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ANOMALOUS CONDUCTIVITY IN Au-DOPED CHALCOGENIDE GLASSY SEMICONDUCTORS

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The experimental results for temperature dependence of the glass conductivity of $(As_2S_3)_{100-x}Au_x$ and $(As_2S_5)_{100-x}Au_x$ $(0.04 \geq x \geq 0)$ are presented. There are found: two fractures on the temperature dependence of the conductivity in compounds with small gold concentration, an abnormal behaviour of the conductivity in the temperature range 360>T>300 K. The major part of the impurity atoms fills the volume of the glass semiconductor, saturates all its valence bounds forming a series of solid solutions what leads to a change of band gap E_g. A small part of the impurity atoms, having the unusual closest neighbourhood, not saturates its valence bonds and as a result, forms an electrical active impurity level, defining the conductivity.

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1. Introduction

In order to solve many problems in the physics and engineering of semiconductors, the controlled introduction of impurities into crystalline semiconductors, which form deep levels in the band gap of a semiconductor, is widely used. Specifically, the operation of the overwhelming majority of semiconductor devices and units is based on the use of doped crystals with specified properties. This circumstance also stimulated the investigation of impurity behavior in chalcogenide vitreous semiconductors (chalcogenide glasses). However, even the first investigations [1,2] demonstrated that most of the impurities introduced into glass from a melt during synthesis weakly (if not at all) affects the physical properties of chalcogenide glasses (CGS). The impurities are optically and electrically inactive; i.e., they form no localized states in the band gap. In early works the results are summarized in a review [3]. It is shown that the CGS conductivity (σ) in a glass is much less than in a crystal, and does not depend upon the impurity concentration. The characteristic fracture, corresponding to the transition from the intrinsic conductivity to the impurity one, vanishes on the conductivity - temperature curve.

2. Theoretical analysis

The absence of the impurity fracture, i. e. the absence of the electric activity of the impurities in the glass was explained by the possibility that the impurity atom uses all its valence electrons for creation of bonds with neighbours in the disordered structure. Therefore, donor or acceptor character of the impurity is not revealed in the glassy state. An influence of metal impurities upon the physical properties of CGS is studied on the glasses of stoichiometric compound, which have a high crystallization tendency. Such an anomaly in the behavior of impurities introduced into CGS was many years considered as their distinctive feature. However, there are facts that are indicative of impurity influence on the physical properties of CGS. It was demonstrated that some impurities, for example, Cu and Ag, substantially change the conductivity that is caused by a decrease in the band gap E_g of a newly formed compound. Despite this fact, the fundamental questions concerning the search for impurities that would make it possible to

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effectively control the physical properties of CGS remain unresolved, and the anomalous behavior of most impurities in glasses has not been explained up to date. This is due primarily to the fact that there are few direct methods for studying the state of an impurity (the structure of the impurity center, its nature, charge states, and local symmetry in the glass matrix) in CGS. The applicability of these methods is restricted.

The study of an influence of Au low concentration impurity upon the electroconductivity of CGS stoichio- and nonstoichiometric compound and the revealing of their features is the aim of this work. The stoichiometric $(As_2S_3)_{100-x}Au_x$ and nonstoichiometric $(As_2S_5)_{100-x}Au_x$, where $0.1> x \geq 0$, were chosen for the study.

3. Experiment and method

Undoped and Au-doped glasses were synthesized by direct alloying the corresponding amounts of elemental As and S with Au of 99.99999% purity in evacuated quartz ampoules using vibrational stirring of the melt. To prevent explosion of ampoules, synthesis was carried out in two stages. In the first stage the ampoules were heated in a tubular furnace up to 800-850 K at a rate of 0.1-0.2 K/s with subsequent holding at this temperature for 15-20 hours. In the second stage, the furnace temperature was increased up to the melting point of the element with the highest melting temperature at a rate of 0.05-0.1 K/s and kept constant for 20-25 hours. The melt was then quenched in salt water with ice. The absence of lines in the Debye-Scherrer powder patterns, diffuse X-ray scattering, and absence of microinclusions and inhomogeneities on polished surfaces and cleavages of the samples visually inspected through a Neophot microscope served as criteria of the vitreous state of the materials. The electroconductivity of the samples was measured by the method of clamping contacts. The plane-parallel samples of thickness d=(0.85 ÷ 2 mm) were clamped between two soft graphitic pivot ∅10 mm, squeezed into the copper blocks. The resistance of pivot together with copper blocks is 0.2 Ω. The current leakage was reduced to zero.

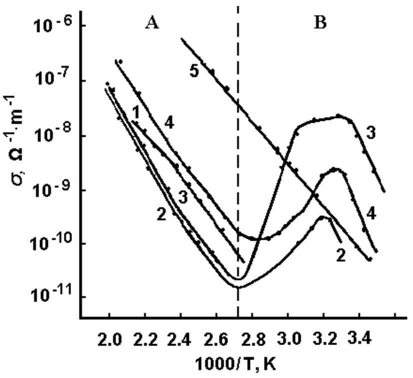

Fig. 1. Temperature dependence of the electrical conductivity on the constant current of glasses $(As_2S_3)_{100-x}Au_x$: values x (at %) 1 - 0; 2 - 0.00001; 3 - 0.0001; 4 - 0.01; 5 –0.02.

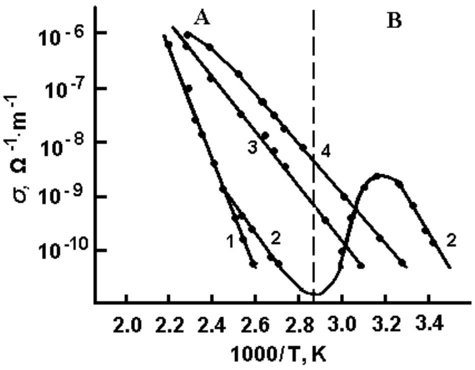

Fig. 2. Temperature dependence of the electrical conductivity on the constant current of glasses $(As_2S_5)_{100-x}Au_x$: values x (at %) 1 – 0 and 0.00001; 2 - 0.0001; 3 - 0.02; 4 -0.04.

The experimental results for temperature dependences of the glass conductivity of the investigated system are represented in Figs. 1 and 2. Figs. 1 and 2 can be divided into two parts: effect A and effect B. A-effect is determined by the extrinsic conductivity, B-effect – transition from semiconducting to metallic conductivity. The temperature increase (T>300 K) leads to the conductivity increase of several orders up to T~310 K. The further temperature increase, T>310 K, leads to the conductivity decrease in several orders (to metallic conductivity). The activation energies of studied glasses are shown in the Table 1. One can see, that activated energy of conductivity decreases with Au content increase in glasses. The electroconductivity As_2S_3 and As_2S_5 is written by the expression $\sigma=\sigma_0\exp(-E_a/kT)$ with energy activation. Glasses containing the gold x=0.00001 at% and higher show fractures and two activation energies. When doping 0.01 at% of gold the glass conductivity increases by two orders. The activation energy decreases by 0.3 eV. The increase of content of gold in As_2S_3 decreases the softening temperature by 20 K and in As_2S_5 by 10 K. It should be noted that in As_2S_3, undoped and doped by gold (0.02 at%) the electroconductivity is described with one activation energy. In the temperature range 360>T>300 K the electroconductivity appreciably rises with the increase of temperature, reaches a maximum and then sharply decreases to minimum values by several orders below 10^{-11} $\mathrm{Ohm^{-1}\cdot cm^{-1}}$. Further increase of temperature T>360 K for the doped glasses gives rise to conductivity with two activation energies. The study for the temperature dependence of the conductivity of doped glasses in several heating-cooling regimes leads to vanishing of the conductivity in the range 360>T>300 K and the conductivity is observed only with two activation energies.

Table 1. The activation energies of studied glasses.

$(As_2S_3)_{100-x}Au_x$					
x=0	x=0.00001	x=0.0001	x=0.01	x=0.02	
0.818 eV 1.005 eV	1.322 eV(a) 0.915 eV(b) 1.536 eV(c)	1.322 eV(a) 0.915 eV(b) 1.536 eV(c)	1.126 eV(a) 0.850 eV(b) 1.700 eV(c)	0.561 eV(a) 0.816 eV(b)	
$(As_2S_5)_{100-x}Au_x$					
x=0	x=0.00001	x=0.0001		x=0.02	x=0.04
1.985 eV	1.985 eV(a)	1.985 eV(a) 1.236 eV(b) 1.270 eV(c)		0.926 eV(a) 0.992 eV(b)	0.664 eV(a) 0.895 eV(b)

4. Discussion

Let us describe a possible picture of formation and the properties of second slope on the plot of conductivity versus temperature.

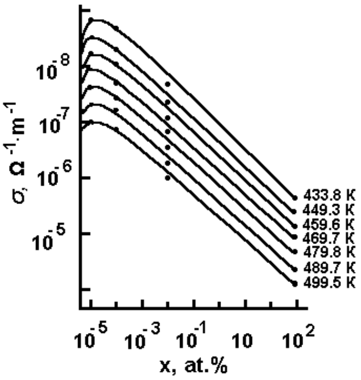

Fig. 3. Dependence of the electrical conductivity on the constant current of glasses $(As_2S_3)_{100-x}Au_x$ at different temperatures.

In a disordered structure, the distances between atoms are not identical with those in crystals. Weak fluctuations of interatomic distances appear equally in compression and extension. At the same time a strong extension is more probable owing to a strong increase of repulsion between atoms for the relatively large slopes. This extension is determined by doping with large radius atom Au into the glass network. Au density changes in glass state are induced by the presence of relatively strong extensions. The density of Au doped samples is less by several percents than in initial compounds. Connecting this difference with the presence of extension fields ("microcavity") one defines that a part of occupied general volume is $(\rho_I - \rho_L)/\rho_I \approx 0.01$ (ρ_I, ρ_L are the density of initial and doped glass semiconductor).

Authors [4] proposed the similar qualitative picture for glass and corresponding crystal semiconductors. Appeared at the edge of such "microcavity" the impurity atom (Au) can not use all its valence electrons to form bonds, as, at least, from one side its nearest neighbour will be at the distance larger than a characteristic length of the valence band. Thus, the doping atom, getting the "microcavity", can form an electrical active impurity level. At the same time the impurity level will be "bonded" to the edge of that band which decreases the E_g. Both formation of level and increase of E_g are determinated by the bonds of doping atom with matrix atoms. In the first case a role is played by a small quantity of doping, getting the “microcavity”. In the second case is impossible to have a mass of doping atoms going into the volume and saturating all the valence bonds. In work [5] it is discussed the different type of embedding of doping atoms at getting the CGS. The decrease of density in weakly doped glass leads to the decrease of the conductivity at the beginning. The increase of the glass density, that, consequently, increases the conductivity, is probably connected with further increase of impurity concentration (Fig. 3). Fig. 3 represents the dependences of conductivity upon a glass composition x in $(As_2S_3)_{100-x}Au_x$ for different temperatures. Similar dependences are observed for glasses $(As_2S_5)_{100-x}Au_x$. It should be noted that in glass semiconductor $(As_2S_3)_{99.99999}Au_{0.00001}$ the conductivity is less than in the initial As_2S_3.

In our last paper [8] we have shown that gold impurity is electrically active, i.e. promote the formation of the impurity level, that allows to observe the impurity conduction.

5. Conclusions

For Au impurity dissolved in glass, the Mossbauer spectrum looks like a quadrupole doublet with the following parameters: isomeric shift $\delta = (1.20 \pm 0.10)$ mm/s, and quadrupole splitting $\Delta = (4.45 \pm 0.15)$ mm/s. The binary compounds of gold with arsenic (AuAs) and sulphur (Au_2S_3, AuS and Au_2S) have been synthesized by the fusion method, but the Mössbauer spectra of these alloys corresponded to the metallic gold. Thus, gold in the given conditions of glass synthesis does not form binary compounds with arsenic and sulphur and we propose that the Mössbauer spectra of ^{197}Au impurity atoms in glassy Au_2S_3 correspond to complicated compound of gold and glass components. It should be noted that crystallization of Au-doped glasses is accompanied by the phase separation of metallic gold, so this compound remains stable only within the structural network of the glass and can not be synthesized as a standalone crystal modification. An analysis of the Mössbauer spectra of ^{197}Au impurity atoms in glassy Au_2S_3 showed that gold is trivalent in glass (Au-III), with the electron configuration of Au atoms $5d^8(5d6Sp^2)^{1.88}$ and effective charge Z=+1.12 e [6]. The effective charge of Au atom can be also derived from the shift of binding energy in Au electron spectra. The electron spectrum of Au in Au_2Se_3 glassy semiconductor consists in a single line corresponding to the binding energy of $4f_{7/2}$ electrons E=(84.16±0.07) eV, that is 0.68 eV higher than the binding energy of $4f_{7/2}$ electrons in the metallic gold and corresponds to the effective charge of Au atoms in glass Z=1.07 e. This value is in a good agreement with the value of Z=1.12 e, obtained from Mössbauer spectra study. Monolayers of Au nanoparticles with 5 nm diameter were deposited recently on a substrate in the form of thin carbon membrane. Au crystals form hexagonal lattice. Au nanocrystals are electrically and mechanically shared with organic molecules [7]. This ensures the structural integrity of the whole monolayer and provides the controlled tunnel barrier for electron transfer between the particles. Such a carbonic monolayer appears on the water surface and can be transferred, with its structure preservation, onto various flat solid substrates. The best solution of the important task to establish electric connection between the ultra small devices would be that if it could be possible to transfer not the whole layer but its separate parts in the form of thin strips. In our case (B-effect) it is possible that the glass matrix acts like a wire between Au nanoparticles. In the 360>T>310 K temperature range, the metallic conductivity between the nanoparticles is probably prevailing.

Acknowledgement

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References

[1] B. T. Kolomiets, T. F. Nazarova, Solid State Physics, Nauka, Moscow (1959).
[2] B. T. Kolomiets, Proc. 6-th Intern. Conf. Amorph. And Liq. Semic., Leningrad, 1975, p. 23.
[3] B. T. Kolomiets, Phys. St. Sol. **7,** 359 (1964).
[4] B. L. Gelmont, K. D. Tsendin, Fiz. Tekhn. Poluprov., **17,** 1040 (1983).
[5] M. Kastner, Phil. Mag. B. **37,** 127 (1978).
[6] I. V. Nistiruk, P.V. Nistiruk, F.S. Nasredinov, P.P. Seregin, Proc. Conf. “Amorphous Semiconductors-80”, Kishinev, 1980, p. 205.
[7] Nanotechnology Research girections, IWGN Workshop Report, Kluwer Academic publishers Dordrecht, Boston, London (2002).
[8] A. A. Babaev, I. K. Kamilov, S. B. Sultanov, A. M. Askhabov, P. P. Khokhlacev, J. Optoelectron. Adv. Mater. **5**(5), 1237 (2003).