 and 2, the values of dielectric constant at different temperatures were estimated according to Eq. (2) and are listed in the same Table. It is observed that the values of \in at any given temperature for InSbTe₃ films are higher than those for InSbSe₃ films. This can be explained on the basis of chemical bonds present in the two system^{32,33} as well as the electro negativity of Se atoms is stronger than Te atom^{34,35} (see Table 3). Accordingly, the bonding energy In–Se and Sb–Se are stronger than In–Te and Sb–Te bonds, respectively. So InSbTe₃ can responsed to the electric field much easier than InSbSe₃.

Table 3:

Elements	In - Te	Sb - Te	In - Se	Sb - Se
Electronegativity difference	0.4	0.2	0.7	0.5

I-T characteristics

The temperature dependence of current was measured for several constantly applied voltages, having in mind the importance of these characteristics for the proper choice of charge transfer model. Fig. 5 (a & b) show the temperature dependence of the current for the InSbSe₃ and InSbTe₃ films, respectively at different constant applied voltages in the temperature range (303–393 K). It is clear from this figure that all obtained relations are straight lines indicating that the conduction in these films takes place through an activated process having a single activation energy in the considered temperature range.



Fig. 5: (a) I (in logarithmic scale) vs 1000/T for InSbSe₃ film at different applied voltage (b) I (in logarithmic scale) vs 1000/T for InSbTe₃ film at different applied voltage

The activation energy $\Delta E \sigma$ was calculated using the following relation:

$$I = I_0 \exp - \Delta E_0 / Kt \qquad \dots (3)$$

Where I_0 is the current extrapolated to 1/T = 0. The slopes of the lines do not vary appreciably with the applied voltage (see $\Delta E\sigma$ values in Table 4). It was found that the electrical conductivity of InSbTe₃ is higher than that of InSbSe₃.³⁶ This result is attributed the nature of chemical bonding in the system being tested. Since the bonding energies of In-Se and Sb-Se are stronger than In–Te and Sb–Te bonds^{32,33}. This is confirmed by the values of electro negativity difference for elements given in Table 3. Larger the difference, the more likely bond will form³⁵.

InSbTe ₃		InSbTe ₃	
Applied bias	Activation energy	Applied bias	Activation energy
(V)	(ΔEσ), eV	(V)	(ΔEσ), eV
0.4	0.176	0.2	0.108
0.5	0.190	0.3	0.099
0.6	0.194	0.4	0.095
		0.6	0.108

Table 4: Activation energy of InSbTe₃ film of thickness 230 nm and InSbSe₃ film of thickness 250 nm at various applied bias

Poole-Frenkel mechanism and its modification

To determine, whether the Poole-Frenkel effect is the dominant mechanism in the high field region, the data of Fig. 3 (a & b) were plotted in accordance with normal high electric field theory to establish the Poole-Frenkel effect, if it dominant. Fig. 6 (a & b) shows a plots of IE⁻¹ (in logarithmic scale) vs E^{1/2} as required by the Poole-Frenkel equation²⁷. The derived value of β_{PF} and \in are listed in Table (18 : 2) for both systems. It is observed that the field lowering coefficient β_{PF} increases with increasing temperature through the investigated range.

Based on the Jonschers model³⁷, which takes account of the emission of electrons from sites in one particular direction in space with respect to the applied field, the data given in Fig. 2 (a & b) for both InSbSe₃ and InSbTe₃ films can be analyzed. Accordingly, plots of IE^{1/2} (in logarithmic scale) vs E^{1/2} are showning Fig. 7 (a & b) for the two systems. The obtained values of β and ε are listed in Tables 1 and 2. Fitting the room temperature

data to the Jonschers model is an indication that a modified Poole-Frenkel process is operating.



Fig. 6: (a) IE^{-1} (in logarithmic scale) vs $E^{1/2}$ plots for the InSbSe₃ film at different temperatures (b) IE^{-1} (in logarithmic scale) vs $E^{1/2}$ plots for the InSbTe₃ film at different temperatures



Fig. 7: (a) $IE^{1/2}$ (in logarithmic scale) vs $E^{1/2}$ plots for the InSbSe₃ film at different temperatures (b) $IE^{1/2}$ (in logarithmic scale) vs $E^{1/2}$ plots for the InSbTe₃ film at different temperatures

Fig. 8 (a & b) shows the $IE^{-1/2}$ (in logarithmic scale) vs $E^{1/2}$ characteristics for conduction model in which carrier motion are assumed to travel for a constant period of time before being trapped. The deduced values of β and ϵ are also given in Tables 1 and 2. From these tables, it is noticed that a large change in β and ϵ occurred with increasing temperature for the two systems.



Fig. 8: (a) $IE^{-1/2}$ (in logarithmic scale) vs $E^{1/2}$ plots for the InSbSe₃ film at different temperatures (b) $IE^{-1/2}$ (in logarithmic scale) vs $E^{1/2}$ plots for the InSbTe₃ film at different temperatures.

Both normal Poole-Frenkel and Jonscher models are capable to explain a change in B and \in for the tested systems with temperature in the investigated range as shown in Tables 1 and 2.

CONCLUSION

The electrical conduction in $InSbX_3$ (X = Te or Se) films has been analyzed. The I-V characteristics of thermally evaporated $InSbX_3$ (X = Te or Se) amorphous thin films were obtained in the temperature range (303-393 K) and thickness range (230-490 nm). The characteristics exhibited a transition from an ohmic region at low applied voltage to a non-linear region at higher voltage arises from lowering of the potential barriers by a high electric field. The behavior of the non-ohmic region of the I-V characteristics can be understood in terms of both simple and modified Poole-Frenkel mechanisms.

The dependence of ohmic current on the temperature corresponds to a thermally activated process with single activation energy. The values of activation energy and the dielectric constant for both InSbSe₃ than for InSbTe₃ films were investigated.

REFERENCE

- 1. A. N. Sreeram, A. K. Varshneya and D. R. Swiler, 1 Non Cryst. Solids, **130**, 225 (1991).
- 2. S. R. Ovshinsky, Phys. Rev. Letters, **21**, 1450 (1968).
- 3. F. M. Collins, J. Non Cryst. Solids, 2, 496 (1970).
- 4. J. L. Hartke, Phys. Rev., **125**, 1177 (1962).
- 5. B. J. Bagley, Solid State Commun., 2, 4663 (1972).
- 6. D. Emin, C. H. Seager and P. K. Quinn, Phys. Rev. Lett., 28, 813 (1972).
- 7. R. M. Hill, Phil. Mag., 23, 59 (1972).
- 8. M. Wobst and Z. Metalked, Phys. Rev., 58, 481 (1967).
- 9. D. P. Belotskii, P. F. Babyuk and N. V. Demyanchuk, Low Temperature Termoelectric Materials, J. Non Cryst. Solids, Kishinev (in Russian) (1970) p. 29.
- N. M. Gasanly, B. A. Natig, A. E. Bakhyshov and K. G. Shirinov, Phys. Stat. Sol., (b) 153, k89 (1989).
- 11. M. Spiesser, R. P. Gruska, S. N. Subbarao, C. A. Castro and A. Wold, J. Solid State Chem., 26, 111 (1978).
- 12. I. Kuliyeva, L. Kh. Khasanova and N. M. Salimova, Izv. Akad. Nauk Azerh SSR Ser. F iz Tekh. Mat.~Nauk (USSR), **5**, 87 (1986).
- 13. J. Horak, K. Cermak and L. Koudelka, I. Phys. Chem. Sol., 42, 805 (1986).
- 14. J. Horak, Z. Stary, P. Lostak and J. Pancir, J. Phys. Chem. Sol., 49, 191 (1988).
- 15. J. Kroutil, J. Navratil and P. Lostak, Phys. Stat. Sol., 131, K 73 (1992).
- K. Dovletov, F. Ragimov, S. Nuryev and N. K. Sama Khotina, Sov. Phys. Semicond., 16, 770 (1982).
- 17. P. Lostak, R. Novatny, J. Kroutil and Z. Stary, Phys. Stat. Sol., (a) 104, 841 (1987).
- V. A. Kulbachinskii, Z. M. Dashevskii, M. Inoue, M. Sasaki, H. Negishi, W. X. Gao, P. Lostak and J. Horak, Phys. Rev., B 52(15), 10915 (1995).
- D. Eddike, A. Ramdani, G. Brun, J. C. Tedenac and B. Liautard, Mat. Res. Bull., 33, 519 (1998).

- 20. J. Horak, S. Karamozov and P. Lostak, Phil. Mag., B 72, 627 (1995).
- 21. H. E. Atyia, Ph. D. Thesis, Ain Sharns University, Egypt (2003).
- 22. J. T. Kerr, J. Non Cryst. Solids, 2, 203 (1970).
- 23. N. A. Hegab, J. Phys. D: Appl. Phys., 33, 2356 (2000).
- 24. E. Abd E1-Wahabb, M. M. Abd E1-Aziz and M. Fadel, Vacuum, 57, 365 (2000).
- 25. N. A. Hegab and A. E. Bekheet, J. Mater. Sci., 36, 3817 (2001).
- 26. W. Schottky, Z. Physik, 15, 872 (1914).
- 27. J. Frenkel, Phys. Rev., 54, 647 (1938).
- 28. C. A. Mead, Phys. Rev., 128, 2088 (1962).
- H. S. Soliman, B. A. Khalifa, M. M. E1-Nahass and E. M. Ibrahim, J. Physica, B 11, (2004).
- 30. J. G. Simmon, Phys. Rev., **155**, 657 (1967).
- 31. J. Yeargam and H. L. Taylor, J. Appl. Phys., 39, 5600 (1968).
- 32. E. V. Shkolnikov, Sov. J. Glass Phys. Chem., 11, 40 (1985).
- 33. John A. Dean, Pmge's Hand Book of Chemistry, 14th Edition, Russia (1992).
- 34. L. Pauling, The Chemical Bond, Cornell University Press, New York (1967).
- 35. A. R. Hilton, C. E. Jones and M. Barau, Phys. Chem. Glasses, 7, 105 (1966).
- N. F. Mott and A. Davis, Electronic Processes in Non Crystaline Materials Clarendon, Oxford. (1971).
- 37. A. K. Jonscher, Thin Solid Films, 1, 213 (1967).

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