Investigation of density of states of Se-Te-Ag thin films by SCLC measurements

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The present paper reports the DC conductivity measurements in vacuum evaporated thin film of a-$Se_{96-x}Te_4Ag_x$ (x = 0, 4, 8, 12 and 16 at. %) sample. Current voltage (I-V) characteristics of these films have been studied at different temperatures with varying the voltage from 0 to 400V. In all the samples, ohmic behaviour is observed at low electric fields up to 3.75×10^2 V/cm. However, at high fields ($>3.75 \times 10^2$ V/cm), the DC measurement indicates that the electrical transport is governed by the space charge limited conduction (SCLC) mechanism. The detailed analysis of current–voltage limited conduction mechanism characteristics on the basis of SCLC theory reveals the presence of uniform distribution of localized states in the mobility gap of these materials. The addition of silver in a-$Se_{96-x}Te_4Ag_x$ decreases the density of localized states in the mobility gap.

1. Introduction

The relationship between structure and electronic properties has been the object of invariable attention in the physics of condensed matter. This problem is most important for non-crystalline semiconductor, and specifically for chalcogenide glassy semiconductor with low coordination of atoms, which leads to labiality of their structure [1-4]. Recently, silver doped chalcogenide semiconductor have been extensively studied, because of their interesting fundamental properties and wide commercial applications, especially in the solar cell technology for terrestrial uses. The potential applications of chalcogenide semiconductors are now in the field of optics, the interest being chiefly from either their infrared transmitting properties or the many photo-induced effects they exhibit. They have also potential uses in many solid-state devices such as switching, memory devices, imaging sensors and optical data storage [5-9]. Enormous interest has been shown in a-Se-Te alloys due to their great hardness, higher photosensitivity, higher crystallization temperature and smaller aging effects as compared to pure amorphous Se or Si [10]. Amorphous semiconductor has inherent defects states in the mobility gap and the density of such localized states (g_0) controls many physical properties of these materials [11-12]. One of the most direct methods for the determination of g_0 involves the measurements of space charge limited current that can easily be observed at high electric fields in amorphous materials because of their low conductivity. The density of localized states near the Fermi level is calculated using the theory of SCLC for the case of uniform distribution of traps. Silver ion conducting system in glassy/amorphous phase attracted widespread academic as well as technological interests recently due to the reason that they exhibited several advantageous material properties due to very high conductivity at room temperature. Silver as a dopent element to a-Se-Te system causes structural changes in the material which in turn modify band structure, and hence the electrical properties due to its ionic nature [13-15]. The purpose of the present study is to report some electrical conduction mechanism to determine the influence of silver content on the properties of a-Se-Te system and characterize its dependence on temperature and electric field. That is, the Se part of the a-Se-Te content is substituted by silver, with the Te set at a fixed content. A lot of work have been done on electrical, optical and dielectric properties of this mixed system by various workers [14,16-21] in detail, but there is a little research work into the high field conduction studies of a-

$Se_{96-x}Te_4Ag_x$ (x = 0, 4, 8, 12 and 16) system. In the present work, we have studied the current–voltage (I-V) characteristics as a function of temperature and electric field dependence on thermally evaporated a-$Se_{96-x}Te_4Ag_x$ thin film. An attempt has also been made to study the transport mechanism in these glassy alloys.

2. Experimental

$Se_{96-x}Te_4Ag_x$ (x = 0, 4, 8, 12 and 16 at. %) glasses are prepared by the melt quenching technique. Appropriate quantity of 5N purity elements were sealed in quartz ampoules under a vacuum of 10^{-5} Torr. The sealed ampoules were then placed in a Microprocessor-Controlled Programmable Muffle Furnace where the temperature was increased at the rate of 4 K per min. up-to 1300 K and kept at that temperature for 12 hours with frequent rocking to insure the homogeneity of the melt. After rocking for about 12 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and quickly dropping into ice water. The quenched samples of a-$Se_{96-x}Te_4Ag_x$ were taken out by breaking the quartz ampoules. The amorphous nature of the samples was confirmed by the absence of any sharp peaks in the x-ray diffraction pattern in fig. 1. However, in fig. 1(a) has some peaks of the selenium elements in the $Se_{96}Te_4$ system. These peaks have very small intensity, and the sharpness is not clear in the fig. 1(a) as well as in 1(b). These peaks may be due to the grain growth of the selenium in the $Se_{96}Te_4$ system. In fig. 1(b) there is an only single peak at the incident angle 30^0. It is only due to selenium elements, so the present system $Se_{96-x}Te_4Ag_x$ as amorphous materials.
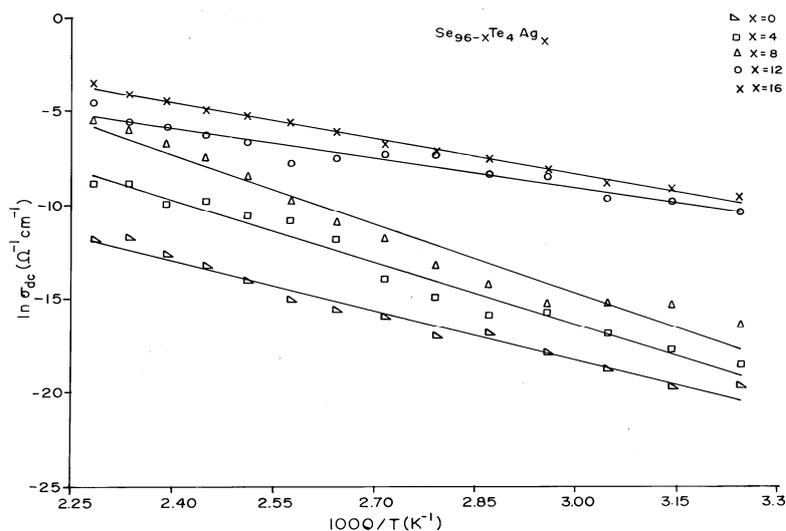

Fig. 1. DC conductivity Vs 1000/T for thin films of a- $Se_{96-x}Te_4Ag_x$ glassy system ($0 \leq x \leq 16$).

Thin films of these glassy alloys were prepared by the vacuum evaporation technique using a standard coating unit (model EU-300). Well-degassed corning glasses plates, having pre-deposited indium electrode for electrical contact, were used as a substrate for depositing amorphous films in the planer geometry and different electrode gap. These films were prepared at a base pressure of ~10^{-5} Torr by keeping the substrate at room temperature. Thickness of the thin films ($5000A^0$) has been measured by using the single crystal thickness monitor. The deposition parameters were kept almost the same for all the samples so that a comparison of results could be made for various glassy samples. DC conductivity and I-V measurement were carried out in a specially designed sample holder where a vacuum of ~10^{-3} Torr was maintained throughout the measurement. For DC conductivity measurement, a dry cell of 1.5 V was used as a constant dc source. A dc voltage (0–400V) was applied across the sample and the resulting current was measured by a digital electrometer (Keithley model 617). The temperature was measured by mounting a copper–constant thermocouple. Keithly LCZ meter (3330) was used for measurement

of capacitance of the bulk samples at lower frequency (200 Hz) and at temperature 358 K, which is involved in the calculation of density of states.

3. Results discussion

Fig. 1 shows the temperature dependence of dc conductivity for a thermal evaporated thin film of a- $Se_{96-x}Te_4Ag_x$ (x = 0, 4, 8, 12 and 16) system. It is clear from figure 1 that the plot of ln σ_{dc} vs 1000/ T is linear in nature in the temperature range 300 –440K. This indicates that the electrical conduction in the film form is through an activated process with single activation energy in this temperature range. The dc conductivity can therefore be expressed by the conventional relation [22]

$$\sigma_{dc} = \sigma_0 \exp(- \Delta E/ kT) \qquad (1)$$

where σ_0 and ΔE represent the pre- exponential factor and activation energy respectively. The calculated values of σ_{dc}, σ_0 and ΔE (from fig. 1), given in Table 1 for these films, suggest that the conduction is due to thermally assisted tunneling of charge carriers in the localized states present in the band tails. The activation energy ΔE alone does not provide any information as to whether the conduction takes place in the extended states above the mobility edge or by hopping in the localized states. As both the conduction mechanism occur simultaneously, with the conduction via localized states dominating at low temperatures, the activation energy in the former case represent the energy difference between the mobility edge and Fermi level. In the later case, it represents the sum of the energy separation between the occupied localized states and Fermi level, and the mobility activation energy for the hopping process between the localized states. In order to obtained a clear distinction between these two conduction mechanism, Mott [1] has suggested the conduction mechanism in amorphous materials such as the conduction at the localized states is two-three orders less than the extended states and should become smaller in magnitude than the conduction in the localized states near to the fermi level. The value of σ_0 reported for the selenium or other selenium alloy films are of the order of 10^3 to 10^4 or greater than it, for conduction in the extended states [23].
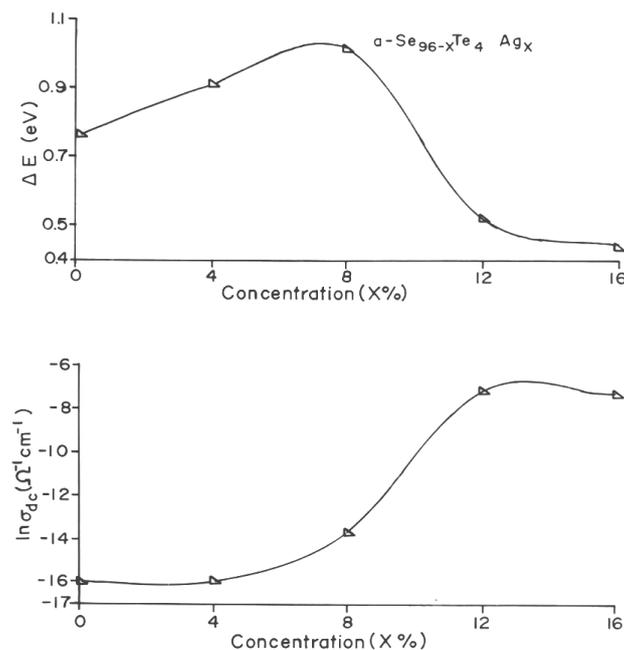

Fig. 2 Variation of activation energy and DC conductivity Vs concentration for a-$Se_{96-x}Te_4Ag_x$ glassy system ($0 \leq x \leq 16$).

In our present system, σ_0 is increases from 10^3 to 10^7, thus the conduction takes place in the extended states [1]. Similar results of selenium-based alloys also have been found by other researchers [24-26]. As the σ_0 increases with silver concentration, similarly the activation energy dc conductivity increases for x = 0, 4 and 8% of silver, after that for higher concentration of silver x = 12 and 16%, σ_0 is decrease thus the activation energy and dc conductivity also have been decreases but for all the silver concentration, density of states decreases from 10^{18} to 10^{16} (eV^{-1}cm^{-3}). The other workers have also been found the same density of states in the selenium-based alloys like the product of total no density of states and total no of pairs [27-30]. Again, the increase in the values of activation energy (ΔE) and pre-exponential factor with silver concentration (up to x = 0, 4 and 8%) shows that the mobility (conduction) of charge carriers in the trap states increases with silver content which can be attributed either to increase optical gap or to increase the width of the localized states region, however dc conductivity is almost constant for each silver concentration. At higher concentration of silver, the decrease in the value of pre-exponential factor can be attributed to the decrease in the density of localized states. Fig. 2 shows the variation of activation energy and dc conductivity with the silver concentration in the present sample. An increase in dc conductivity with a corresponding decrease in the activation energy is found to be associated with the shift of the fermi level in impurity doped chalcogenide glasses [31-32].

Several workers [33-36] have pointed out that when a metal undergoes chemical combination, it forms compound where the distribution of charge takes place in the outer level to the most likely level or surface that can be affected by the redistribution of electrons in the fermi level or surface. This is, when a metal undergoes chemical combination and forms a compound its Fermi level should change. This can also be explained on the basis of the change in electronegativity. According to Sanderson [37], when an element combines with other elements, they come together at an intermediate value of electronegativity, which is the geometric mean of the combining atoms.
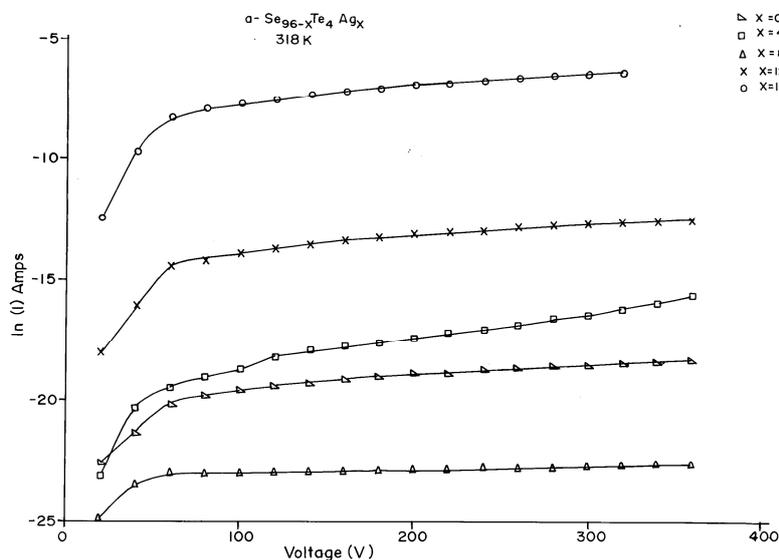

Fig. 3. Distinction between ohmic and SCLC region for a-Se$_{96-x}$Te$_4$Ag$_x$ glassy system for electrode gap "d" = 0.12 cm

For the present system, the electronegativity (X_c) has been calculated by Sanderson's equalization using, Husain et al. [38], values of electronegativity for different elements and calculated values are shown in Table 1. It is observed that the electronegativity of the system decreases as the Silver concentration increases. So, one can infer that the decrease in electronegativity, increases dc conductivity of the system.
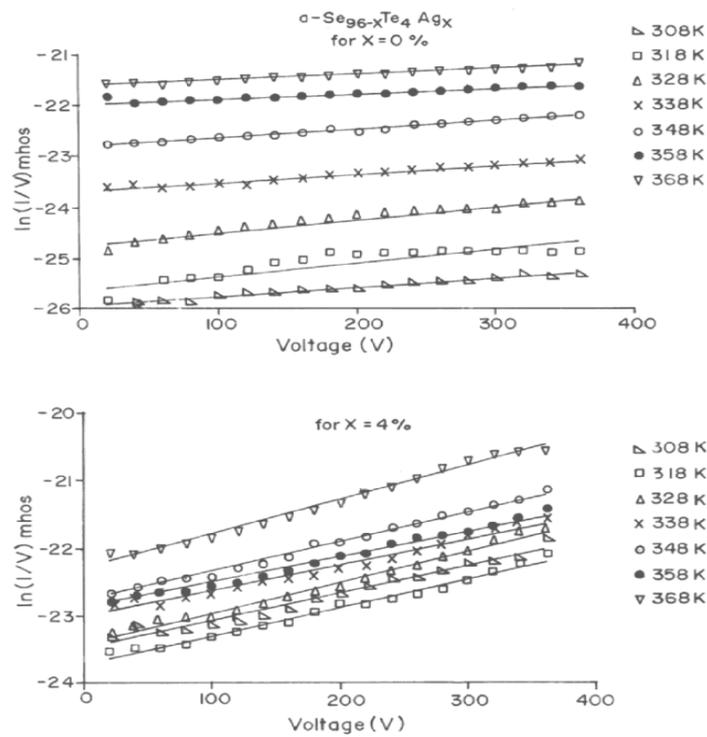
Fig. 4. ln I/V Vs voltage (V) plots for a-$Se_{96}Te_4$ and a-$Se_{92}Te_4Ag_4$ for electrode gap
"d" =0.12 cm
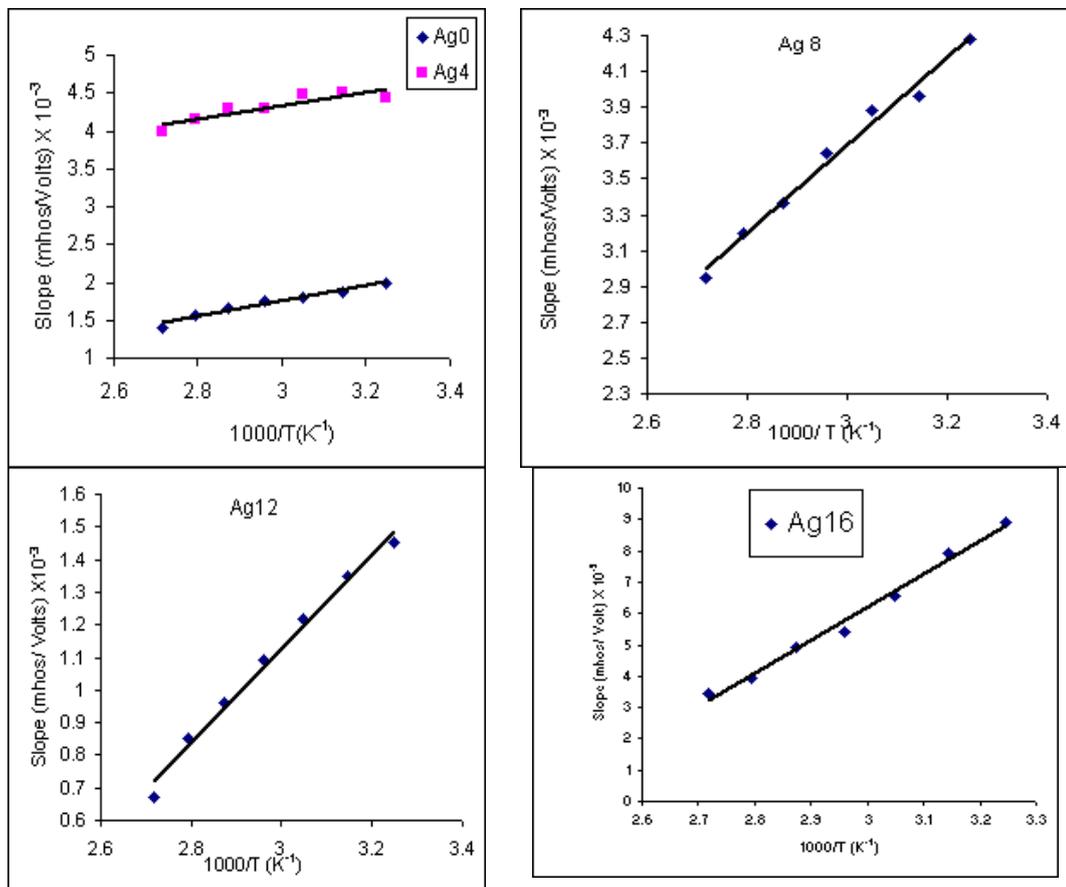

Fig. 5. Slope of lnI/V Vs voltage against 1000/T for electrode gap "d" = 0.12 cm

The I-V characteristics for a-$Se_{96-x}Te_4Ag_x$ thin film indicates its ohmic behavior up to 3.75×10^2 volt / cm as shown in Fig 3. However, at higher field (>3.75 x 10^2 V/cm), the non-ohmic behavior is observed due to the predominance of charge carrier injection from electrode into the sample. Fig. 4 (a and b) shows the ln (I / V) Vs voltage plot for a-$Se_{96}Te_4$ and a-$Se_{96}Te_4Ag_4$ at different fixed temperature in the range 300-370K for electrode gap 0.12cm. Similar results were obtained for other samples for all different electrode gaps (results are not shown here). From Fig. 4 it is clear that the plot of ln (I/V) Vs V is a straight line for all the fixed temperature and the slope is not constant (same) at all the measuring temperature. This type of behavior has also been reported by other workers in chalcogenide glasses [37-39]. Now the values of these slopes (From fig. 4) plotted as a function of temperature are shown in Fig. 5 for all the studied samples for electrode gap d = 0.12cm. It is observed that the slope decreases as the temperature increases in the present sample (in Fig. 5). According to the theory of SCLC, in the case of uniform distribution of localized states g_0, current I at a particular voltage V is given by the relation [40-41]

$$I = KV \exp (SV) \tag{2}$$

where K is a constant and S is given by

$$S = 2\varepsilon_0\varepsilon_r /qg_0d^2kT \tag{3}$$

where ε_0 is the Permittivity of free space, ε_r is the relative dielectric constant, d is the electrode gap, k is the Boltzmanns constant and g_0 is the density of localized states. It should be noted that equation 2 is not an exact solution of SCLC equation, but it is a very good approximation of the single carrier space charge limited current under the condition of a uniform distribution of localized states. From equation 2, ln (I/V) Vs V curves should be straight lines (Fig. 4) whose slope should decrease with increase of temperatures as evident from equation 3. Similar phenomena are observed in a-$Se_{96}Te_4$ and $Se_{96}Te_4Ag_4$ sample. Fig. 5 shows the slope decreases with the increase of the temperature, which confirms the presence of SCLC in the present sample. Thus, for SCLC mechanism, the slope (S) increases linearly with the electrode gap. Thus, the I-V characteristics for all samples having different electrode gap (d) have been recorded. The calculated values of these slopes in these thin films of a-$Se_{96-x}Te_4Ag_x$ have been plotted against $1/d^2$ as given in Fig.6. It shows that the slope decrease as the electrode gap increases for the silver content up to x= 0, 4, which confirms again the validity of equation 3 in the present case and for higher concentration of silver (x =8,12and 16 %) too, the validity of equation 3 is true (results are not shown). The plot of ln I vs $(E)^{1/2}$ were not found to be a straight line (results are not shown here) and in the case of Pool Frenkel effect, the slope (S) must be independent of the electrode gap (d) [42]. Hence the possibility of such a conduction mechanism is ruled out. The density of localized states (g_0) can be obtained from the slope of S against 1000/T curves when the values of dielectric constant (ε') are known. To calculate the dielectric constant, we use a specially design sample holder from which we measure the capacitance of the sample in pellet form (diameter = 1.2cm and thickness = 0.10 cm) and calculate the dielectric constant by dividing the capacitance in the vacuum. A vacuum of 10^{-3} Torr has maintained in the sample holder at the time of measurement. Using this measured value of dielectric constant at temperature 358K and frequency 200Hz, the values of g_0 were calculated for the present samples.

Table1. Electrical parameter and density of states of a $Se_{96-x}Te_4Ag_x$ system

| Sample	Activation Energy(ΔE) (eV)	DC Conductivity (σ_{dc})($\Omega^{-1}cm^{-1}$)	σ_0 ($\Omega^{-1}cm^{-1}$)	ε'	Slope (S) (mhos -V^{-1})	Density of States (g_0) ($eV^{-1}cm^{-3}$)	X_c (Electro-negativity)
$Se_{96}Te_4$	0.76	11.58×10^{-8}	5.7×10^3	90	0.94×10^{-3}	2.76×10^{18}	2.132
$Se_{92}Te_4Ag_4$	0.91	11.74×10^{-8}	7.39×10^5	128	0.70×10^{-3}	5.25×10^{18}	2.121
$Se_{88}Te_4Ag_8$	1.01	13.58×10^{-8}	2.18×10^7	54	2.50×10^{-3}	6.23×10^{17}	2.108
$Se_{84}Te_4Ag_{12}$	0.52	76.6×10^{-5}	1.59×10^4	52	1.52×10^{-3}	9.87×10^{17}	2.096
$Se_{80}Te_4Ag_{16}$	0.44	65.8×10^{-5}	1.01×10^3	31	9.16×10^{-3}	9.76×10^{16}	2.087
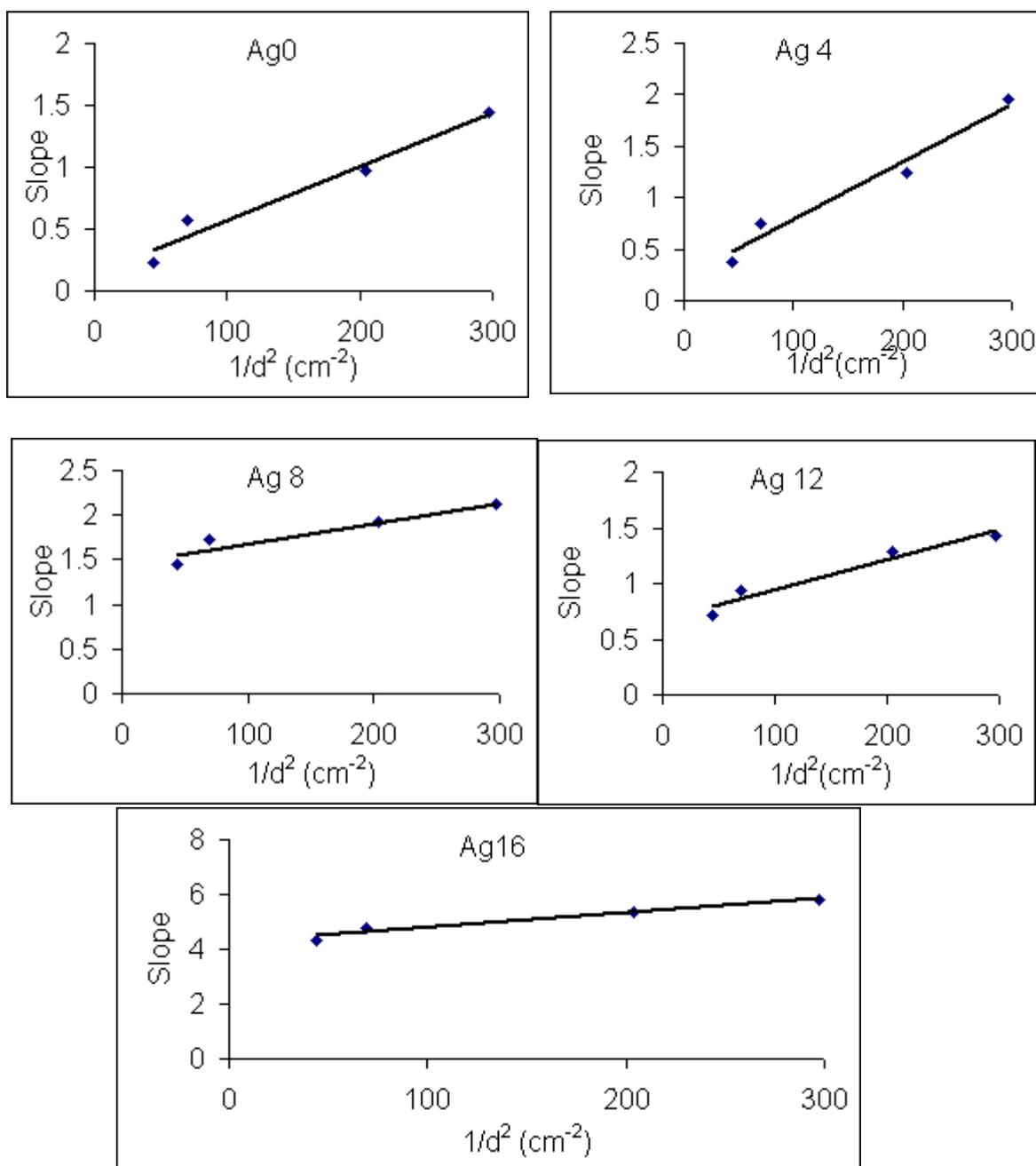
Fig. 6. Variation of slope Vs electrode gap ($1/d^2$) for a-$Se_{96-x}Te_4Ag_x$ system.
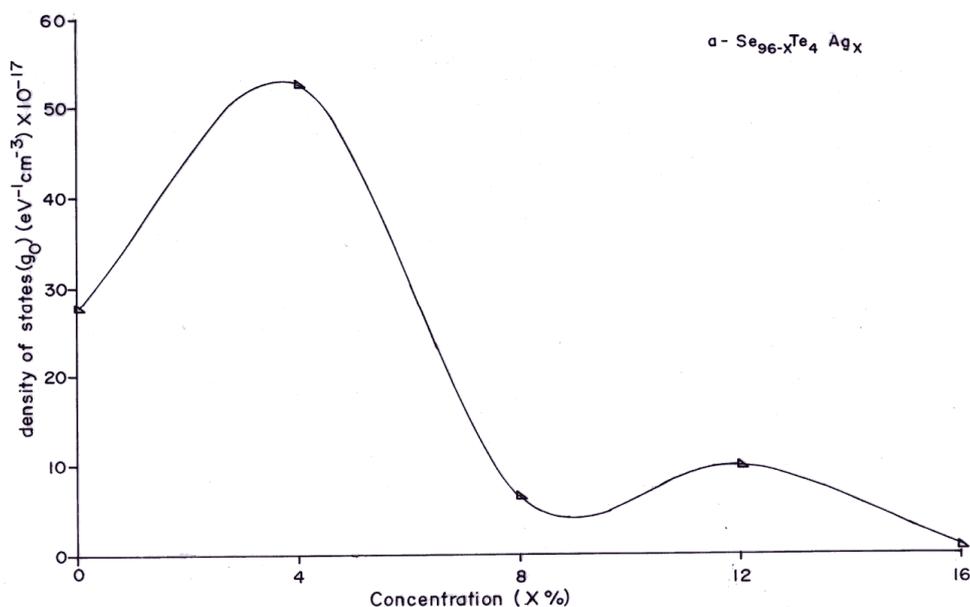
Fig. 7. Density of states "g_0" Vs concentration (X %) curves in a-$Se_{96-x}Te_4Ag_x$ by the SCLC measurements.

The density of localized states decreases as the silver concentration increases, given in Table 1. Fig. 7 shows the variation of density of localized states in the mobility gap with the silver concentration. The lone pairs and the other configuration, which the system might have undergone at the time of quenching, could be responsible for the decrease in the density of localized states. The variation can be explained in terms of charged impurity in the structure of Se-Te bonds. Schottmiller et.al have studied the effect of addition of various elements (S, Te, Bi, Ag & Ge etc.) on the structure of glassy Se by IR and Raman spectra. According to them, in glassy Se about 40 % of the atoms have a ring structure and 60 % atoms are bonded as polymeric chains. An incorporation of Te decrease the Se ring concentration favoring Se-Te polymeric chains and mixed rings [42-43]. On addition of Ag into Se-Te systems, might chains have decreased and rings get increased which decreases the defect states (D^+, D^-) in the Se-Te rings and chains, this is because silver decreases the localized states. The present results indicate that, at low concentration of silver, the atoms might have entered into the polymeric chains of Se-Te, which may increase the density of states (g_0). However at higher concentration, these atoms may enter into the ring structure of Se-Te, which could decrease the g_0. Also the density of localized states decreases with decrease the electro negativity of the system.

4. Conclusion

The temperature dependence of dc conductivity of a-$Se_{96-x}Te_4Ag_x$ (x = 0, 4, 8, 12 and 16) thin films has been used to calculate the activation energy and pre-exponential factor, which inferred that the conduction mechanism of charge carriers in the extended states. On increasing the concentration of silver, the increase in dc conductivity and decrease in activation energy is due to decrease of localized states in the band gap. The SCLC mechanism holds validity in the above study. Addition of Ag into Se-Te system might decrease the chain and increases the rings of Se-Te, which in turn decreases the defect states (D^+, D^-). This is probably the reason that silver decreases the localized states. The present results indicates that, at low concentration of Ag, the silver atoms may enter into the polymeric chains of Se-Te, which increases small change in density of states (g_0). However at higher concentration, these atoms may enter the ring structure of Se-Te, which could decrease the density of localized states (g_0) in the band gap. As the

electronegativity of the system decreases, the corresponding dc conductivity increase and the density of states decreases with the increase of silver concentration of the system.

References

[1] N. F. Mott, Davis E. A., Electron Processes in Non-Cryst. Mate. (Oxford: Clarendon), **2**, 660 (1979)
[2] Satish Kumar, M. Husain, M. Zulfequar, J. Optoelectron. Adv. Mater**. 9**(9) 2743 (2007)
[3] K. D. Tsendin, Electronic Phenomena in Chalcogenide Glassey Semiconductor (St Petersburg: Nauka), 486 (1996)
[4] A. A. Aivazov , Disorder Semiconductors (Moscow: Publisher MEI), 352 (1995).
[5] I. Shimizu, H. Kokade, E. Inoue, Photogr. Sci. Engg., **19**,139 (1975)
[6] Y. Ashara, T. Izumitani, Phys. Chem. Glasses, **16**, 29 (1975)
[7] K. J. Tai, E. Ong, R. G. Vidinsky, Proc. Electro-Chem. Soc., **9**, 83 (1982)
[8] K. Tanaka, Y. Imai and A. Odajima, J. Appl. Phys., **57**, 4897 (1985)
[9] J. Shirafuji, G. Kim and Y. Inuishi, Jpn. J. Appl. Phys.**16**, 671(1977)
[10] B. T. Kolomieto, Phys. Status Solidi, 7 (1964) 713
[11] N. A. Hagab, J. Phys. D: Appl. Phys. **33**,2356 (2000)
[12] M. A. Majeed Khan, M. Zulfequar, M. Husain, Physica B, **366**,1 (2005)
[13] Z.U. Borisova. Glassy Semiconductors, Plenum Press, New York, 128 (1981)
[14] K. Tanaka. J. Non-Cryst. Solids, **164,** 1179 (1993)
[15] M. Ohto, M. Itoh and K. Tanaka. J. Appl. Phys., **77** 1034 (1995)
[16] D. L. Price, S. Susman, K. J. Volin and R. J. Dejus, Physica B, **156,** 189 (1988)
[17] K. Tanaka, M. Itoh, N. Yoshida and M. Ohto, J. Appl. Phys., **78**, 3895 (1995)
[18] T. Kawaguchi, S. Maruno and S.R. Elliott, J. Appl. Phys., **79**, 9096 (1996)
[19] M. Ohto, Phys. Stat. Solidi A., **159**, 461 (1997)
[20] S. K. Dwivedi, A. Kumar, S. Kumar, Advanced Materials for Optics and Electronics, **9**, 235 (2000)
[21] S. A. El-Hakim, F. A. El-Wahab, A. S. Mohamed, M. F. Kotkata, Phys. Stat. Sol. (a), **198**, 128 (2003)
[22] N. F. Mott, E. A. Davis, Philos. Mag., **22**,903 (1970)
[23] E. A. Davis, N. F. Mott, Philos. Mag., **22,** 7 (1970) 903
[24] S. A. Khan , M. Zulfequar, Z. H. Khan, M. Husain, Journal of Optics, **50(1),** 5 (2003)
[25] S. A. Khan , M. Zulfequar, M. Husain, Current Aplied Physics, **3**, 337 (2003)
[26] M. A. Majeed Khan, M. Zulfequar, Z. H. Khan, M. Husain, Journal of Materials Science, **8**, 549 (2003)
[27] N. Mehta, A. Dwividi, R. Arora, S. Kumar, A. Kumar, Bult. Mater. Sci., **28(6)**, 579 (2005)
[28] Ashwani K. Sharma, K. L. Bhatia, Journal of Non-Crystalline Solids, **109**, 95 (1989)
[29] K. Koughia,a! Z. Shakoor, and S. O. Kasap, Journal of Applied Physics, **97,** 33706 (2005)
[30] G. J. Adriaenssens, A. Stesmans, Journal of Optoelectronics and Advanced Materials, **4(4),** 837 (2002)
[31] M. A. Lampert, M. Park, Current Injection in Solids, Acad. Ress, New York, 1970
[32] S. P. Singh, S. Kumar, A. Kumar, Chalcogenide Letters, 1(8) (2004) 105
[33] B.T Kolomites,E.A. Lebedev & N.A. Rogachev, Fiz. Tekh, Ppuprov**, 8,** 545 (1974)
[34] S. Okano, M. Suzula, Kimura, N. Fukada and A. Hiraki, J. Non-Cryst. Solids, **59 & 60,** 969 (1983)
[35] A. V. Pendharkar, C. Mande, Physica , **66**, 204 (1973)
[36] V. K. Konderawer, C. Mande, Curr. Scie., **42**, 562 (1973)

[37] R. T. Sanderson, Inorganic Chemistry , Affiliated East-West Press, New Delhi, (1971)
[38] M. Husain, A. Batra, K. S. Srivastava, Polyhedra, **8**, 1233 (1989)
[39] S. P. Singh, S. Kumar, A. Kumar, Chalcogenide Latt. **1**, 105 (2004)
[40] Shaila Wagle, Vinay Shirodker, Brazilian Journal of physics, **30**, 380 (2000)
[41] C. Viswnathan, S. Gpal, M. Thamilselvan, K. Prem Nazeer, D. Mangalaraj, Sa. K.
 Narayandass, Junsin Yi, David C. Ingram, Joural of Materials Science: Materials in
 Electronics, **15 (12)**, 787 (2004)
[42] Shagufta B. Husain, M. Zulfequar, M.A. Majeed Khan , M. Husain, Current Applied Physics,
 4, 445 (2004)
[43] J. Schottmiller, M. Tabak, G. Lucvsky, A. Ward, J. Non - Cryst. Solids, **4,** 80 (1970)

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