JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 11, No. 12, December 2009, p. 2049 - 2052

Analysis of conductivity of glasses from the $(As_2S_3)_{100-x}Bi_x$ system in direct and alternating regimes

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The work presents results of the conductivity measurements in both direct and alternating regimes for a series of samples from the system $(As_2S_3)_{100-x}$ Bi_x, x = 0.5, 2, 6 and 8 at.%. Temperature dependence in the *dc* regime indicates a semiconducting character of all investigated glasses. A linear fit of experimental results was used to determine the pre-exponential factor and energy of activation. On the basis of the analysis of these parameters it was possible to establish a dominant mechanism of conduction, as well as an increased participation of localized states in the transfer processes with an increase in Bi concentration. Conductivity measurements in the *ac* regime were performed with the aim of studying the nature of defect centers. The glasses with 0.5, 2 and 6 at.% Bi showed a frequency dependence of the *ac* conductivity that is typical for amorphous semiconducting materials. The absence of frequency dependence for the glass with 8 at.% Bi at higher temperatures in the major part of the measuring interval, significantly higher conductivity, as well as its temperature dependence, compared to the other glass samples, indicate the possibility of treating this sample as an inhomogeneous double-layer structure, an indication of this being also the results of x-ray analysis.

(Received July 5, 2009; accepted November 12, 2009)

Keywords: Chalcogenide glasses, Impurity atoms, Conductivity mechanism, Type of conductivity, Defect states

1. Introduction

It is generally known that chalcogenide glasses exhibit p-type of conductivity. This characteristic is ascribed to two phenomena. Namely, the effect of structural disorder influences less the lone-pair orbitals of the top of the valence band compared to nonbonding orbitals, so that the area of localized states in the valence band tail is smaller than that in the conduction band. A consequence of this is that the number of electrons excited above the band gap to the conduction band is smaller than the number of holes excited to the valence band. Further, in thermal activation, the life time of free holes excited from the positively charged defect centers is longer than the life time of free electrons excited from negatively charged defect centers which, because of that, mainly undergo recombination [1].

With the aim of improving physical characteristics, chalcogenide semiconductors are sometimes doped with certain impurity atoms, which has also significant consequences on their electronic structure, that is the type of conduction [2]. This work presents and analyzes results of *dc* and *ac* measurements of conductivity of the glasses from the $(As_2S_3)_{100-x}Bi_x$ system, indicating the way of changing electrical properties of glasses in the p-n transition.

2. Experimental

Samples of the investigated system $(As_2S_3)_{100-x}Bi_x$, belonging to the class of chalcogenide semiconductors were prepared by the procedure described by Goryunova, Kolomiets and Shilo [3]. Amorphousness of the synthesized samples was checked by X-ray method, which showed that the samples with lower Bi content were amorphous, while the sample with 8 at. % Bi contained crystalline centers of the type Bi, As and As_2S_3.

Electrical conductivity of a representative series of samples from the system $(As_2S_3)_{100-x}Bi_x$ was determined in stationary and dynamic modes of measurements. Samples with x = 0.5, 2, 6 and 8 at.% Bi were mechanically polished with abrasive powders of different grain size to obtain plane-parallel plates. In both measurement regimes, samples were mounted on a specially constructed holder placed in the high-temperature chamber of the setup HP 4329A and exposed to *dc* or *ac* voltage during the thermal treatment in the temperature interval of 300-500 K.

Conductivity of the samples in *dc* regime was determined by measuring the ohmic resistance of the material at selected temperatures at a constant working voltage of U=10 V. Total conductivity in the *ac* regime was measured in the frequency range of 10^3-10^6 Hz, by measuring the sample impedance at the corresponding temperatures. The *ac* component was obtained as the difference between the total measured conductivity and *dc* conductivity.

3. Results and discussion

Results of measurements of *dc* conductivity are shown in Fig. 1. Temperature behavior of the conductivity of investigated glasses, apart from confirming their

semiconducting character, satisfies also the Arrhenius equation, that is it indicates that the conductivity of the samples is a thermally activated process [4].

The slope of the temperature dependence of the function $ln\sigma_{dc}$ and its intercept served to determine the pre-exponential factor $ln\sigma_0$ and activation energy ΔE_{σ}. Values of these parameters are listed in Table 1. The increase in *dc* conductivity is accompanied by a decrease in the activation energy, which can be explained as a result of the proportion of conductivity that is due to hopping between defect states in the overall conductivity, or, as a consequence of the shift of the Fermi level [6,7,8].

On the other hand, according to the Davis-Mott model [9], the values of the pre-exponential factor of the investigated samples indicate the dominance of hopping between localized states in the band tails.

Fig. 1 also illustrates the tendency of increasing the *dc* conductivity with increase in Bi content, especially pronounced in the sample with the highest ratio of doping atoms, whose conductivity is by several orders of magnitude higher compared to the other samples that are poorer in Bi (Table 1).

Table 1. Parameters of dc conductivity of tha glesses of $(As_2S_3)_{100-x}$ Bi_x system

x [at.%]	σ_{300K} [$\Omega^{-1}m^{-1}$]	ΔE_{σ} [eV]	σ_0 [$\Omega^{-1}m^{-1}$]
0.5	$2.54\cdot10^{-14}$	0.96(4)	77.76
2	$8.69\cdot10^{-13}$	0.84(6)	20.67
6	$1.27\cdot10^{-11}$	0.69(4)	226.83
8	$2.74\cdot10^{-6}$	0.49 (2)	398.72

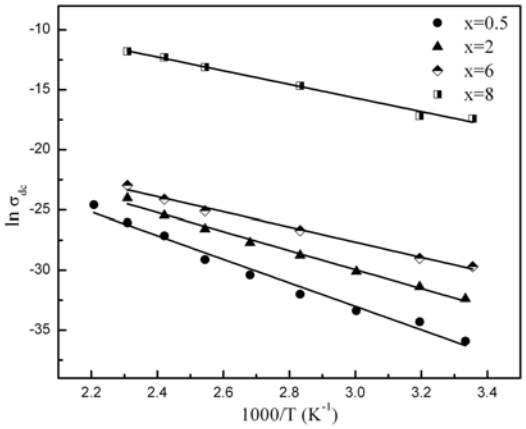

Fig. 1. Dependence of $ln\sigma_{dc}$ on 1/T for the glasses of the $(As_2S_3)_{100-x}$ Bi_x system

This effect can be explained as a consequence of glass doping with Bi atoms, which, in view of entering the matrix in the form of Bi^{3+} defects, provide additional electrons in delocalized states of the conduction band [5]. This is also manifested as an increased value of the σ_0 factor (Table 1).

A general characteristic of chalcogenide semiconducting glasses is their frequency dependence of *ac* conductivity, which can be described by the general relation:

$$\sigma_{ac}(\omega) == const \cdot \omega^{s} \qquad (1)$$

where ω is the angle velocity and s is the frequency factor. This is explained in terms of the relaxation of charge carriers that are tunneling or hopping between equilibrium states [10].

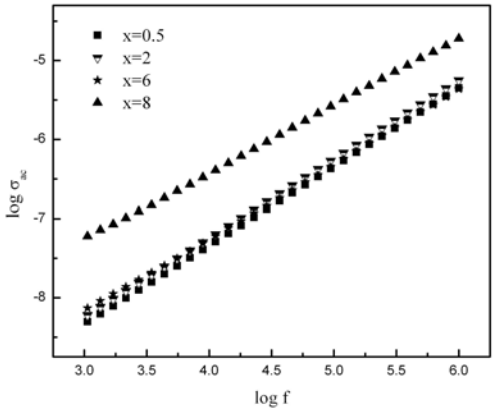

Fig. 2. Frequency dependence of σ_{ac} for the glasses from the $(As_2S_3)_{100-x}$ Bi_x system at room temperature

Fig. 2 shows the frequency dependence of σ_{ac} for the investigated glasses at room temperature. It is evident that the frequency behavior of σ_{ac} for all samples can be described by equation (1). The increase in the conductivity of the sample with highest impurity content suggests the increase in the density of localized states in the band tails, and it is the only one from the representative series of samples that exhibits a significant temperature dependence. (Fig. 3). This is explained by an increase in the density of neutral defect states D^0, that is by a higher contribution of single polarons in the *ac* conduction regime [11]. The weak dependence of the conductivity on temperature for the rest of the samples indicates the low activation energy and corresponds to the mechanism of hopping between localized states adjacent to the Fermi level as dominant in the overall conductivity [12].

A characteristic property of metal-doped dielectrics is that their *ac* conductivity increases only at higher temperatures [13], due to the reduction of charge shift. With the glass $(As_2S_3)_{92}Bi_8$, this effect appears at higher temperatures, which could be explained in terms of the Koops [14] or Maxwell-Wagner [15] model of structural orderliness. In this sense the composition with 8 at.% Bi may be thought of as being an inhomogeneous double-layered structure – one layer consists of the crystalline Bi centers and represents the conduction layer, and the other made of the As-S matrix in which these centers are incorporated.

The smaller *ac* activation energy and increase in σ_{ac} with increased field frequency for the investigated samples

confirm that the model of correlated barrier hopping (CBH model) can be used for interpretation of the results [11,16,17]. According to this moedel, the value of the frequency factor *s* at room temperature is in the span of 0.7-1.0 and decreases with increase in temperature, i.e. it satisfies the relation [17]:

$$s = 1 - \frac{6k_BT}{W_m + (k_BT\ln(\omega\tau_0))} \approx 1 - \frac{6k_BT}{W_m} \qquad (2)$$

where k_B is the Boltzmann constant, τ_0 is the characteristic relaxation time, W_m stands for the height of the potential barrier, and T is the temperature.

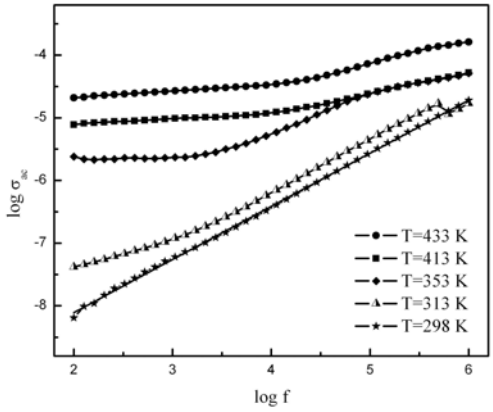

Fig. 3. Frequency dependence of σ_{ac} for the glass $(As_2S_3)_{100-x}Bi_x$ at different temperatures

The height of the potential barrier is obtained by linear fitting to the functional dependence given by relation (2) and it is W_m=0.123 (8) *eV*. By comparing with the activation energy of *dc* conductivity of the glass $(As_2S_3)_{92}Bi_8$, (Table 1), which corresponds approximately to the middle of the optical band gap, it can be concluded that the conductivity of this sample in the *ac* regime is primarily due to hopping between D^0 and D^-, that is D^0 and D^+ states. The increase of the proportion of the single polaron type of hopping with increase in the impurity content is a consequence of the shifting of the Fermi level towards the conduction band [22]. The introduction of Bi into the arsenic-sulfide matrix disturbs the equilibrium between the D^+D^- defect pairs as a consequence of converting particular S_3^+ states to S_1^- states, yielding thus to a decrease in the number of free holes as well as of the number of traps capturing electrons excited to the conduction band.

On the other hand, the increase in the number of S_1^- states results in an increase of the acceptors capturing the holes from the valence band. The change of the conduction type is accompanied by a significant decrease in the band gap, which was confirmed by measuring optical characteristics of the Bi-As-S system [23]. Pattanaik and Srinivastan [24] showed that the change in conduction type in the Ge-Se glasses doped with Pb can be ascribed to microcrystalline clusters as responsible for the detected effect. The X-ray measurements indicated the existence of crystalline centers exactly in the sample with 8 at.% Bi.

Hopping of the charge carriers between the pairs of localized states near the Fermi level is also influenced by the density of localized states $N(E_f)$, calculated from the following relation [25]:

$$\sigma_{ac} = (1/3)\pi e^2 k_B T N^2(E_f)\omega\alpha^{-5}\left[\ln(\nu_{ph}/\omega)\right]^4 \qquad (4)$$

where *e* is the elementary charge, α is the exponentially decreasing parameter of the wave function of localized states, and υ_{ph} is the phonon frequency. Taking that $\upsilon_{ph}=10^{12}$ Hz and α^{-1}=10 *Å* [26], we calculated the density of states for the investigated glasses at the frequency logf=4.15 for the corresponding temperatures (Table 2).

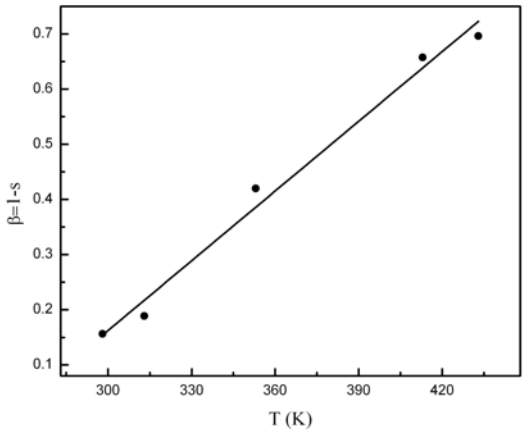

Fig. 4. Temperature dependence of the factor s *for the glass $(As_2S_3)_{100-x}Bi_x$*

The decrease in the number of defect states with increase in temperature with the glasses x = 0.5 and 2 at.% Bi corresponds to a decrease in the bipolaronic contribution due to the state conversion at higher temperatures. In the glass with x = 6 at.% Bi at higher temperatures and in the glass with x = 8.% Bi in the whole temperature interval the single polaron mechanism is fully dominating. On the other hand, the increase in defect states around the Fermi level with increase in Bi content in the composition of investigated glasses is in accordance with the conclusion of both *dc* and *ac* regime of conductivity measurement.

Table 2. Number of defect states in dependence of temperature and glass composition

T (K)	N (10^{15} eV^{-1} m^{-1})			
	x=0.5	x=2	x=6	x=8
300	4.922	5.478	5.309	13.64
313	-	5.363	5.021	12.00
353	4.653	5.108	5.008	46.74
393	-	4.849	6.403	-
413	4.301	4.743	6.466	58.96
433	4.267	4.637	6.386	96.68

4. Conclusion

Measurement of conductivity of the glasses of the $Bi_x(As_2S_3)_{100-x}$ system in *dc* regime pointed out to the semiconducting character of the investigated samples. It was also established that the introduction of Bi into the arsenic-sulfur matrix yielded a significant increase in the conductivity, accompanied by a decrease in the activation energy of hopping of charge carriers between localized states.

The results of the measurement of *ac* conductivity were explained in accordance with the CBH model. The pronounced temperature dependence of glass conductivity with the highest dopant content was explained by a higher participation of neutral neutral defect states in the transition processes, due to the shift of the Fermi level toward the conduction band. The change of conductivity type was explained in terms of coupling the two effects that arise as a consequence of introducing Bi atoms: additional electrons in the conduction band and increased number of negatively charged defect centers.

Acknowledgment

This work was realized in the frame of the project "Amorphous and Nanostructural Chalcogenides" (No. 141026B), financed by the Ministry of Science and Technological Development of the Republic of Serbia.

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