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DC conductivity measurements of $(As_2S_3)_{1-x}$ $(AgI)_x$ thin films♣

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Thin films from the $(As_2S_3)_{1-x}$ $(AgI)_x$ system have been prepared by vacuum thermal evaporation from the corresponding bulk glasses. Films with less than 25 mol % of AgI are amorphous, as shown by XRD investigations. The thin film morphology and surface have been investigated with SEM and AFM. Sandwich systems consisting of a deposited bottom electrode, a chalcogenide film and an upper electrode have been utilized for electrical studies. The DC conductivity has been measured in a linearly increasing electrical field up to 10^8 Vm^{-1}, at ambient temperature. The obtained results have been interpreted with a view of Christov's theory for injected electron currents.

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1. Introduction

Chalcogenides are transparent in a wide spectral region, possess a relatively high index of refraction, low acoustic losses of ultrasonic waves, etc. [1-4]. Investigations of the mechanical, electrical, and optical properties of chalcogenide glasses (ChG) have shown that these properties depend substantially on the system composition.

Recently, interest in Ag and silver iodide (AgI) as additives in network glasses, such as chalcogenides and oxides, has risen because the resulting composite glasses possess a high electrical conductivity with potential applications for batteries, sensors and displays [5-8].

The goal of this work is to study the direct current conductivity of thin films from the $(As_2S_3)_{100-x}(AgI)_x$ system, at electric fields up to 10^8 $V.m^{-1}$ at room temperature. The experimental current-voltage characteristics of the samples are compared with the theory of Christov [9] for injected electron currents in semiconductors and insulators.

2. Experimental

Bulk samples of $(As_2S_3)_{(100-x)}$ $(AgI)_x$ system (x = 0, 10, 20) were prepared by a standard melt-quenching technique from As_2S_3, previously synthesized by us, and commercial AgI (Alfa Aesar, Johnson Matthey) [10]. For investigation of the DC conductivity, a "sandwich" (Au/ChG/Au) layer system of consecutively deposited bottom gold electrode, chalcogenide film and upper gold electrode were prepared by thermal vacuum evaporation, in a standard vacuum set-up ("Hochvacuum" B 30.2). The process conditions were as follows: 1.33 x 10^{-3} Pa residual pressure in the chamber and a 0.12 m source-substrate distance. An inductively heated tantalum evaporator was used for the chalcogenide layer depositions, and an open ribbon tantalum evaporator for deposition of the electrodes.

The thickness of the films, measured by means of an interference microscope with an accuracy of ± 5 nm, varied from 265 to 285 nm.

The glassy nature of the samples was verified by X-ray diffraction analysis. XRD spectra were recorded by a Philips APD15 X-ray diffractometer. The diffraction data were collected at a constant rate of 0.2 °/min over an angle range of 2θ = 20 – 70 °, using $Cu_{K\alpha}$ radiation (λ=1.54178 Å).

The morphologies of the films were investigated by scanning electron microscopy (SEM, Hitachi S-4000), while their topography was examined by atomic force microscopy (AFM, CP–II) in a tapping mode.

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The current-voltage characteristics of the structures were measured at linearly increasing electrical fields of up to 10^8 Vm^{-1}, at ambient temperature. The computerized experimental set-up utilized for the investigations included a precision amplifier and a picoammeter providing current measurements within an accuracy of 10 pA. All experiments were carried out at constant temperature, measured by a thermocouple to an accuracy of 0.2 K, in a special designed chamber.

3. Theoretical approach

According to the theory of Christov, the current density due to electron transitions over and through the potential barrier at the metal/semiconductor interface is given by the equation:

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

where j'', j_2' and j_1' are the current densities corresponding to the thermionic emission, thermionic field and field emission regions, respectively; Qj'', Q_2' and Q_1' are quantum corrective factors, functions of the field intensity ε and the temperature T; j_{RS}, j_{MG}, j_{FN} are the current densities determined by the equations of Richardson-Schottky, Murphy-Good, and Fowler-Nordheim. T_K and T_C are the characteristic Christov temperatures, defined by the expressions:

$$T_C = \frac{heE}{4\pi k\sqrt{2m_C \chi t(y)}} \quad (2)$$

$$T_K = \frac{h(e\varepsilon)^{1/4}}{\pi^2 k\sqrt{m_c}} E^{3/4} \quad (3)$$

where h and k are Planck's and Boltzmann's constants, respectively, e is the electron charge, m_c is the effective electron mass, ε is the relative dielectric function of the semiconductor film, χ is the electron work function and E is the transition field intensity.

The application of Christov's theory is a very suitable approach for determination of the basic parameters of the films and the metal/chalcogen interface, namely the electron work function and effective electron mass.

4. Results and discussion

The amorphous nature of the films was proved by X-ray diffraction spectra (Fig. 1). The very similar broad halos corroborate that the samples were typical glasses.

A SEM image of an $(As_2S_3)_{80}$ $(AgI)_{20}$ thin film is presented in Fig. 2, as a typical pattern of the studied films. The top-view SEM picture (Fig. 2a) reveals a uniform, homogeneous, and featureless surface of the film. The cross–sectional view (Fig. 2b) demonstrates that the film also possesses an internal amorphous and compact structure.

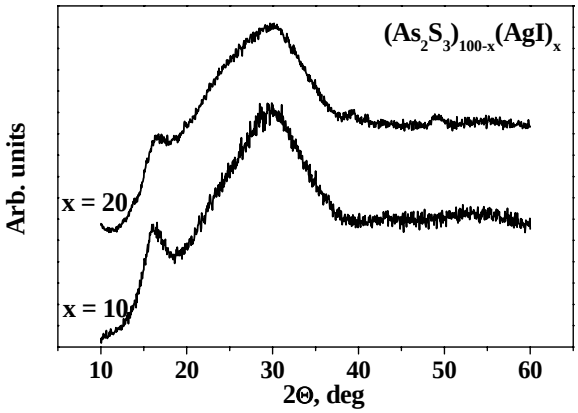
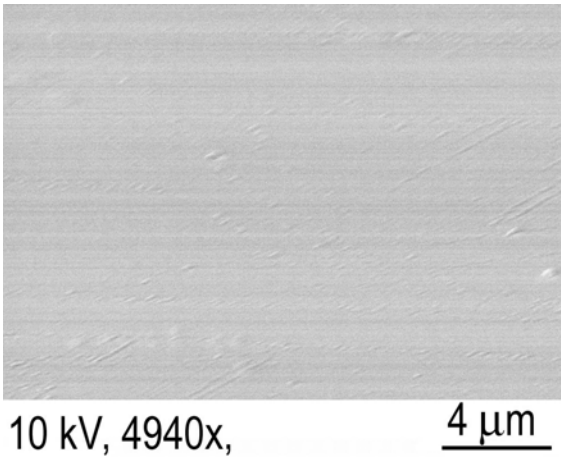
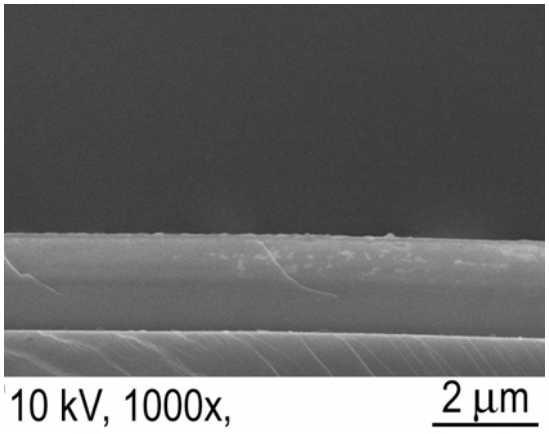


Fig. 1. X-ray diffraction patterns for some glass compositions of the $(As_2S_3)_{100-x}(AgI)_x$ system.



a



b

Fig. 2. SEM images of an $(As_2S_3)_{90}(AgI)_{10}$ thin film: (a) top-view and (b) cross-section.

The results from the AFM microscopic analyses are in good agreement with those obtained by the SEM investigation. The AFM images (Fig. 3) confirm that the evaporated films have relatively smooth surfaces with low degrees of roughness. The rms values increase with AgI content, but nevertheless do not exceed several nanometres in films with 20 mol.% AgI.

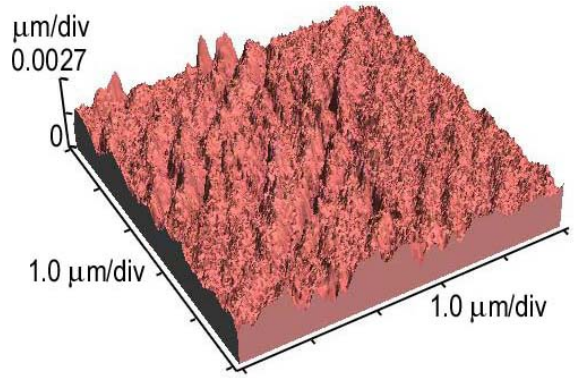


Fig. 3. AFM 3D image of an $(As_2S_3)_{90}(AgI)_{10}$ thin film.

These data, as well as our previous results on the optical properties, imply that most probably the incorporation of up to 20 mol.% AgI in a As_2S_3 host glass exclude the appearance of metallic conductivity. The suggestion is supported by the observed gradually decrease in the optical band gap with AgI content [11]. Obviously, the studied $(As_2S_3)_{1-x}$ $(AgI)_x$ glasses could be interpreted as intrinsic semiconductors, similar to most of the chalcogenide glasses [12]. For such materials, the Christov theory is suitable to be applied.

The current voltage characteristics of all samples under study, recorded in electrical fields up to 10^8 V.m^{-1}, showed a non-linear rise of the current with the AgI content. From the current-voltage characteristics of Au/ChG/Au systems represented in $\ln j = f(E^{1/2})$ Schottky coordinates (Fig. 4), one can determine the dielectric function of the chalcogenide film.

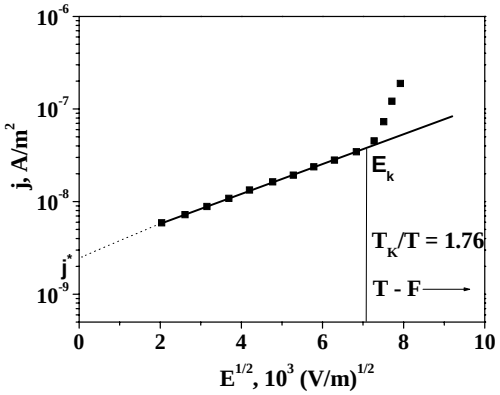


Fig. 4. V-A characteristic in Schottky coordinates.

From the slope, α, of the linear part of the relationship indicating the thermionic emission region, the dielectric function can be determined according to the formula,

$$\varepsilon d = \frac{e^3}{4\pi\varepsilon_0 (kTtg\alpha)^2} \qquad (4)$$

Where d is the film thickness, T is the temperature, ε_0 is the dielectrical constant, and k is the Boltzmann constant.

The values of the dielectric function in Table 1 suggest that the dielectric behaviors of our films depend on the AgI incorporation. The AgI dopant increases the conductivity, and hence the value of the dielectric function decreases slowly.

The effective electron mass in the metal is assumed to be equal to the free electron mass m. However, the effective electron mass in the

Table 1. The values of the dielectric function, ratio of the effective electron mass and the electron work function of the $(As_2S_3)_{(100-x)}(AgI)_x$ system.

	As_2S_3	$(As_2S_3)_{90}(AgI)_{10}$	$(As_2S_3)_{80}(AgI)_{20}$
ε, [V/m]	6.02	5.95	5.82
$\frac{m_c}{m}$	0.05	0.11	0.2
χ_{TE}, [eV]	0.85	0.87	0.95
χ_{TF}, [eV]	0.865	0.89	0.96

conduction band (m_c) of the semiconductor differs from m, and depends on the band structure. The effective electron mass could be evaluated by the formula:

$$\frac{m_c}{m} = \left(\frac{h\sqrt[4]{e\varepsilon}}{1.76\pi kT} \right)^2 E_k^{3/2} \qquad (5)$$

where h is Planck's constant, E_k is the field intensity and lies at the point corresponding to the transition of the $\ln j = f(E^{1/2})$ characteristic from a linear to a nonlinear shape. This is valid for any temperature, if only the critical field E_k is reached. The obtained values of the effective electron mass are presented in Table 1. This method allows one to achieve an accuracy of 5 %, that is better compared to the method of cyclotron resonance also used for effective electron mass measurements where an accuracy of 8 % was reported [13].

The non-linear increase of the effective mass values most probably is due to the filling of higher levels of the conduction band by new electrons. The latter is facilitated by the decrease of the band gap.

In the region of pure thermionic emission, where the electron transition occurs over the interface potential barrier, the current density is determined by the equation of Richardson-Schottky. The linear dependence $\ln j = f(E^{1/2})$ can be used as an evidence for the thermionic emission region. The values of the electron work function in the region of thermionic emission can be calculated by the expression:

$$\chi_{TE} = -kT \ln \frac{j^*}{AT^2 m_c / m} \qquad (6)$$

where j^* is the ordinate of the relationship $\ln j = f(E^{1/2})$ (Fig. 4) and A is the Richardson constant ($A=4\pi ek^2m_c/h^3$).

The values of the electron work function in the region of thermionic emission, calculated with accuracy of ±0.02 eV, are presented in Table 1. The higher content of AgI does not influence the electron work function values. They depend mostly on the chalcogenide matrix, showing the absence of metal conductivity.

Using the Schottky potential barrier and the Fermi-Dirac energy distribution function for free electrons, Murphy and Good have proposed a new type of emission, named thermionic-field (T-F). In this narrow intermediate emission range, the current density depends strongly on both the temperature and field. The borders of the linear dependence $\ln(j/\varepsilon)=f(\varepsilon^2)$ (Fig. 5), presented in a Murphy-Good coordinate system, represent the area of thermionic-field emission.

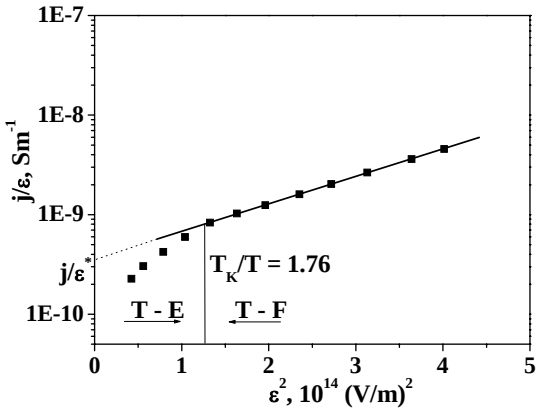


Fig. 5. V-A characteristic in Murphy–Good coordinates.

The values of the electron work function in the region of thermionic-field emission can be calculated by expression

$$\chi_{TF} = -kT \ln\left[\frac{h(j/E)^*}{e^2\sqrt{2\pi m_c kTt(z)}}\right] \qquad (7)$$

where $(j/E)^*$ is the ordinate of the relationship $\ln(j/\varepsilon) = f(\varepsilon^2)$ (Fig. 5), and $t(z) \approx 1$.

The calculated values of the electron work function in the region of thermionic-field emission are listed in Table 1. The results received show a good coincidence with those from the thermionic emission region.

5. Conclusions

Thin amorphous films from the $(As_2S_3)_{100-x}(AgI)_x$ system, prepared by thermal vacuum evaporation from previously synthesized bulk glasses, have been characterized as amorphous with smooth, featureless and uniform surfaces, irrespective of the AgI amount revealed by morphological and topological studies.

From the experimentally collected data on the electrical conductivity, the following conclusions can be drawn:

1) The AgI concentration does not affect substantially the dielectric function values;

2) The effective electron mass in the conduction band strongly depends on the AgI concentration, and increases non-linearly in samples with 20 mol.% of AgI;

3) The electron work function values are defined by the chalcogenide matrix. The values derived in both the regions of thermionic and thermionic-field emission show good agreement.

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