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ELECTRICAL PROPERTIES OF AMORPHOUS As_2Se_3-$GeSe_2$-SnTe THIN FILMS

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Electrical properties of vacuum evaporated thin As_2Se_3-$GeSe_2$-SnTe films have been studied. The thermal activation energy of the films with different SnTe concentration is determined by the temperature dependence of conductivity. From electrical investigations some basic physical characteristics of the investigated semiconductor films were calculated applying the Christov's theory for injected electron currents. Effective electron mass (m_c/m) in the conduction band, relative dielectric permittivity ε of the films and the electron work function (χ) at the Al/(As_2Se_3-$GeSe_2$-SnTe) interface as a function of SnTe content were determined.

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1. Introduction

The multicomponent chalcogenide, chalcohalide and oxichalcohalide glasses are a subject of intensive investigation on the last two decades. The increased interest on that class of chalcogenide glasses is determined by their relatively easy synthesis and the wide field of possible applications. It's known that when the number of components in a system is increased, the variety of materials properties will be broadened. These predetermine the possibilities for their application - in IR optics [1], for functional elements in integral-optic systems [2], for optical waveguide [3] and fibers preparation [4,5], for optical layer [6], photoresists [7], materials for ion-selective electrodes [8], as well as optical recording media [9]. The presence of more then one glasificator with different atom coordinations and different types of chemical bonds in them determine the great number of structural units and diversity of their properties.

The glasforming region of As_2Se_3-$GeSe_2$-SnTe system was investigated in previous work [10]. The present investigation is a part of a general characterization of these glasses.

The aim of the present work is to investigate some physical properties of thin films from the As_2Se_3-$GeSe_2$-SnTe systems by measuring their dc conductivity. The experimental results are compared to the theory of injected electron currents in semiconductors and insulators.

2. Theoretical considerations

According to the most general theory of Christov [11-13] for the electron emission from metal to dielectric (semiconductor) the current density in thin film systems from metal-dielectric-metal is given by the equation:

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$$j(E,T) = j_1^{/} + j_2^{/} + j^{//} = Q_1^{/}(T/T_C).j_{FN} + Q_2^{/}(E,T)j_{MG} + Q^{//}(T_K/T)j_{RS} \quad (1)$$

where:

j_{RS}, j_{MG} and j_{FN} are the currents determined by the equations of Richardson-Schotkky, Murphy-Good and Fower-Northheim, for the regions of thermo-ionic, thermo-ionic field and field emission and $Q_1^{´}$, $Q_2^{´}$ и $Q^{˝}$ are quantum correction coefficients - functions of field and temperature.

The dependence of the thermo-ionic emission component j'' ($j''\sim expE^{1/2}$) of the current density, the thermo-ionic-field emission component j_2' ($j_2'\sim expE^2$) 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 transition of the characteristics $lnj(E^{1/2})$ 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:

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

where m is the free electron mass, h is Planck constant, k is Boltzmann constant, e is the electron charge, ε is the relative permittivity of the material. The relation is valid for any temperature if only the critical field E_k is reached. Vodenicharov has proposed a method for the determination of the ratio m_c/m (effective electron mass) using the general theory of Christov for metal/semiconductor/metal systems [12,13,14].

From the above defined emission regions the electron work function of the "metal-semiconductor" interface can be calculated. For the thermionic emission region it is obtained:

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

where A is the Richardson's constant and j^* is a current density at $E = 0$, deduced from the $lnj(E^{1/2})$ graphical dependence.

3. Experimental

The bulk materials were prepared by direct monotemperature synthesis from binary compounds - As_2Se_3, $GeSe_2$ and SnTe, which were previously prepared by the same method. The preparation regime of the As_2Se_3-$GeSe_2$-SnTe systems was described in Ref. [10].

The starting materials, sealed in evacuated quartz ampoules (1.33×10^{-3} Pa) were heated up to 1100 K in an oven with vibrational stirring followed by quenching in air. Thin films were prepared by vacuum sublimation from a special vaporizer. Optical glass, monocrystalline Si and NaCl crystals were used as substrates. The thickness of the deposited films varies in the range of 80-150 nm and has been measured by interference microscope. The microstructure of films was investigated by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) using EM 400, Philips (Holland) electron microscope. For TEM observations of film surfaces C+Pt replicas were applied while SAED was performed directly on the films. Their chemical composition was followed by Auger electron spectroscopy (AES) with aid of apparatus Ribère 309 (France). A good agreement between the composition of the deposited films and the initial glassy samples was found.

Electrical measurements were performed on sandwich samples with two Al electrodes deposited on the bottom and top of the films. The capacitance of structures and dielectric losses were measured at room temperature with precised RLC bridge at frequency 8 kHz. The dc conductivity was studied in the temperature range of 290-405 K. Current-voltage characteristics were investigated by applying a linearly increasing voltage on the samples.

From the volt-ampere characteristics of the structures some basic electrical characteristics were obtained by applying the Christov's theory.

4. Results

TEM observations show that the surface microstructure of all films corresponds to homogeneous amorphous state without crystalline or immiscibility formations (Fig. 1).

Table 1. Properties of As_2Se_3-$GeSe_2$-SnTe thin films.

Composition	ε	m_c/m	χ, eV	E_a, eV
$(As_2Se_3)_{45}(GeSe_2)_{45}(SnTe)_{10}$	5.32	0.39	0.73	0.86
$(As_2Se_3)_{40}(GeSe_2)_{40}(SnTe)_{20}$	5.29	0.45	0.75	0.79

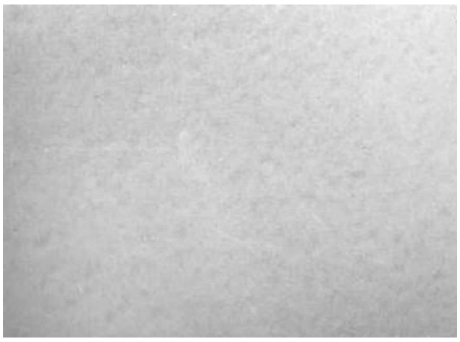

Fig. 1. TEM micrograph of film surface with composition $(As_2Se_3)_{45}(GeSe_2)_{45}(SnTe)_{10}$.

The obtained SAED patterns also correspond to the amorphous microstructure of the films (Fig. 2).

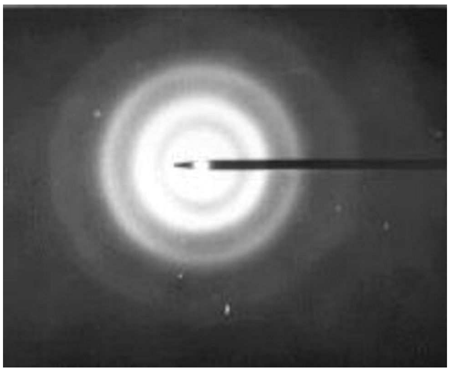

Fig. 2. SAED patterns of film with composition $(As_2Se_3)_{45}(GeSe_2)_{45}(SnTe)_{10}$.

The profilograms obtained by AES (Fig. 3) show homogeneous component distribution in the thin films both in the surface and in the volume.

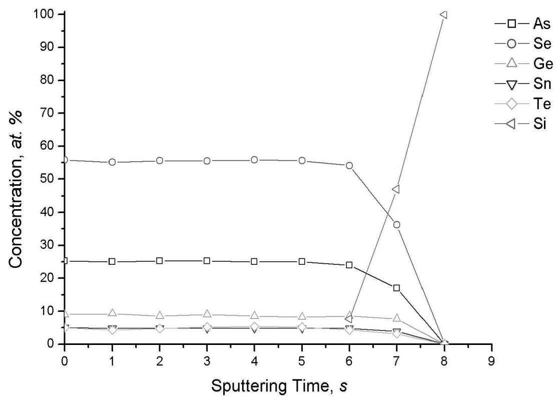

Fig. 3. AES profilograms of thin film with composition $(As_2Se_3)_{63}(GeSe_2)_{27}(SnTe)_{10}$.

The investigation of the dc conductivity is carried out in the temperature range 290-405 K (Fig. 4), and the slope of the graph relation $\sigma = C exp\ (-\Delta E/kT)$ determines the values of activation energy. The investigated temperature region is limited by the glass transition temperature T_g of the glasses [10]. The results are given in Table 1. A weak relation has been found, between the activation energy and SnTe concentration.

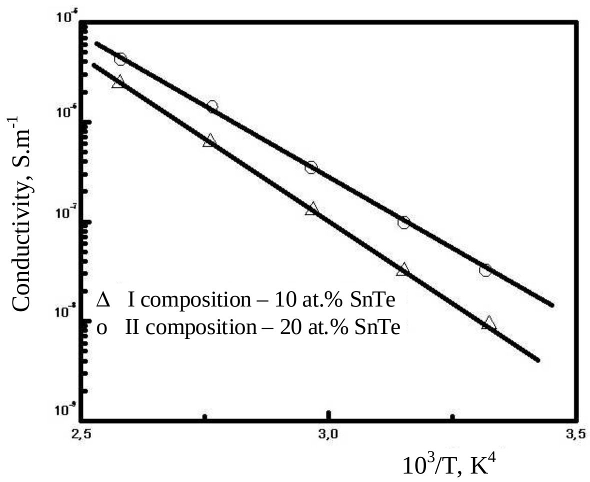

Fig. 4. DC conductivity versus 1/T, of thin As_2Se_3-$GeSe_2$-SnTe films.

The VA characteristics of the films were investigated at room temperature up to electric fields reaching their dielectric strength (3.10^8 V/m).

Dielectric measurements show very good dielectric features of the chalcogenide films; their dielectric strength reaches 10^8 V/m and dielectric losses are very small ($tg\delta < 0.03$).

The value of relative dielectric permittivity of the films, requisite according to equation (2) for determine m_c/m is calculated by two independent methods:

- by measuring the capacitance of thin films structures Al/As_2Se_3-$GeSe_2$-SnTe /Al;

- by the slope $tg\alpha = dlnj/dU^{1/2}$ of VA characteristics presented in Schotkky co-ordinates lnj vs. ($E^{1/2}$).

The results for $\boldsymbol{\varepsilon}$ obtained by the above two methods are in good agreement. The average value of $\varepsilon = 5.3$ (determined by both methods) and it is independent on the SnTe content. This value of ε has been used in the calculations of m_c/m.

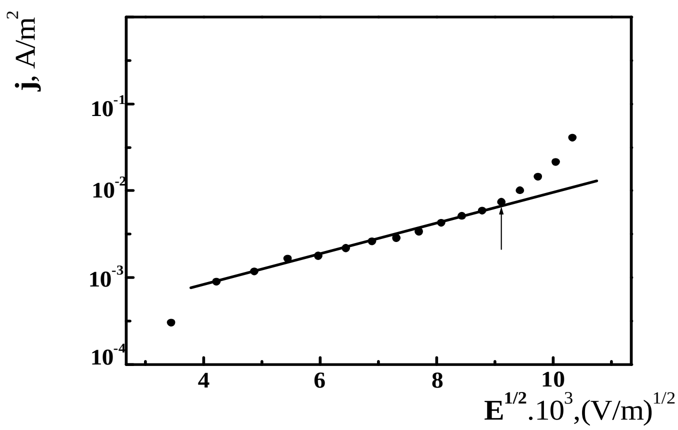

Fig. 5. VA characteristics of sample with composition $(As_2Se_3)_{45}(GeSe_2)_{45}(SnTe)_{10}$.

The critical value of the applied field (E_k) at the transition from thermionic emission region to the thermionic-field emission is determined by the last point laying on the linear part of the $lnj(E^{1/2})$ characteristics (Fig. 5). Using the value of E_k from Eq. (2) we can determine the m_c/m ratio. This method proposed by Vodenicharov [13] ensures relatively good accuracy at the determination of the effective electron mass, the standard deviation being $\pm$ 0.03. The values of m_c/m obtained for different compositions are presented in Table 1. The values of m_c/m increase with SnTe content .

From the thermionic region of emission the electron work function χ_{TE} at the interface “metal/semiconductor” was evaluated by equation (3), extrapolating the linear part of the current-voltage characteristics to cross the ordinate at a point $E = 0$ and $j = j$. The values of χ_{TE} at the Al/(As_2Se_3-$GeSe_2$-SnTe) interface are given for each sample, on Table 1.

5. Discussion

The investigation of the temperature dependence of conductivity suggests that only one type conductivity is presented in the investigated temperature range. The linear character of the dependence shows that significant structural changes do not occur. The thermal activation energy in chalcogenides is a function of the electronic energy levels of the chemically interacting atoms and hence of the energy band gap. The increase in SnTe content from 10% to 20% leads to decrease E_a and it is probably due to a complication of the band gap structure in the investigated glasses.

The linear section from current-voltage characteristic of the samples with As_2Se_3-$GeSe_2$-SnTe composition in Schottky co-ordinates indicates a presence of a thermionic emission region. This linear part of the characteristics, is in the range of electric field intensities from 1.4×10^7 to 4.8×10^7 V/m. According to Christov's criteria, the corresponding change in T_k/T is between 0.46 to 1.05. This means that the linear part is limited only to the extended thermionic emission region, i.e. a region of “pure” thermionic emission is not observed. This could be responsible for appearance of another conduction mechanism, such as space-charge-limited currents, related with a presence of volume charge region, which becomes dominant and suppresses the “pure” thermionic emission. This is most likely if we take of mind, that the amorphous thin films prepared by thermals sublimation are characterized with their high defect concentration [15].

The good accordance in the values of ε determined by two independent methods, demonstrates the coincidence between capacity and Schottky film thickness, testifying to the usefulness of the Schottky mechanism of electron transfer.

The obtained values for the electron wotk function χ_{TE} at the interface “metal/semiconductor” are listed in Table 1 and show that parameters of the potential barrier of the Al-(As_2Se_3-$GeSe_2$-SnTe) interface do not depend on SnTe concentration.

The increase of the values of m_c/m with SnTe content, is probably due to an increase of current charges in the conductivity band and could be explained by the local ordering of As_2Se_3-$GeSe_2$-SnTe chalcogenide glasses.

6. Conclusions

The electrical properties of the thin films in the As_2Se_3-$GeSe_2$-SnTe system were investigated in relation to the film's composition.

The investigation of the temperature dependence of conductivity suggests that the increase in SnTe content from 10% to 20% leads to decrease E_a.

The analysis of the voltage-current characteristics in the regions of thermal emission and thermal field emission could be used for determining of some physical parameters of the films: i.e. the effective electron mass m_c/m in the conduction band as a function of the SnTe content (up to 20 at.%), and the relative dielectric permittivity ($\varepsilon = 5.30 \pm 0.03$).

The value of the electron work function ($\chi_{TE} = 0.74 \pm 0.03$ eV) at the Al / As_2Se_3-$GeSe_2$-SnTe interface was determined from the region of thermal emission. The experimental data confirm Christov's theory of injected electron currents.

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