Chalcogenide Letters Vol. 1, No. 7, July 2004, p. 83 - 90

STEADY STATE PHOTOCONDUCTIVITY IN a-$Se_{90}Ge_{10-x}In_x$ THIN FILMS

S. Singh, R. S. Sharma, R. K. Shukla, A. Kumar*

Department of Physics, Harcourt Butler Technological Institute,
Kanpur-208 002, India

Temperature and intensity dependence of photoconductivity is studied in a-$Se_{90}Ge_{10-x}In_x$ thin films prepared by vacuum evaporation. Temperature dependence of photoconductivity shows a maximum at a particular temperature. The study carried out on intensity dependence of photoconductivity shows that the values of γ is found to be between 0.5 and 1.0 for all the samples. This indicates that there exists a continuous distribution of localized state in the mobility gap of a-$Se_{90}Ge_{10-x}In_x$ thin films. Composition dependence of steady state photoconductivity shows that photoconductivity as well as photosensitivity is found to be minimum at 4 at. % of In. A discontinuity in various electrical parameters at 4 at. % of In is related to formation of mechanically stabilized structure at a particular average coordination number 2.2. This is consistent with the theory of Phillips and Thorpe for the topological model in case of chalcogenide glasses.

1. Introduction

Chalcogenide glasses are promising materials for many applications in solid state devices. Recently, special interests have dedicated to in the amorphous films of chalcogenide glasses in connection with the modification of their properties on doping with metal impurities [1]. In thermally evaporated amorphous films of chalcogenide glasses these impurity atoms are electrically active and allow to obtain new materials with the improved properties. The changes in physical properties of amorphous films is caused by the modification of their structural and chemical disordering due to presence of high concentration of defects [2]. Trapping and recombination processes, which depend on the distribution and concentration of these defects, strongly influence the photoelectrical characteristics of the amorphous materials [3].

The electrical properties of chalcogenide glasses are not, in general, affected appreciably by the incorporation of impurities because the random network of atoms can accommodate an impurity without creating an extra electron or hole. This concept is based on the fact that an impurity atom can satisfy its valence requirements by adjusting its nearest neighbour environment, thus causing the negligible effect on the electrical properties [4]. Another argument is that the high density of localized states present in the forbidden gap effectively pins the Fermi level. However, experimental results reported by various researchers have shown that there are selected cases in which the addition of impurity atoms does change the electrical properties of chalcogenide glasses significantly [5-8]. It has also been found that the effect of impurities depends strongly on the composition of the glass, the chemical nature of the impurity and the method of doping. Impurity concentration obviously is a critical factor in such cases because all impurities cannot behave in an electrically active manner. Several of the physical properties are found to improve by the addition of certain impurities. Therefore, investigations on the influence of impurities on the properties of chalcogenide glasses are of relevance both from the basic science and application point of view.

In the present paper the results of d. c. conductivity and steady state photoconductivity of ternary chalcogenide glassy system, namely Se-Ge-In, are presented. The system can be considered as consisting of the basic Se-Ge network with appropriate amounts of indium added as impurity in the glass forming region of the Se-Ge-In system.

* Corresponding author: dr_ashok_kumar@yahoo.com

2. Experimental

Glassy alloys of $Se_{90}Ge_{10-x}In_x$ (x = 2, 4, 6 and 10) were prepared by quenching technique. The exact proportions of high purity (99.999%) elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4}gm. The materials were then sealed in evacuated (~ 10^{-5} Torr) quartz ampoules (length ~ 5cm and internal diameter ~ 8 mm). The sealed ampoules containing were heated to 1000 ^{o}C and were held at that temperature for 12 hours inside a furnace. The temperature of the furnace was raised slowly at a rate of 3 - 4 ^{o}C / minute. During heating, all the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogeneous glassy alloys.

After rocking for about 12 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water rapidly. The quenched samples were then taken out by breaking the quartz ampoules. The glassy nature of the alloys was ascertained by x - ray diffraction patterns.

Thin films of these glasses were prepared by vacuum evaporation technique keeping glass substrates at room temperature. Vacuum evaporated indium electrodes at bottom were used for the electrical contact. The thickness of the films was ~ 500 nm. The coplanar structure (length ~ 1.2 cm and electrode separation ~ 0.5 mm) was used for present measurements.

The electrical conductivities in dark as well as in presence of light were studied by mounting them in a specially designed sample holder in which illumination could be achieved through a transparent window. A vacuum of about 10^{-2} Torr was maintained throughout these measurements. The temperature of the films was controlled by mounting the heater inside the sample holder and measured by a calibrated copper constantan thermocouple mounted very near to the films. The heating rate was kept quite small (0.5 K/min.) for these measurements. The light source for these measurements was a 200 W tungsten lamp. Intensity of light was measured by a Luxmeter (Testron, model LX - 101) and the current was measured by a digital electrometer (Keithley, model 614).

3. Results and discussions

3.1 D.C. Conductivity

The d. c. conductivity was measured as a function of temperature (285 K to 375 K) for glassy $Se_{90}Ge_{10-x}In_x$ with x = 2, 4, 6 anmd 10. The results of these measurements are plotted in Fig. 1. It is clear from the figure that ln σ_{dc} vs. 1000/T curves are straight lines for all the samples indicating that the conduction in these glasses is through an activated process having single activation energy in the temperature range (285 K to 375 K) The d. c. conductivity can, therefore, be written as

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

where ΔE is the activation energy for d. c. conduction and k is the Boltzmann's constant.

The values of σ_{dc} at a particular temperature 303 K for various samples are calculated and plotted in Fig. 2 as a function of In concentration. The values of ΔE and σ_0 are also calculated using the slopes of the curves of Fig. 1 and equation 1 and plotted in Figs. 3 and 4. The results of these calculations are given in Table 1. It is clear from these figures that σ_{dc} first decreases as indium concentration increases from x = 2 to x = 4 and then increases with the increase of concentration of indium. ΔE and σ_0 are also found to be maximum at x = 2 at. % of In.

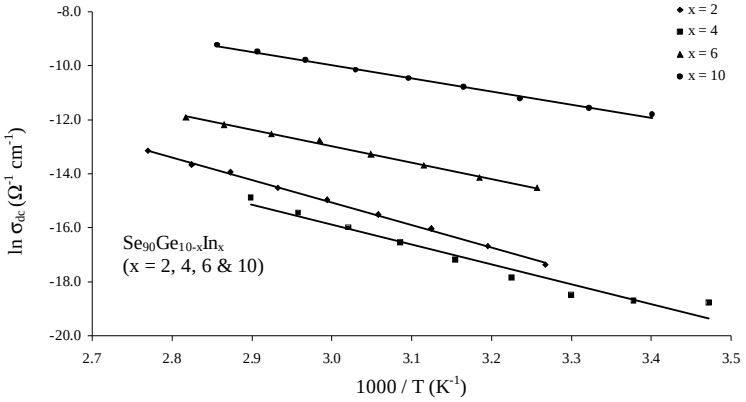

Fig. 1. Temperature dependence of dark conductivity for various samples in a - $Se_{90}Ge_{10-x}In_x$ thin films.

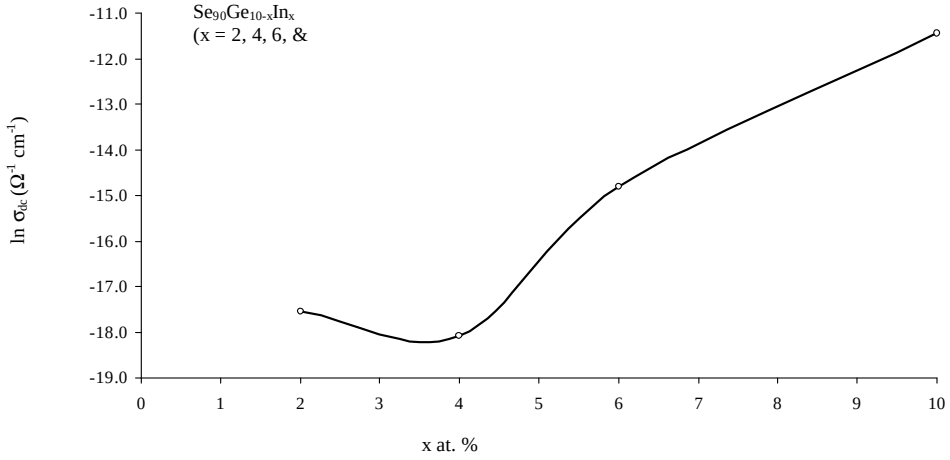

Fig. 2. ln σ_{dc} versus x at. % in a - $Se_{90}Ge_{10-x}In_x$ thin films.

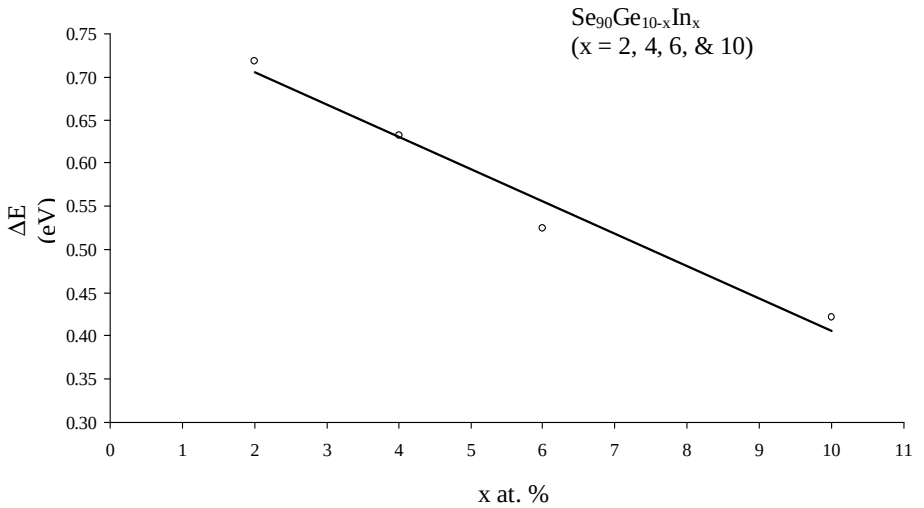

Fig. 3. ΔE versus x at. %in a - $Se_{90}Ge_{10-x}In_x$ thin films.

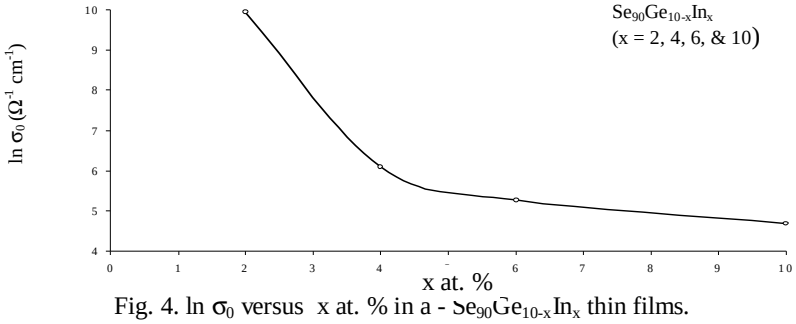

Fig. 4. ln σ_0 versus x at. % in a - $Se_{90}Ge_{10-x}In_x$ thin films.

Table 1.

S. No.	Composition (x)	ΔE (eV)	$\sigma_{dc}(\Omega^{-1}cm^{-1})$ at 303 K	$\sigma_0(\Omega^{-1}cm^{-1})$
1.	2	0.72	2.39×10^{-8}	2.09×10^{4}
2.	4	0.63	1.41×10^{-8}	4.47×10^{2}
3.	6	0.52	3.71×10^{-7}	1.93×10^{2}
4.	10	0.42	1.08×10^{-5}	1.08×10^{2}

3.2 Steady state photoconductivity

3.2.1 Temperature dependence of photoconductivity

Temperature dependence of steady state photoconductivity has been studied in a-$Se_{90}Ge_{10-x}In_x$ system with x = 2, 4, 6 and 10 in the temperature range 285 K to 375 K. Temperature dependence of photoconductivity at various intensities (6400 Lux, 8600 Lux and 10750 Lux) for a particular composition $Se_{90}Ge_8In_2$ is shown in Fig. 5. A maximum in photoconductivity is observed at a particular temperature of the film. Below maxima, ln σ_{dc} vs. 1000/T curves are straight lines.

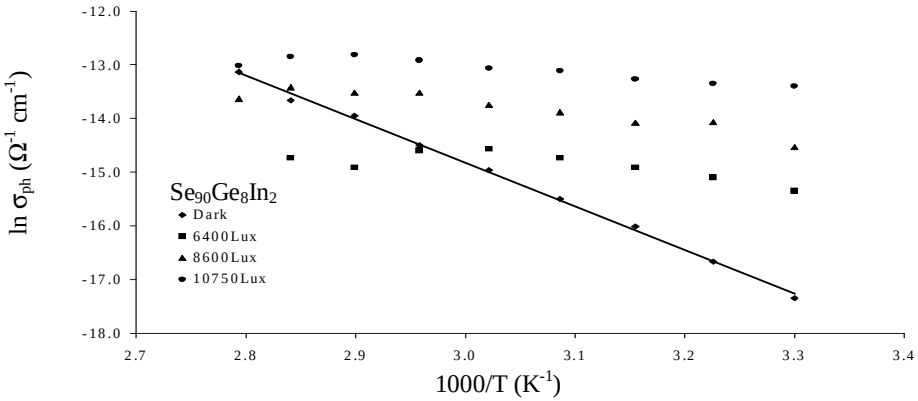

Fig. 5. Temperature dependence of photoconductivity in a - $Se_{90}Ge_8In_2$ thin film.

The first model of photoconductivity in amorphous chalcogenides at higher temperature was proposed by Street and Mott [9]. In this model recombination of photo-generated carriers is dominated by deep centers situated close to the Fermi level [10]. According to this model σ_{ph} must be proportional to product of the quantum efficiency η and the light intensity F, when the photocurrent I_{ph} is less than the dark current I_d, whereas at larger values of F, which yields $I_{ph} > I_d$, σ_{ph} must be proportional to $(\eta F)^{1/2}$.This model describes well the experimental data on these materials.

A maximum in the photoconductivity is a general feature of amorphous semiconductors [11-33] and various theories have been put forward to explain these maxima. According to ABFH (Arnoldussen-Bube-Fegen-Holemberg) model [11] for photoconductivity in amorphous chalcogenide alloys, this type of behaviour is found in type I photoconductors. For type I photoconductors, photoconductivity is greater than the dark conductivity upto a particular temperature T_{max} where the photoconductivity attains its maxima value. If the temperature is increased beyond T_{max}, photoconductivity decreases. On the basis of the energy level diagram suggested by the ABFH model, there are transitions which are from (i) localized to extended state for $T > T_{max}$ and (ii) localized to localized states for $T < T_{max}$ that dominate in type I photoconductors. The similar behaviour has also been reported by Mathew and Philip [12,13] in case of As-Sb-Se, Se-Ge-In and Ge-Se-Bi glassy system.

Main and Owen [14] has also found the similar behaviour of photoconductivity in case of amorphous As_2S_3. The well defined activation energies involved in the temperature dependence of photoconductivity suggests that the recombination centers are located at relatively discrete levels of localized states. Main and Owen [14] have interpreted their data on the basis of a simple four level model containing an electron trap and hole trap. To identify the origin of the gap states, which are responsible for recombination, Street and Mott [9] and Mott et al. [34] postulated the model of the so called dangling bonds. Their first hypothesis was that the chalcogenide glasses contain a high number of frozen in structural defects and the missing chalcogen atoms leaving broken or dangling bonds on other atoms could be the source of localized defect states.

Maxima in photoconductivity with temperature have been reported in As-Te and As-Se systems [15] and the Si-Te-As system [35] near room temperature whereas it was found to be absent in $Te_{85}Ge_{15}$ and $Te_{85}Ge_{10}sb_5$ [16] and $Sb_{15}Ge_{10}Se_{75}$ [36].

3.2.2 Intensity dependence of photoconductivity

Besides temperature dependence of photoconductivity, intensity dependence of photoconductivity has also been studied in the same glassy system at various fixed temperatures (306 K, 341 K and 374 K) in the intensity range 1300 – 10750 Lux. Intensity dependence of photoconductivity at a particular temperature 306 K is shown in Fig. 6. It is clear from this figure that ln σ_{ph} vs. ln F curve is a straight line. Intensity dependence of photoconductivity at other temperatures are also of the same nature. This shows that photoconductivity follows a power law with intensity, i.e., $\sigma_{ph} \propto F^{\gamma}$. The values of γ are calculated from the slopes of ln σ_{ph} vs. ln F curves are found to lie between 0.5 and 1.0 for all the samples.

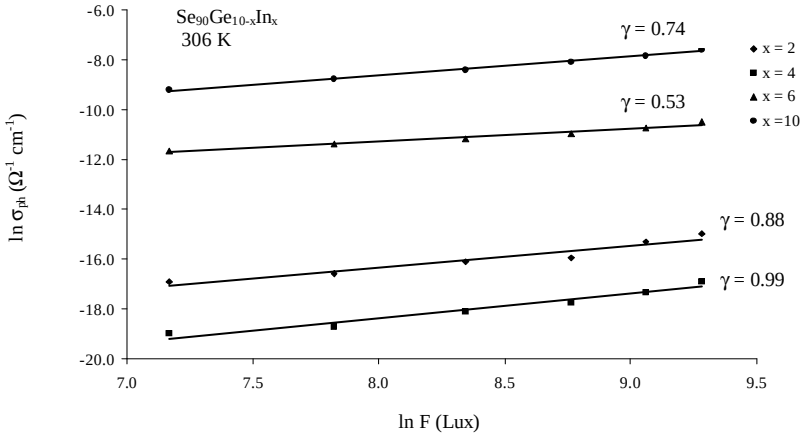

Fig. 6. Intensity dependence of photoconductivity in a - $Se_{90}Ge_{10-x}In_x$ thin film.

Rose [37] has pointed out that the power between 0.5 and 1.0 can not be understood by assuming a set of discrete trap levels but demands the existence of continuous distribution of traps in the band gap.

As γ is always between 0.5 and 1.0 in the present case, the interpretation given by Rose [37] is in good agreement with our experimental results and indicates that there exists a continuous

distribution of localized state in the mobility gap of a-$Se_{90}Ge_{10-x}In_x$ thin films with x = 2, 4, 6 and 10 at various temperatures.

3.2.3 Composition dependence of photoconductivity

The important parameter in photoconductivity measurements is photosensitivity (σ_{ph}/σ_d) at a particular temperature and intensity. The value of σ_{ph}/σ_d for a particular material decides the use of that material in the photoconductivity devices. We have, therefore, calculated the values of σ_{ph} and σ_{ph}/σ_d at a particular temperature 303 K and plotted in Fig. 6 as a function of x in a- $Se_{90}Ge_{10-x}In_x$ system. It is clear from these figures that σ_{ph} and σ_{ph}/σ_d are found to be minimum at 4 at. % of In.

Photosensitivity depends upon the lifetime of excess carriers which in, turns depends upon the density of localized states in a particular material. Higher the density of localized states, lower will be the lifetime and photosensitivity will therefore decrease.

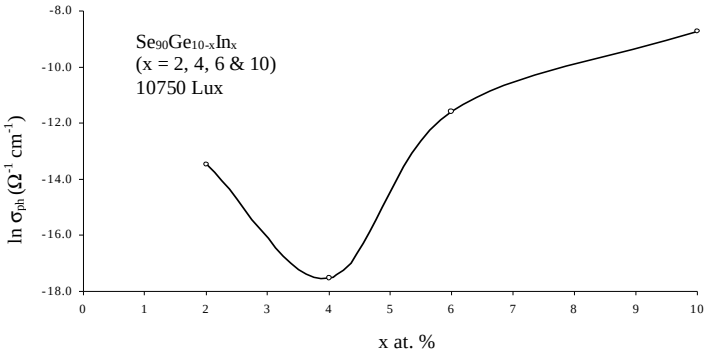

Fig. 7a. ln σ_{ph} versus x at. % in a - $Se_{90}Ge_{10-x}In_x$ thin films.

Many approaches have been proposed to explain the compositional dependence of various physical properties of chalcogenide glasses [38-46]. One of these approaches is the so-called chemically ordered network model (CONM) [38-41], in which the formation of hetropolar bonds is favored over the formation of homopolar bonds. In this model, the glass structure is assumed to be composed of cross-linked structural units of the stable chemical compounds (hetropolar bonds) of the system and excess, if any, of the elements (homopolar bonds). Due to chemical ordering, features (such as extremum, a change in slope or kink) occur for the various properties at the so-called the tie line or stoichiometric compositions at which the glass structure is made up of cross-linked structural units consisting of hetropolar bonds only. The tie line compositions, where the features seen have chemical origin, are also referred as the chemical threshold of the system [47, 48].

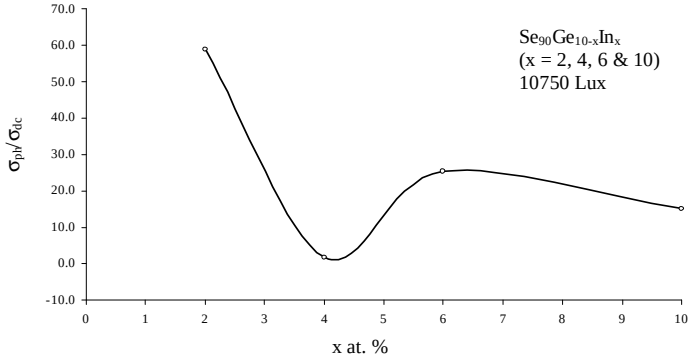

Fig. 7b. σ_{ph}/σ_{dc} versus x at. % in a - $Se_{90}Ge_{10-x}In_x$ thin films.

Other approaches are the so-called topological models which are based on the constraint theory [42-45] and on the structural dimensionality considerations [46]. In these models, the properties can be discussed in terms of the average coordination number (Z), which is indiscriminate

of the species or valence bond. In the constraints model [42-45], by equating the number of operating constraints to the number of degrees of freedom, Z of the most stable glass is shown to be ~ 2.4. At this value of Z, the glass network changes from an elastically floppy (polymeric glass) type to a rigid (amorphous solid) type.

By extension of the topological model to the medium-range structures, other features at Z ~ 2.67 have also been observed [46]. However, the features observed at Z ~ 2.67 were attributed to a change from two-dimensional layered structure to a three-dimensional network arrangement due to crosslinking.

In the present case a discontinuity in electrical parameters is observed at 4 at. % of In showing a discontinuity at an average coordination number <Z> = 2.2, which is closer to topological models based on constraints theory described above.

4. Conclusion

Temperature dependence of d. c. conductivity is studied in a-$Se_{90}Ge_{10-x}In_x$ where x is varied from 2 to 10. The values of ΔE and σ_0 are calculated. The results of these calculations show that σ_{dc} first decreases as indium concentration increases from x = 2 to x = 4 and then increases with the increase of indium concentration. σ_0 is also found to be maximum at x = 2.

Temperature and intensity dependence of photoconductivity are studied in a-Se_{90} Ge_{10-x} In_x thin films. A maximum is observed in the case of $Se_{90}Ge_8In_2$ thin film and the models proposed by ABFH [11] and Main and Owen [14] are attractive for the explanation of this type of behaviour. The values of γ is found to be always between 0.5 and 1.0 for all the samples which indicates that there exists a continuous distribution of localized state in the mobility gap of a-$Se_{90}Ge_{10-x}In_x$ thin films with x = 2, 4, 6 and 10 at various temperatures.

Composition dependence of steady state photoconductivity shows that photoconductivity reaches the minimum at 4 at. % of In. We have also calculated σ_{ph}/σ_d at 303 K for various intensities (6400 Lux, 8600 Lux and 10750 Lux). The values show that σ_{ph}/σ_d is minimum at x = 4. The discontinuity in various electrical parameters at 4 at. % of In is related to formation of mechanically stabilized structure at a particular average coordination number 2.2. This is consistent with the theory of Phillips and Thorpe [44] for the topological model in case of chalcogenide glasses.

References

[1] D. V. Harea, I. A. Vasilev, E. P. Colomeico, M. S. Iovu, J. Optoelectron. Adv. Mater. **5,** 1115 (2003).
[2] N. F. Mott, E. A. Davis, Electronic Processes in Non-crystalline Materials, Clarendon Press, Oxford, (1979).
[3] M. Popescu, A. Andriesh, V. Ciumash, M. Iovu, D. Tsiuleanu, S. Shutov "Fizica sticlelor calcogenice" (roum.) I. E. P., Stiinta Press Chisinau-Editura Stiintifica Bucuresti (1996).
[4] N. F. Mott, Adv. Phys. **16**, 49 (1976).
[5] E. A. Davis, N. F. Mott., Phil. Mag. **22**, 903 (1970).
[6] B. T. Colomiets, A. Lebedev, N. A. Rogachev, Fiz. Tekh. Poluprov **8**, 545 (1974).
[7] S. Okano, M. Suzuki, T. Imura, N. Fukuda, A. Hiraki, J. Non-Cryst. Sol. **59-60**, 969 (1983).
[8] R. Mishra, S. Goel, A. K. Agnihotri, A. Kumar, J. Mat. Sci. Lett. **11**, 212 (1992).
[9] R. A. Street, N. F. Mott, Phys. Rev. Lett. **35**, 1293 (1975).
[10] N. F. Mott, E. A. Davis, Electronic Processes in Non-crystalline Materials, Mir, Moskva, (1982).
[11] T. C. Arnoldussen, R. H. Bube, E. A. Fagen, S. Holmberg, J. Non-Cryst. Sol. **8-10**, 933 (1972).
[12] G. Mathew, G. Philip, Pramana- J. Phys. **53**, 891 (1999).
[13] G. Mathew, G. Philip, J. Phys. Condens. Matter **11**, 5283 (1999).
[14] C. Main, A. E. Owen, Electronic and Structural Properties of Amorphous Semiconductors ed. P. G. Le Comber, J. Mort (London: Academic Press) 527 (1973).

[15] J. M. Marshall, C. Main, A. E. Owen, J. Non. Cryst. Sol. **8-10**, 760 (1972).
[16] M. Igalson, R. Tryokozoko, Sol. St. Commun. **40**, 99 (1981).
[17] T. C. Arnoldussen, R. H. Bube, E. A. Fagen, S. Holmberg, J. Appl. Phys. **43**, 1798 (1972).
[18] J. G. Simmons, G. W. Taylor, J. Non-Cryst. Sol. **8-10**, 947 (1972).
[19] B. T. Kolomiets, V. M. Lyubin, Soviet Phys. Solid State **2**, 46 (1960).
[20] B. T. Kolomiets, V. M. Lyubin, Soviet Phys. Solid State **4**, 291 (1962).
[21] E. Fagen, H. Fritzsche, J. Non-Cryst. Sol. **4**, 480 (1970).
[22] W. E. Howard, R.Tsu, Phys. Rev. B **1**, 4709 (1970).
[23] K. Weiser, R. Fisher, M. H. Brodsky, in: Proc. Tenth Intern. Conf. On the Physics of Semiconductors, Cambridge, Mass., p.667 (1970).
[24] B. T. Kolomiets, E. M. Raspopova, Soviet Phys. Semiconductors **4**, 1041 (1971).
[25] V. I. Kruglov, L. P. Strakhov, Soviet Phys. Semiconductors **4**, 1316 (1971).
[26] B. T. Kolomiets, Yu. Rukhlyadev, V. P. Shilo J. Non-Cryst. Sol. **5**, 389 (1971).
[27] R. H. Bube, H. E. Mahan, R. T. S. Shiah, H. A. Vander Plas, Appl. Phys. Lett. **25**, 419 (1974).
[28] T. D. Moustakas, K. Weiser, Phys. Rev. B **12**, 2448 (1975).
[29] M. Hammam, G. J. Adriaenssens, W. Grevendonk, J. Phys. C: Solid State Phys. **18**, 2151(1985).
[30] B. T. Kolomiets, Yu. Rukhlyadev, V. P. Shilo, J. Non.Cryst. Sol. **5**, 402 (1971).
[31] S. K. Tripathi, A. Kumar, J. Non-Cryst. Sol. **104**, 229 (1988).
[32] N. Qamhieh, G. J. Adriaenssens, J. Non-Cryst. Sol. **292**, 80 (2001).
[33] M. Hammam, G. J. Adriaenssens, J. Non-Cryst. Sol. **59-60**, 961 (1983).
[34] N. F. Mott, E. A. Davis, R. A. Street, Phil. Mag. **32**, 961 (1975).
[35] G. W. Taylor, J. G. Simmons, J. Phys. C **7**, 3051 (1974).
[36] A. S. Mann, A. K. Sharma, D. R. Goyal, A. Kumar, J. Non-Cryst. Sol. **104**, 273 (1988).
[37] A. Rose, Concept in Photoconductivity and Allied Problems (New York: Interscience, 1963).
[38] G. Lucovsky, F. L. Galeener, R. H. Geils, R. C. Keezer, in: P. H. Gaskell (Ed.), The Structure of Non - Crystalline Materials, Taylor and Francis, London, 127 (1977).
[39] G. Lucovsky, R. J. Nemanich, F. L. Galeener, in: W. Spear (Ed.), Proceedings of Seventh International Conference on Amorphous Liquid Semiconductors, Center for Industrial Consultancy and Liaison, Univ. of Edinburgh, Edinburgh, 130 (1977).
[40] F. Betts, A. Bienesock, S. R. Ovshinsky, J. Non-Cryst. Sol. **4**, 554 (1970).
[41] G. Lucovsky, F. L. Galeener, R. C. Keezer, R. H. Geils, H. A. Six, Phys. Rev. B **10**, 5134 (1974).
[42] J. C. Phillips, J. Non-Cryst. Sol. **34**, 153 (1979).
[43] J. C. Phillips, J. Non-Cryst. Sol. **57**, 355 (1983).
[44] J. C. Phillips, M. F. Thorpe, Sol. Stat. Commun. **53**, 699 (1985).
[45] K. Tanaka, Phys. Rev. B **39**, 1270 (1989).
[46] C. H. Hurst, E. A. Davis, in: W. Brenig (Eds.), Proceedings of Fifth International Conference on Amorphous and Liquid Semiconductors **1,** Taylor and Francis, London, 349 (1974).
[47] P. Boolchand, Key Eng. Matter **13-15**, 131 (1987).
[48] S. Mahadevan, A. Giridhar, J. Non-Cryst. Sol. **110**, 118 (1989).