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ELECTRODE-LIMITED CONDUCTIVITY OF AMORPHOUS CHALCOGENIDE THIN FILMS FROM THE $GeSe_2$-Sb_2Se_3-ZnSe SYSTEM

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The results of an experimental test of Christov's theory for injected electron current into dielectric or semiconductor materials, in amorphous $GeSe_2$-Sb_2Se_3-ZnSe thin films, are reported. The effective electron mass in the conduction band, the electron work function at the Al/chalcogenide interface, and the relative dielectric permitivity of the layers have been determined. The temperature dependence of the electrical conductivity and the thermal band-gap have also been investigated.

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1. Introduction

In the last decades a large number of studies have been carried out on chalcogenide semiconducting materials prompted by fundamental and technological interest [1, 2]. The investigation of the electron transport in these glasses have been performed due to the importance of the electrical properties of the semiconductors [3, 4].

Ge_xSe_{1-x} is one of the best glass formers in the chalcogenide family of glasses that forms a bulk glass for compositions $x < 0.43$. The addition of Ge in them increases the conductivity and decreases the density of states at the Fermi level. These glasses with polyvalent elements (arsenic and germanium) exhibit properties which are the result of the formation of three-dimensional structural units. The Ge and As atoms form spatial units with the chalcogen elements, break their characteristical configurations and contribute to the establishment of more homogeneous structure, a fact which explains some of their physical properties. The addition of Sb_2Se_3 in $GeSe_2$ glassy network significantly increases the glass-forming ability, that results in an extended glass-forming region [5]. ZnSe is an important material for the development of optoelectronic devices with wide band gap at room temperature. Small quantities of Me (Me = Cu, Bi, Sn, Sb, Zn etc.) or MeX (X = S, Se, Te) added to Ge-Se host matrix notably change the physical behaviour of the semiconducting material [6].

The present work reports the results from investigations of the electrical d.c. conductivity of thin films from $GeSe_2$-Sb_2Se_3-ZnSe system. The experimental results are compared to the results of the theory of injected electron currents in semiconductors and insulators.

2. Theory

The physical parameters, such as dielectric permitivity, ε, and effective electron mass, m_c/m, in the conduction band depend on the structure of the semiconductor film, while others, such as electron work function, χ_{TE}, depend on the potential barrier at the interface metal/semiconductor. Vodenicharov [7] has proposed a method for determination of the ratio m_c/m using the general theory of Christov for

metal/semiconductor/metal systems. The other method, that of the cyclotron resonance, is an accurate method for the determination of the m_c/m but it is rather complex and applicable only to limited number of substances. The Vodenicharov's method is simple and very accurate in the range between the regions of thermionic to thermionic-field emission. The Christov's theory was proved as valid for chalcogenide systems with Ge and shows the applicability for complex systems.

Christov has proposed the most general theory of electron emission from metal in vacuum [8]. This theory has been modified taking into account the emission in semiconductors and insulators [9, 10]. According to the theory, the total injected current j as a function of electrical field E and temperature T is:

$$j(E,T) = j_1' + j_2' + j'' = Q_1'(T/Tc)j_{FN} + Q_2'(E,T)j_{MG} + Q''(Tk/T)j_{RS} \quad (1)$$

where j_{FN}, j_{MG}, j_{RS} are defined by the well-known formulas of Fowler-Nordheim, Murphy-Good and Richardson-Schottky for the regions of field, thermionic-field and termionic emission, respectively; Q_1', Q_2' and Q'' are determined functions of the field and temperature.

The dependences of the thermionic emission component j" ($j'' \sim \exp(E^{1/2})$) and the thermionic-field emission component j_2' ($j_2' \sim \exp(E^2)$) on the current density, and their sum $j = j'' + j_2'$ on the field intensity in Schottky co-ordinates reach an intersection point of the curves for which $j'' = j_2'$. This point corresponds to a transition of the characteristics $\ln j \sim f(E^{1/2})$ from linear to nonlinear shape. The point lies at a field intensity E_k and is defined by the condition $T_k/T = 1.76$. Using the value of E_k one can determine the ratio m_c/m by the expression:

$$m_c/m = [h(\varepsilon e)^{1/4}/1.76\,\pi^2\,kT]^2 E_k^{3/2} \quad (2)$$

where m is the free electron mass, h is Planck's constant, k is Boltzmann's constant, e is the electron charge, ε is the relative permittivity of the material. The relation is valid for any temperature only if the critical field E_k is reached.

From the thermionic region of emission the electron work function χ_{TE} at the interface metal/semiconductor can be evaluated by relation:

$$\chi_{TE} = -\,kT \ln (j^*/AT^2 m_c/m) \quad (3)$$

where A is Richardson's constant, and j* is the value of the current density for E=0 from the relationship $\ln j = f(E^{1/2})$.

The electron work function χ_{TF} in the region of the thernionic-field emission is given by the expression:

$$\chi_{TF} = -\,kT \ln[\,h(j/E)^*/\varepsilon^2 (2\pi m_c kTt(z))^{1/2}] \quad (4)$$

where it is assumed that t(z) = 1, and (j/E)* is the value of the function $\ln (j/E) = f(E^2)$ for E = 0.

3. Experimental details

Bulk samples of the studied system were prepared by the high temperature synthesis. The initial compounds were of purity 5 N. The final temperature of the synthesis was 1100 K and the glass formation was carried out with a cooling rate of around 150 $Kmin^{-1}$. The compositions of the samples are listed in Table 1.

Thin films were prepared by vacuum evaporation from a special evaporator [11] in a conventional vacuum installation. Film morphology and structure were investigated by X-ray diffraction (Philips TUR 69, Netherlands) and by transmission electron microscopy (Philips TEM 301, Netherlands). The surface roughness of the thin films was examined by atomic force microscope (AFM) "Dimension" 3100 in attractive regime.

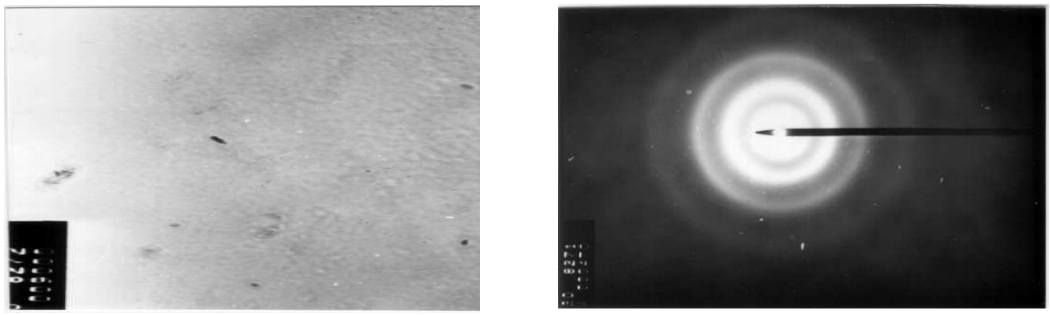
Films' compositions was found by Auger spectroscopy (Ribere N 309, France). The film thickness varied from 50 to 200 nm and was measured with an interference microscope. Optical glass,

single-crystalline Si and NaCl crystals were used as substrates. Evaporated layers of pure Al (99.999%) were used as electrodes.

Capacitance and dielectric losses were measured at room temperature using a precise RLC bridge (RFT 8470, Germany) at a frequency of 8 kHz. Current-voltage characteristics were measured with a picoammeter "MV-40" in the temperature range 300-420 K. Linearly increasing voltage was applied on the samples, and a precise compensation set-up was used. A special computer program processed the experimental data with high accuracy.

4. Results

All thin films of the $GeSe_2$-Sb_2Se_3-ZnSe system have been found amorphous by X-ray diffraction investigations. Fig. 1a,b presents an electron transmission and diffraction patterns of a film with composition $(GeSe_2)_{54}(Sb_2Se_3)_{36}(ZnSe)_{10}$. The films are characterized by high homogeneity.



a) b)

Fig. 1. Electron microscope pictures of thin $(GeSe_2)_{54}(Sb_2Se_3)_{36}(ZnSe)_{10}$. a) TEM; b) electron diffraction.

Conditions for the preparation of amorphous complex chalcogenide films are: high evaporation temperature (750 K), low evaporation rate and low substrate temperature (< 300 K).

The films' composition has been analyzed by means of the Auger electron spectroscopy. The profilogramm of the $(GeSe_2)_{72}(Sb_2Se_3)_{18}(ZnSe)_{10}$ layer in Fig. 2 shows that the composition is identical with that of the bulk sample with an accuracy ~1 at. % according to the method of "elemental sensitivity".

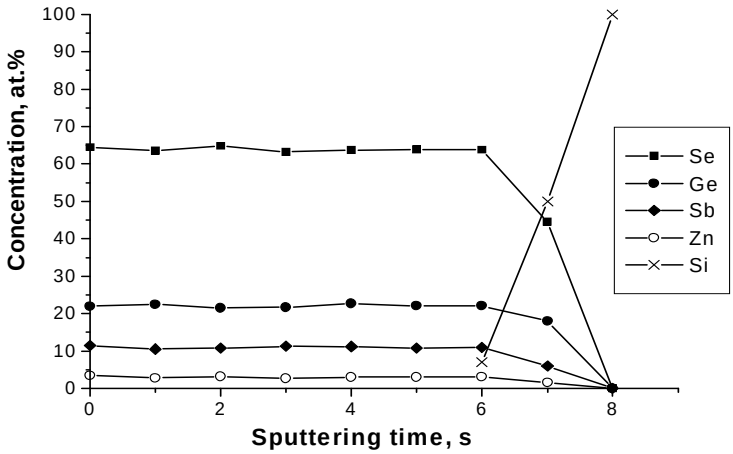


Fig. 2. Auger electron profilogramm of the$(GeSe_2)_{72}(Sb_2Se_3)_{18}(ZnSe)_{10}$ sample.

The results from AFM studies indicates negligible roughness on the films surface (Fig. 3, Table 1).

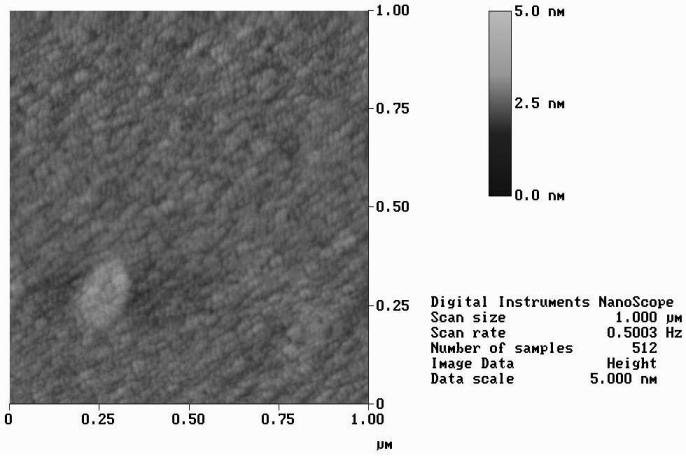


Fig. 3. AFM pattern for the $(GeSe_2)_{54}(Sb_2Se_3)_{36}(ZnSe)_{10}$ sample.

The thermal band-gap ΔE_a for the investigated thin films is determined by analyzing the temperature dependence of the conductivity $\sigma(T)$. The temperature varies from 300 to 420 K. A further increase of the temperature is limited by the glass transition temperature, T_g. ΔE_a is determined with following equations:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{2kT}\right), \tag{5}$$

where σ_0 is the conductivity at 0 K.

$$E_a = 2k10^3 \frac{\Delta(\ln\sigma)}{\Delta\left(\frac{1000}{T}\right)} \tag{6}$$

For the amorphous $GeSe_2$-Sb_2Se_3-ZnSe thin films σ varies from 1×10^{-12} to 1×10^{-10} S/cm at room temperature.

Fig. 4 is a graphic representation of the typical dependence $\ln\sigma = f(1000/T)$.

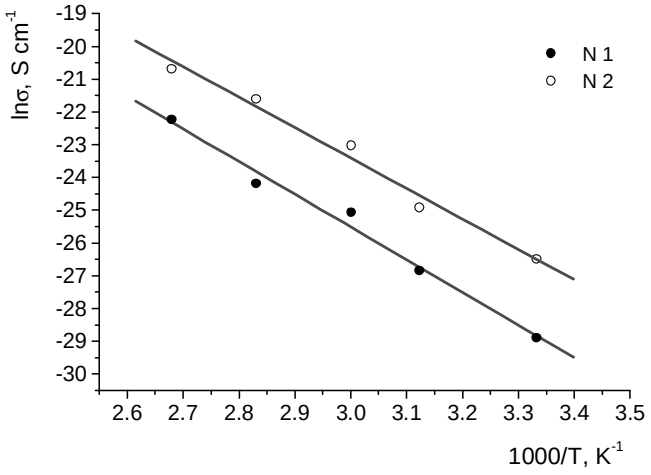


Fig. 4. The Arrhenius dependence for $GeSe_2$-Sb_2Se_3-ZnSe amorphous thin films.
N 1 - $(GeSe_2)_{80}(Sb_2Se_3)_{20}(ZnSe)_0$; N 2 - $(GeSe_2)_{54}(Sb_2Se_3)_{36}(ZnSe)_{10}$.

The calculated values for the thermal band gaps are listed in Table 1.

Table 1. Compositions, thermal band-gaps and average roughness of thin films from the $GeSe_2$-Sb_2Se_3-ZnSe system.

No	Composition, mol. %	ΔE_a, eV	Average roughness, nm
1	$(GeSe_2)_{80}(Sb_2Se_3)_{20}$	1.60	5.7
2	$(GeSe_2)_{54}(Sb_2Se_3)_{36}(ZnSe)_{10}$	1.43	1.5
3	$(GeSe_2)_{72}(Sb_2Se_3)_{18}(ZnSe)_{10}$	1.67	-
4	$(GeSe_2)_{81}(Sb_2Se_3)_{9}(ZnSe)_{10}$	1.58	9.3
5	$(GeSe_2)_{64}(Sb_2Se_3)_{16}(ZnSe)_{20}$	1.60	15.0

The d.c. investigations are conducted in the field range up to 1×10^8 V/m in order to cover the thermionic and thermionic-field emission regions. The thermionic and thermionic-field components of the current on the boundary between these regions, determined from the condition $T_k = 1.76$ T have been obtained to be equal (T_k is Chistov's characteristic temperature and T is the experimental one). The critical field intensity E_k of this boundary has been determined accurately from the current - voltage characteristics (Fig. 5). The linear part of the dependence ln j versus $E^{1/2}$ determines the thermionic emission region.

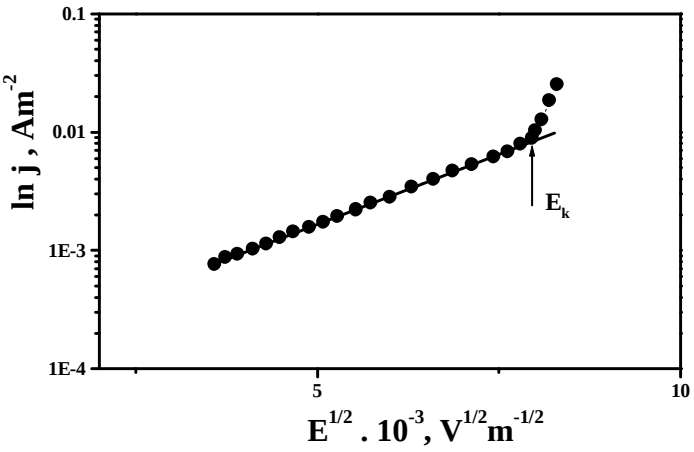


Fig. 5. Relationship $\ln j = f(E)^{1/2}$ of the $(GeSe_2)_{54}(Sb_2Se_3)_{36}(ZnSe)_{10}$ sample.

Fig. 6 depicts the transition from thermionic emission to thermionic-field emission. The plot is presented in co-ordinates $\ln j/E = f(E^2)$ and shows a linear increase. The values of χ_{TF} are calculated from the graph and compared to the values of the work function received from the thermionic emission region.

The results of the effective electron mass and work function on the surface, calculated from eqs. (2-4), are presented in Table 2.

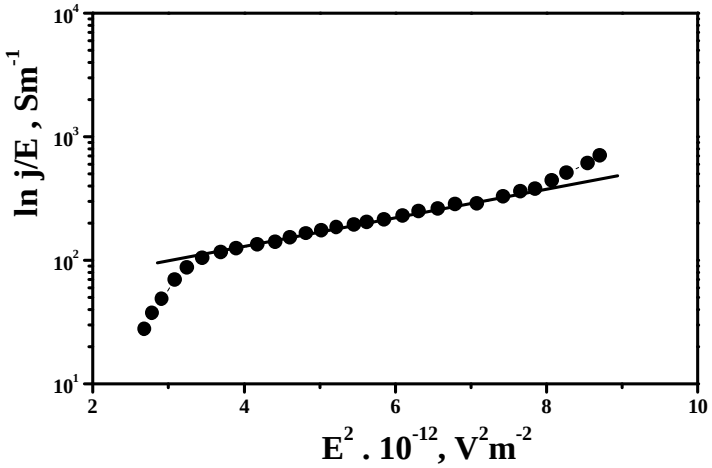


Fig. 6. Relationship $\ln(j/E) = f(E)^2$ of the $(GeSe_2)_{54}(Sb_2Se_3)_{36}(ZnSe)_{10}$ sample.

The samples show good dielectric behaviour shown by the ε values in the Table 2. These values are determined by two independent methods: from the capacitance data and from the slope of current-voltage characteristics in Shottky co-ordinates by using the equations (7) and (8). An average value from both measurements is given in the table.

$$\frac{d(\ln j)}{d(\sqrt{U})} = tg\alpha = \frac{1}{kT}\sqrt{\frac{e^3}{4\pi\varepsilon\varepsilon_0 d}}, \tag{7}$$

where d is the films thickness and

$$\varepsilon = \frac{e^3}{4\pi\varepsilon_0 d(kT \cdot tg\alpha)^2}. \tag{8}$$

Table 2. Physical constants of the studied samples.

No	Composition, mol. %	$m_c\backslash m$	ε	χ_{TE}, eV	χ_{TF}, eV
1	$(GeSe_2)_{80}(Sb_2Se_3)_{20}$	0.35	4.78	1.10	1.12
2	$(GeSe_2)_{54}(Sb_2Se_3)_{36}(ZnSe)_{10}$	0.77	5.95	1.03	1.01
3	$(GeSe_2)_{72}(Sb_2Se_3)_{18}(ZnSe)_{10}$	0.53	5.87	1.11	1.12
4	$(GeSe_2)_{81}(Sb_2Se_3)_9(ZnSe)_{10}$	0.48	5.36	1.23	1.20
5	$(GeSe_2)_{64}(Sb_2Se_3)_{16}(ZnSe)_{20}$	0.81	7.41	1.08	1.09

5. Discussion

The process of thin film preparation is a typical evaporation process of the multicomponent chalcogenide glasses. The preparation conditions ensure a homogeneous and gradual evaporation of the initial bulk glasses. It could be assumed that the low rate of the process ensures a co-evaporation of $GeSe_2$, Sb_2Se_3 and ZnSe units which have similar enthalpies of evaporation (about 250 kJ/mol) and nearly the same evaporation rates.

The values of the dielectric function calculated by both methods (described in the experimental part) show a good reproducibility and similar trend of increase as ZnSe content increases. The maximum values are shown in the film with composition $(GeSe_2)_{64}(Sb_2Se_3)_{16}(ZnSe)_{20}$ that contains a maximum ZnSe concentration and a lower $GeSe_2$ content. ZnSe is a typical insulator, while the increase in Ge concentration improves the conductivity.

The values of effective electron mass show an increase with ZnSe content at a constant ratio $GeSe_2$:Sb_2Se_3 = 4. This increase probably is due to the complex structure of the material. ZnSe units are incorporated in the glass network formed by $GeSe_{4/2}$ tetrahedra and Sb_2Se_3 pyramids. The determination of these values with respect to the Ge and Sb content show a gradual decrease of m_c/m values as the Ge content increases. The decrease could be explained if we assume that new electrons are placed on different positions. Probably electrons fill in the lower levels of the conductive band or new higher levels in the valence band and as a result their effective mass increases.

The values of the electron work function given in Table 2 reveal a good recurrence in calculations for both investigation regions (thermionic and thermoionic-field emission). This is an evidence for the reliability of the used method. The $\chi_{TE}(\chi_{TF})$ values are negligibly dependent on the films' composition. It is observed a tendency of slight decrease of this parameter for increasing Sb_2Se_3 and ZnSe content, respectively. The incorporation of $SbSe_{3/2}$ and $ZnSe_{2/2}$ structural units in $GeSe_{4/2}$ structural network leads to the lower values of potential barrier on metal-semiconductor (chalcogenide glass) surface. This means that Sb_2Se_3 and ZnSe form new energetic levels with small density in band gap around Fermi level. It could be also supposed that the larger influence of the $GeSe_2$ content on the electron work function is due to an increase in the compactness of the material.

The thermal band-gap values show a slight irregularity in the dependence on the films composition. Because of the high complexity of the investigated multicomponent glasses it is difficult to assert which component has a major influence on the electrical properties. Fig. 7 illustrate the dependences of the investigated physical parameters: ε, ΔÅ$_a$, m_c/m and χ_{TF} on $(GeSe_2)_x(Sb_2Se_3)_y(ZnSe)_z$ thin films compositions, where x + y + z = 100 mol.%.

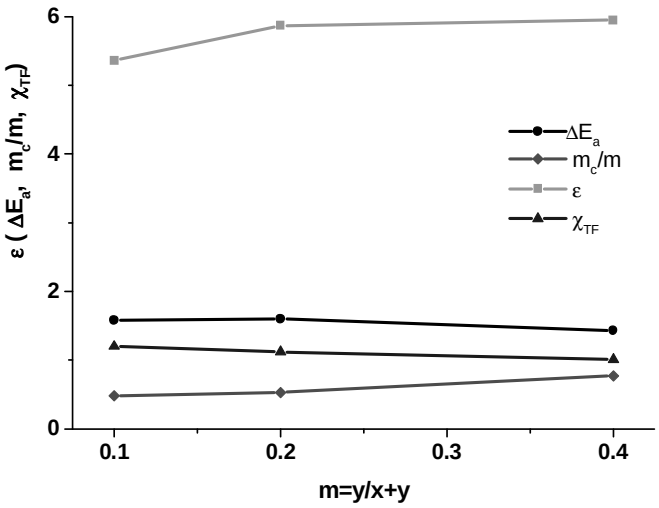


Fig. 7. The ε, ΔÅ$_a$, m_c/m and χ_{TF} dependence on m (m=[Sb_2Se_3]/[Sb_2Se_3]+[$GeSe_2$]) at z = const.

Similar behaviour was reported in Ref. 12 and Ref. 13. concerning other multicomponent Ge- chalcogenide glasses.

6. Conclusions

The obtained results support Christov's theory for injected electron currents in insulators and semiconductors. It should be emphasized that the possibility for accurate determination of the transition field E_k from the experimental current-voltage characteristics is a great advantage of the method used above with an accuracy comparable with that of cyclotron analysis.

From the performed studies the following parameters of the system have been determined:

(i) the values of dielectric permitivity ε are in the range from 5.4 ± 0.1 to 5.9 ± 0.1 obtained by two independent methods from capacitance data and from the slope of current-voltage characteristics in Schottky co-ordinates). The values are dependent of the ZnSe content;
(ii) effective electron mass in the conduction band m_c/m are varied from 0.48 eV to 0.77 eV and increase with the decreasing of $GeSe_2$ content;
(iii) the value of the electron work function at the Al-(Chalcogenide glass) interface calculated from both thermionic and thermionic-field emission regions is dependent on the $GeSe_2/Sb_2Se_3$ ratio and increase with the increasing of the $GeSe_2$ content;
(iv) the thermal band-gap are varied from 1.43 eV to 1.60 eV and slightly depends on the $GeSe_2$:Sb_2Se_3 ratio.

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