JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 8, No. 2, April 2006, p. 785 - 788

Electron transport in amorphous $(GeSe_5)_{1-x}B_x$ films

P. PETKOV*, S. PARVANOV, T. PETKOVA[a]
Department of Physics, Thin Films Technology Lab, University of Chemical Technology & Metallurgy, 8 Kl. Ohridsky Blvd., 1756 Sofia, Bulgaria
[a]*Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bonchev Bl. 10, 1113 Sofia, Bulgaria*

The charge-transport behavior of $(GeSe_5)_{1-x}B_x$ films (x = 0, 10, 20 mol.%) have been studied and their dependence on field, temperature and composition has been observed. The investigations have been carried out at room temperature and below room temperature in temperature range 173 - 293 K and applied electric fields up to 10^8 Vm^{-1} on sandwich Al/Chal/Al structures. The I-V characteristics show a linear (ohmic) dependence at low voltage and non-ohmic dependence at higher voltage region. In the intermediate region electron transport behaviors are determined by space charge limited conduction (SCLC) mechanism. Quantitative information about the transport parameters has been derived as a function of film composition applying the relevant SCLC theory. The magnitude and energy distribution of the space charge has been obtained by the method of Manfredotti for current- voltage characteristics analyses. Electron localized states have been obtained in the region from 0.32 to 0.90 eV. The density of localized states varies with film composition from 5.9×10^{23} to 4.1×10^{26} m^{-3}.

(Received January 3, 2006; accepted March 23, 2006)

Keywords: Chalcogenide glasses, Thin films, Electrical properties, Band gap structure

1. Introduction

Intrinsic semiconductor behaviors of amorphous materials fit into the scheme of energy levels, whose bands extend as tails of the localized states. In view of the low mobility of charge carriers this results in the energy gap even in the cases of the real systems with the overlapping tails. In the case of some chalcogenide glasses, the energy gap thus defined, whose existence is due to the lack of mobility of charge carriers have been better characterized by the approach derived from the Cohen-Fritzche-Ovshinsky [1] and, S. Hosokawa [2]. Equally important results related to forming the models of these materials have been obtained on the basis of the approach by Street and Mott, based on the existence of defect centers [3]. Real glassy network is known to show structural disorder such as broken chemical bonds, modified forms of the structural units and topology disorder, which increase the density of the localized states, and leads to their distribution in the band gap depth partially overlapping the "tails" as described in the Street-Mott [3] and Kastner-Adler-Fritzsche model [4] for the charged defects. In the vicinity of the middle of the forbidden gap, (i.e. the mobility gap), a real glass possesses a narrow band of localized states with a sufficiently high density to fix the Fermi level to this region. These energy states are strongly influenced by the components involved and structure defects, whose number depends on the nature of components introduced and the method of sample preparation. The mechanism of conductivity influenced by the traps is the space charge limited conduction (SCLC) mechanism.

The electron transport investigation in disordered systems is of considerable significance due to the strong effect on the electrical properties of semiconductors [5, 6]. Our previous investigations show that the introduction of boron into the basic Ge-Se amorphous matrix additionally disturbs the ordering and coordination in the glass matrix [7]. It has been established that electrode limited conduction mechanism can be applied to explain the low field currents in these chalcogenide glasses at room temperature.

The aim of present work is to study the electron transport behavior of the chalcogenide films in intermediate area between the Ohmic (low electric field) and the Schottky region (high electric field) by measuring the current-voltage characteristics of Al/Ge-Se-B/Al structures in temperature range below room temperature.

2. Experimental

Bulk chalcogenide glasses with constant ratio Ge: Se=1:5 and different content boron: 0, 10 and 20 mol. % were synthesized by melt-quenching technique. Starting elements with 5N purity were mixed and sealed in evacuated quartz ampoules, heated up to 1200 K for 12 h with heating rate of 2-3 K min^{-1}. Melted samples were quenched in a mixture of ice and water.

Thin films were prepared by vacuum evaporation of the respective bulk glasses in a standard installation "Hochvacuum" B 30.2. The experimental conditions of evaporation process: residual pressure of about 1.33×10^{-4} Pa, source-substrate distance of 0.12 m was kept constant; the evaporation temperature 900-1000 K, was varied according to the film composition. A special designed tantalum evaporator was used for preparation of homogeneous films. Corning glass substrates were rotated during the deposition process to prevent non-uniformity in

the film thickness. Film thickness varied between 80 and 190 nm measured by optical interference method. Experiments were performed on sandwich structures Al/Ge-Se-B/Al prepared by consecutive evaporation of bottom aluminum electrode, chalcogenide film and upper aluminum electrode. The current-voltage characteristics of the structures were measured at a linear increasing electrical field applied up to 10^8 Vm^{-1}. The temperature range of the investigations was 173 - 293 K monitored by temperature controller.

Computerized experimental set-up utilized for investigations included precise amplifier and picoammeter MV-40, Germany.

3. Theoretical approaches

The space-charge limited current (SCLC) behaviours have been studied by many authors. In general the aim of these investigations has been to determine concentration and depth of trapping centers. Disadvantage of the most of models applied has been connected with the necessity to make a fit between experimental data and theoretical curves calculated from specific trap distribution. The method of Lampert [8] for discrete levels is most suitable for semiconductor materials, since the method is independent on the mechanism of charge carrier generation, and structure of the semiconductor film. Lampert has shown that the current density **j** in the region where the conduction is governed by the SCLC mechanism is given by

$$j = \frac{\mu \varepsilon A V^2}{d^3} \qquad (1)$$

where **j** is current density, ε – relative dielectric constant, **A** – the area of the sample, **d** – thickness of the film, **μ** is the carriers mobility, **V** is applied voltage.

Manfredotti and co-workers [9] has suggested a simplified method for current-voltage characteristics analyses. The parameters of trap distributions (energy and density of localized states) are obtained without introducing a-priori hypothesis regarding the nature of the distributions themselves. The analysis has shown a good agreement with Lampetrs method and has been proved for GaSe [9] and GeSe films [10].

The Manfredotti method is based on the assumptions: constant carrier mobility, homogeneous trap distribution in the space, independency of the electrical length of the sample from the electrical field, trap occupancy determined by the position of Fermi level and the gap state density varies slowly and continuously over energies of the order kT. Thus the energy distribution of the localized states is given by the equation

$$\frac{dn_t}{dE_F} = \frac{1}{e}\frac{d\rho}{dE_F} \qquad (2)$$

where $\mathbf{n_t}$ is the total density of the localized electrons, **ρ** is total space charge density in the sample, $\mathbf{E_F}$ is the energy of the quasi-Fermi level, and **e** is the electron charge.

The expression (2) is valid when the density of the localized carriers is larger than that of the free ones. The derivative $\mathbf{dn_t/dE_F}$ has its maximum for

$$E_{Fm} = E_t + kT \ln g$$

The position and the value of the maximum determine the energy level $\mathbf{E_t}$ of the localized states and their density $\mathbf{N_t}$. With a sufficient precision one can determine the energy depth of the traps with equation (2) in the approximation $\mathbf{E_{Fm} \approx E_t}$, since **g = 2** (degeneracy factor), kT lng reaches a maximum of 0.018 eV at room temperature. Using the value g = 2, (this value has been introduced and proved by Manfredotti [9]) the localized states density can be evaluated by the expression

$$N_t = 4kT\left(\frac{dn_t}{dE_F}\right)_{E_{F\max}} \qquad (4)$$

4. Results and discussion

The current-voltage characteristics are an important tool for analyzing different conduction processes and electron transport in the amorphous materials.

The I-V characteristics of thin film with 20 mol.% B in log-log scale measured in the temperature interval 173 – 293 K are plotted in Fig. 1. The curves reveal an increase in the current values with the temperature. All I-V characteristics yield conduction regions, which fit to different slopes. The slopes correspond to ohmic condition at lower fields where the power dependence is j ~U and non-ohmic conduction (Schottky or Pool-Frenkel region) at higher fields (j ~exp$U^{1/2}$). The non-ohmic region in-between is governed by the relation j ~ U^n. Our study concerns this intermediate conduction region where n=2.

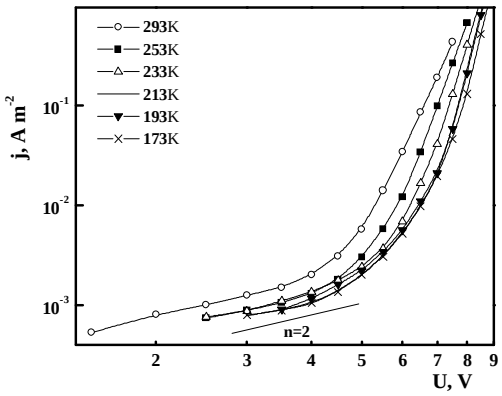

Fig. 1. Current-voltage characteristics of $Ge_{13}Se_{67}B_{20}$ sample in log-log scale(the solid line shows the area where the relation j ~U^2 is valid).

Non-ohmic behaviors have been observed in many chalcogenide materials and have often been interpreted in terms of trap controlled space charge limited conduction (SCLC) [11,12]. However in order to exclude the

existence of Shottky or Poole-Frenkel conduction in the region under study we have to analyze careful the results shown in Fig. 1. Schottky emission occurs due to thermal activation of electrons over the metal-insulator or metal-semiconductor interface barrier because of lowering the barrier height due to applied voltages. Poole-Frenkel mechanism is similar to the Schottky, except that it is applied to thermal excitation of electrons from traps into the conduction band of the insulator. In both cases the relation ($j \sim \exp U^{1/2}$) should be a straight line. In order to check if the Shottky mechanism is favorable in the electric field under study we re-plotted the I-V characteristics in semi-logarithmic scale as $\log j = f(U^{1/2})$ for two different samples with different thicknesses in the voltage region where SCLS conduction is expected. Both curves of $GeSe_5$ and $(GeSe_5)_{80}B_{20}$ presented in Fig. 2 show non-linear dependence and verify the absence of Shottky or Poole-Frenkel conduction mechanism.

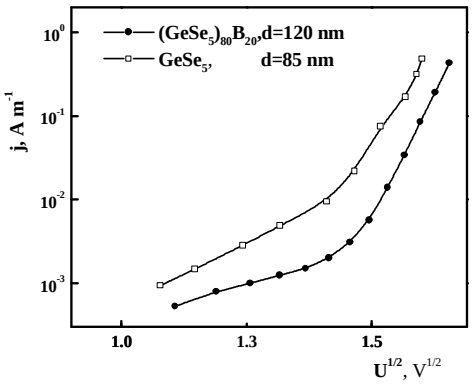

Fig. 2. Current density versus $U^{1/2}$ for $GeSe_5$ and $(GeSe_5)_{80}B_{20}$ thin films.

According to eq. (1) the SCLC mechanism can be corroborated also by linearity of the relation log j versus d^{-3} (film thickness). The current density plotted versus film thickness of the film $(GeSe_5)_{20}B_{20}$ (Fig. 3) exhibits that the current linearly decreases as the film thickness increases and the slope is calculated to be 3.1. The experimental results: non-linearity of j vs. $U^{1/2}$ dependence and the slope in the thickness dependence of the current suggest a trap controlled SCLC mechanism in the region under study.

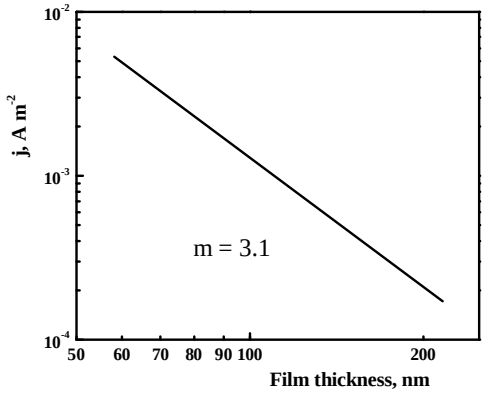

Fig. 3. Relation between current density and film thickness of $(GeSe_5)_{80}B_{20}$ thin films.

Fig. 4 shows relation of dn_t/dE_F on the quasi-Fermi level (E_F) energy in thin film samples without boron (Fig. 4a), with 10 mol% (Fig. 4b) and 20 mol.% boron content (Fig. 4c).

For the E_t and N_t calculations we assume the following parameters derived from the literature and from our earlier studies: $\varepsilon = 6.3$ for the relative dielectric permittivity of the amorphous films, $m_c/m = (0.33 \div 0.95)$ m for the electron effective mass and $\mu = 5 \times 10^{-2}$ m^2 /Vs for the electron mobility in the films at room temperature [7]. The values of energy of the localized states, E_t are determined from the position of the maxima of $dn_t/dE_F = f(E_F)$ using the relation (3). It is obvious that the deviations in maxima position of different samples are very small and do not exceed 1kT. It is to be noted that only the peaks with magnitudes exceeded five times the fluctuation level are taken into account for E_t determination. The peaks are narrow and their full width at half maximum is less than 0.02 eV. This value is considerably less than 3.5 kT values indicating that the localized states thus obtained are discrete states. The value of half maximum is very small compared to E_t. This suggests a uniform distribution of the localized states in the band gap that is typical for the amorphous films as reported by other authors [13]. The mean values of the traps depth, E_t, calculated in Table 1 show small increase in the values with increase in boron concentration.

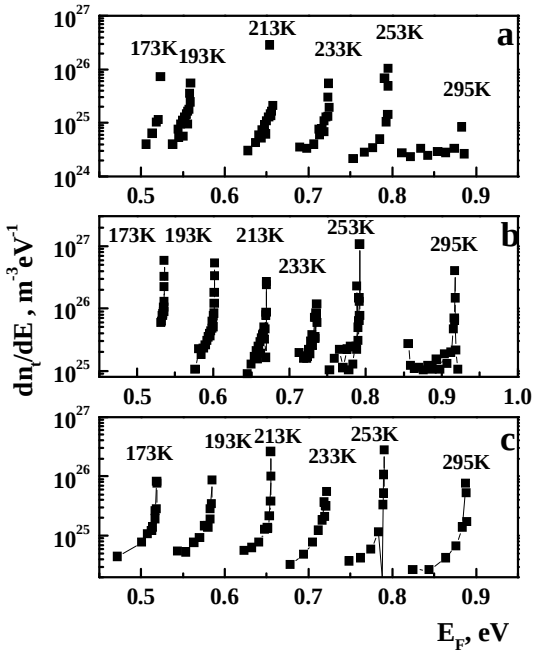

Fig. 4. The dependence of dn_t/dF on the position of the quasi-Fermi level E_F for a. $Ge_{17}Se_{83}$ sample, b. $Ge_{15}Se_{75}B_{10}$ sample, c. $Ge_{13}Se_{67}B_{20}$ sample.

Table 1. Mean values of energy distribution of the localized states, E_t and localized states density N_t of the $Ge_{17}Se_{83}$, $Ge_{15}Se_{75}B_{10}$, $Ge_{13}Se_{67}B_{20}$ films.

$GeSe_5$		$(GeSe_5)_{90}B_{10}$		$(GeSe_5)_{80}B_{20}$	
E_t [eV]	N_t [m^{-3}]	E_t [eV]	N_t [m^{-3}]	E_t [eV]	N_t [m^{-3}]
0.87	7.4×10^{24}	0.90	4.1×10^{25}	0.87	8.5×10^{23}
0.81	4.7×10^{24}	0.87	3.5×10^{25}	0.83	5.9×10^{23}
0.78	2.4×10^{25}	0.85	1.8×10^{25}	0.80	6.1×10^{24}
0.71	4.6×10^{24}	0.78	9.3×10^{25}	0.78	9.1×10^{24}
0.64	1.9×10^{25}	0.72	9.4×10^{24}	0.77	8.5×10^{23}
0.57	5.8×10^{24}	0.66	2.0×10^{25}	0.72	4.4×10^{24}
0.51	4.9×10^{24}	0.59	3.6×10^{25}	0.64	2.1×10^{25}
0.44	4.1×10^{24}	0.56	4.1×10^{26}	0.55	3.2×10^{24}
0.38	1.1×10^{25}	0.53	3.5×10^{25}	0.54	3.7×10^{24}
0.32	7.8×10^{24}	0.49	3.6×10^{25}	0.51	4.3×10^{24}

The density values, N_t, calculated in Table 1 are from 5.9×10^{23} to 4.1×10^{26} m^{-3} depending on the boron concentration. The introduction of 10 mol. % boron increases carrier density in the localized states. S. P. Singh et.al. has reported similar dependence in GeSeIn films [14]. Further increase in boron content (20 mol.%) leads to a small decrease in the density of states. To explain the results observed we should have in mind the structure of Ge-chalcogenide glasses. Ge-Se films are known to have a large number of defects due to dangling bonds that give rise to large number of localized states [14]. These localized states act as carrier trapping centers and after trapping the injected charge from electrodes they become charged and thereby expected to build up a space charge. The boron introduction induces structural changes in the host Ge-Se matrix. This leads to rearrangement in the local environment, helps the creation of new defects that are presented also as traps in the gap and this could result in a shift of the Fermi level. Some new trap states can also appear in the mobility gap as it has been shown in the present study as an increase in the density of states. However the introduction of boron amount more than 10 mol.% probably reduces the number of dangling bonds due to creation of new structural units and reducing the number of defect bonds. Hence the number of the localized states diminishes.

5. Conclusions

The investigations of Al-(Ge-Se-B) -Al samples in the intermediate range between Ohmic and the Schottky regions at the electric field up to $E = 10^8$ Vm^{-1} show a non-ohmic power dependence and suggest the appearance of traps controlled space charge limited currents. Energy distribution of the localized state in the temperature interval 173 to 293 K reveals that the introduction of the third element, boron, leads to a shift of the Fermi level, E_t, from 0.32 eV to 0.51 eV. The density of localized states increases when boron atoms first are introduced probably due to creation of new defect bonds. The defect states in the films form space charge on trapping the injected charge from electrodes and hence determine the SCLC process. When amount of boron is more than 10 mol. % boron atoms are most probably create new structural units in the host Ge-Se matrix and thus leads to a reduction in defect numbers and small decrease in density of states, respectively.

The results show that analysis of the current-voltage characteristics could be successfully performed in both space charge limited currents region at strong electric fields and at low temperatures where dominant mechanism is the electrode limited conductivity.

Acknowledgements

This work has been performed by the financial support of the contracts: POEMES, NNE5/2002/18 and contract X-1203 of the Bulgarian Science Found to which authors are grateful.

References

[1] M. Cohen, H. Fritzsche, S. Ovshinsky, Phys. Rev. Lett. **22**, 1065 (1969).
[2] S. Hosokawa, Y. Hari, K. Nishihara, K. Tamura, M. Tamiguchi, JNCS, **166**, 1199 (1993).
[3] R. A. Street, N. F. Mott, Phys. Rev. Lett. **35**(22), (1975) 1293.
[4] M. Kastner, D. Adler, H. Fritzsche, Phys. Rev. Lett. **37**(22), 1504 (1976).
[5] M. A. Afifi, M. M. Abdel-Aziz, H. Labib, M. Fadel, E. El-Metwally, Vacuum **61**, 45 (2001).
[6] S. Kumar, S. Kashyap, K. Chopra, Thin Solid Films **21**, 146 (1992).
[7] S. Parvanov, P. Petkov, C. Vodenicharov, Thin Solid Films **357**, 242 (1999).
[8] M. Lampert, P. Mark, Current Injection in Solids, Academic Press, New York, 1970.
[9] C. Manfredotti, C. Blasi, S. Calassini, G. Mococci, Phys. Stat. Sol. (a), **36**, 569 (1976).
[10] C. Vodenicahrov, S. Parvanov, Mat. Chem. & Physics **21**, 455 (1989).
[11] K. Yilmaz, M. Parlak, M. Ercelebi, Journ. Mater. Sci: Mater. Electronics **15**, 225 (2004).
[12] S. Dwivedi, A. Kumer, S. Kumar, Adv. Mat. for Optics & Electronics **9**, 235 (1999).
[13] S. Wagle, V. Shirodkar, Brazilian Journal of Physics, **30**(2), 380 (2000).
[14] S. Singh, S. Kumar, A. Kumar, Chalcogenide Letters **1**(8), 105 (2004).

*Corresponding author: p.petkov@uctm.edu