

PHOTOLUMINESCENCE AND CONDUCTIVITY OF As_2S_3 AND As_2S_5 GLASSES WITH SMALL GOLD ADDITIONS

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The photoluminescence (PL) spectra and the excitations of glassy semiconductors of stoichiometric and nonstoichiometric compounds $(\text{As}_2\text{S}_3)_{100-x}\text{Au}_x$, $(\text{As}_2\text{S}_5)_{100-x}\text{Au}_x$ ($0 \leq x \leq 0.04$) at $T=77$ K are studied for the first time. The PL spectrum in the glasses of nonstoichiometric compound with small gold additions splits in two bands one of which being responsible for gold. The experimental results for temperature dependence of the glass conductivity of $(\text{As}_2\text{S}_3)_{1-x}\text{Au}_x$ and $(\text{As}_2\text{S}_5)_{1-x}\text{Au}_x$ ($0.04 \geq x \geq 0$) are presented for the first time. There are found: two fractures on the temperature dependence of the conductivity in compounds with small gold concentration, and an abnormal behaviour of the conductivity in the temperature range $300 \text{ K} < T < 360 \text{ K}$. The major part of the impurity atoms enters into the volume of the glass semiconductor, saturates all its valence bonds by forming a series of solid solutions and this leads to a change of band gap E_g . A small part of impurity atoms, having an unusual closest neighbourhood, do not saturate the valence bonds, and, as a result, forms an electrical active impurity level that defines 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 affect weakly (if at all) the physical properties of chalcogenide glasses (CGS). The impurities are optically and electrically inactive; i.e., they do not form 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 lower than in a crystal, does not depend upon the impurity concentration, the characteristic fracture in the $\sigma(T)$ curve, corresponding to a transition from the intrinsic conductivity to the impurity conductivity, vanishes on the temperature dependence of the CGS.

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 a possibility of the doping atom to use all its valence electrons for creation of bonds with neighbours in the disordered structure. Nevertheless, donor or acceptor character of the impurity was not revealed in the glassy state. The influence of metal impurities upon

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the physical properties of CGS was studied on the glasses of stoichiometric compounds, which exhibits good crystallization ability (except for several ones). Such an anomaly in the behavior of impurities introduced into CGS was considered as their distinctive feature. However, there are facts that are indicative of the influence of impurity on the physical properties of CGS. It was demonstrated that some impurities, for example, Cu and Ag, substantially change the conductivity, and this is caused by a decrease in the band gap E_g of a newly formed compound. The number of studies devoted to the investigation of impurity behavior in CGS continuously increased [8,9]. However, photoluminescence (PL) in CGS and corresponding crystalline analogs was found in [10]. This finding made it possible to perform a series of investigations aimed at revealing the influence of various impurities on PL properties. These investigations showed that doping CGS with various impurities, as a rule, does not lead to the formation of new emission bands within a wide range of energies and temperatures. The centers that are responsible for the radiative recombination with $E \approx E_g/2$ in CGS are intrinsic defects with a negative correlation energy ($-U$). A new band peaked at 0.81 eV was found in the PL spectra of $(\text{GeS}_3)_{100-x}\text{Bi}_x$ glasses, whereas no new emission bands were found in the PL spectra of $(\text{As}_2\text{S}_3)_{100-x}\text{Bi}_x$ glasses [11]. The new band was observed, also, in the PL spectra of powder samples of the same composition [12]. Several studies [11,12] were aimed at revealing the specific features of the influence of Bi impurity on the PL properties of glasses with a tetrahedral and chain-layer structure. It should be noted that the corresponding analogs of CGS are GeS_2 and As_2S_3 crystals, whereas the GeS_3 glass is nonstoichiometric. Despite this fact, the fundamental questions concerning the search for impurities that would make it possible to effectively control the physical properties of CGS remain unresolved, and the anomalous behavior of most impurities in glasses has not been explained 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 study of the influence of low concentration of gold impurity upon PL properties and electroconductivity of CGS stoichiometric and nonstoichiometric compounds, and the revealing of their features is the aim of this work. The stoichiometric $(\text{As}_2\text{S}_3)_{1-x}\text{Au}_x$ and nonstoichiometric $(\text{As}_2\text{S}_5)_{1-x}\text{Au}_x$, where $0.1 > x \geq 0$, are chosen for this study.

3. Experiment and method

Undoped and Au-doped glasses were synthesized by direct alloying of corresponding amounts of elemental As and S with Au of 99.99999% purity in evacuated quartz cells using vibrational stirring of the melt. To prevent explosion of cells, synthesis was carried out in two stages. In the first stage, cells were heated. The ampoules were heated in a tubular furnace 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 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 by a Neofot microscope served as criteria for the vitreous state of the materials.

Steady-state luminescence was excited by a DKSL xenon lamp with a power of 1000 W. The PL and PL-excitation spectra were investigated at $T = 77$ K. To exclude possible distortion of emission spectra due to self-absorption, the emission was detected from the illuminated side of the sample. Silicon and germanium photodiodes were used as photodetectors. The PL-excitation spectra were recorded in the vicinity of the peak of the PL spectrum, whereas the PL spectra were recorded using excitation by quanta with energies corresponding to the peak of the PL-excitation spectrum. Since the "fatigue effect" of PL was observed in the glasses under investigation, the spectra were measured after the establishment of quasi-steady state of emission, i. e. when fatigue effect could be disregarded during spectra recording. The electroconductivity of the samples was measured by a method of clamping contacts. The plane-parallel samples of thickness $d = 0.85 \pm 2$ mm were clamped between two soft graphitic pivots of size $\varnothing 10$ mm, squeezed into the copper blocks. The resistance of a pivot together with copper blocks is 0.2 ohms. The current leakage is reduced to zero.

The investigation of the PL in the glasses of two systems showed that the PL spectrum in specially undoped glasses is represented by a wide band with maximum $E_{PL} \approx E_g/2$ responsible for the intrinsic defects with negative correlation energy. A single peak is observed in the exponential portion of the self-absorption edge of the PL spectrum of glass which corresponds to the value of absorption coefficient $\alpha \approx 10^2 \text{ cm}^{-1}$. The PL and PL-excitation spectra of undoped and doped glasses are shown in Figs. 1 and 2. An increase in the impurity content in stoichiometric glass with $x > 0$ leads simultaneously to the shift of the peak of the main emission band at $E = E_g/2$ to lower energies and to a decrease in intensity. The introduction of small amounts of impurity into the nonstoichiometric glass leads to the emergence of a new emission band. For nonstoichiometric glasses, splitting of the PL spectrum results in the appearance of peaks at $E_{pl1} = 1.26 \text{ eV}$ and $E_{pl2} = 0.95 \text{ eV}$ with the half-maximum $\delta \approx 0.1 \text{ eV}$ observed at $x = 0.01$. The peaks of the emission bands E_{pl1} and E_{pl2} in the PL-excitation spectra correspond to $E_{ex1} = 2.4 \text{ eV}$ and $E_{ex2} = 2.1 \text{ eV}$, respectively. Note that (1) the peaks of the main emission band in the PL and PL-excitation spectra shift to lower energies with increasing impurity content ($x > 0$), (2) the peaks in the PL and PL-excitation spectra at E_{pl1} and E_{pl2} undergo no substantial changes, and (3) a single broad band of emission and excitation of luminescence is observed for glasses $(\text{As}_2\text{S}_5)_{1-x}\text{Au}_x$ with $x > 0.04$.

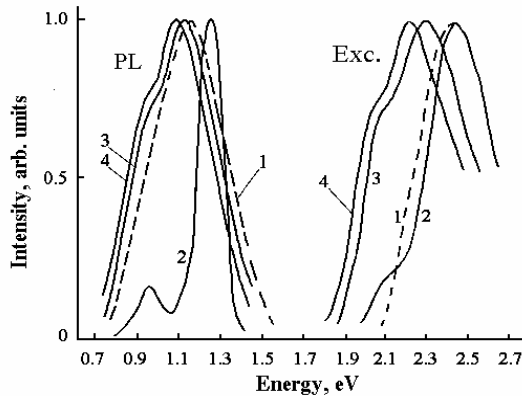


Fig. 1. Photoluminescence (PL) spectra and PL-excitation (Exc) spectra of $(\text{As}_2\text{S}_5)_{1-x}\text{Au}_x$ glasses at $T=77 \text{ K}$. x : (1) 0, (2) 0.01, (3) 0.02, (4) 0.04.

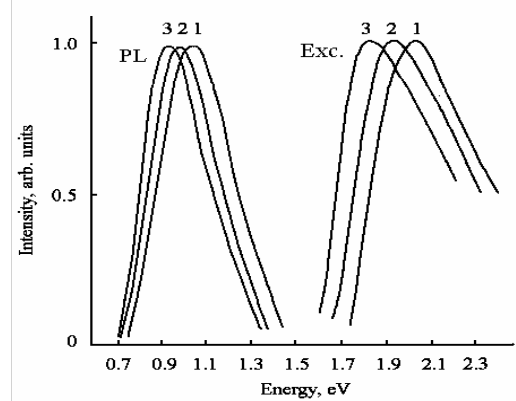


Fig. 2. Photoluminescence (PL) spectra and PL-excitation (Exc) spectra of $(\text{As}_2\text{S}_3)_{1-x}\text{Au}_x$ glasses at $T=77 \text{ K}$. x : (1) 0, (2) 0.01, (3) 0.04.

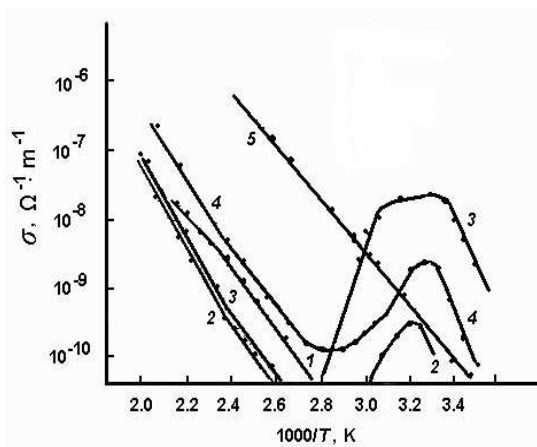


Fig. 3. Temperature dependence of the electrical conductivity on the constant current of glasses $(\text{As}_2\text{S}_3)_{1-x}\text{Au}_x$: values x (at %) 1 - 0; 2 - 0.00001; 3 - 0.0001; 4 - 0.01; 5 - 0.02.

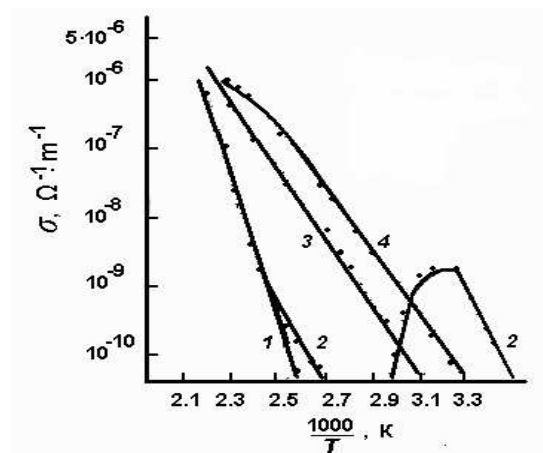


Fig. 4. Temperature dependence of the electrical conductivity on the constant current of glasses $(\text{As}_2\text{S}_5)_{1-x}\text{Au}_x$: values x (at %) 1 - 0 and 0.00001; 2 - 0.0001; 3 - 0.02; 4 - 0.04.

The experimental results for temperature dependences of the glass conductivity in the system studied in this paper are represented in Figs. 3 and 4. The electroconductivity of As_2S_3 and As_2S_5 is described by the expression $\sigma = \sigma_0 \exp(-E_a/kT)$ with the activation energy, E_a . Glasses containing gold ($x=0.00001$ at% and higher) shows curve fractures and two activation energies. When doping by 0.01 at% 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 undoped and doped by 0.02 at% gold the electroconductivity is described with one activation energy. In the temperature range $360 > T > 300$ K the electroconductivity appreciably increases with the increase of temperature, reaches a maximum and then sharply decreases to minimum values by several orders below $10^{-11} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$. 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 the vanishing of the conductivity in the range $360 > T > 300$ K. The conductivities observed exhibit two activation energies.

4. Discussion

If Au doping of small concentration forms electric active centers, a question appears: is Au able to create optically active centers? Let us describe a picture of formation and properties for the second slope in the temperature dependence of the conductivity.

In disordered structure the distance between atoms changes randomly. Weak fluctuations of interatom distances are feasible equally in compression and extension. At the same time a strong extension is possible owing to a strong increase of repulsion between atoms for the relatively large slopes. This extension is determined by the introduction of large atomic radius Au into the glass network. The density changes induced by Au in glass are due to the presence of relatively strong extensions. The density of Au doped samples is less by several per cent than that of the 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). The authors [13] proposed the similar qualitative picture for glass and corresponding crystal semiconductors. Appearing 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 the characteristic length of the valence band. Thus, the doping atom, getting the "microcavity" can form an electric active impurity level. The impurity level will be "bound" to the edge of that band, and this will decrease the E_g . It occurs because both formation of level and increase of E_g are given by the bonds of doping atom with matrix atoms. In the first case the role is played by a small quantity of doping atoms, getting the "microcavity", in the second case it is impossible that the main mass of doping atoms goes into the volume and saturates all its valence bonds. In the paper [14] are discussed different types of embedding of doping atoms at getting the CGS.

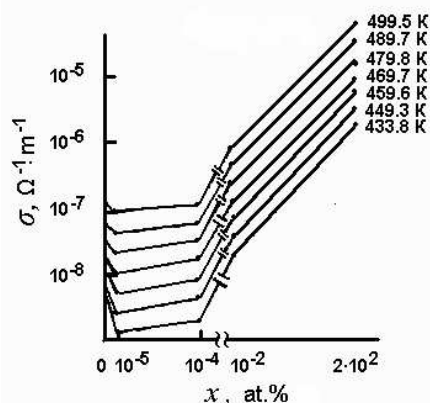


Fig. 5. Dependence of the electrical conductivity on the constant current of glasses $(\text{As}_2\text{S}_3)_{1-x}\text{Au}_x$ at different temperatures.

5. Conclusions

We suppose that donor- and acceptor-like impurities nucleate in doped glasses by pair. Obviously, such pairs consist of the ion Au⁺ (a donor) and charged interrupted D⁻, which are on different edges of one “microcavity”. The studied pairs do not undergo the annihilation at low impurity concentration, as a disappearance of “microcavity” requires a simultaneous movement of a large number of atoms that probably occurs at large concentrations, and the observation of the temperature dependence of the conductivity with one activation energy. Therefore, the main part of atoms, that forms the glass matrix, saturate all their valence bonds. The atoms are electrically passive and lead to the decrease of the forbidden band by forming a series of solid solutions. The remaining number of impurities that makes the “microcavity” do not saturates all its valence bonds. The impurities are electrically active, i.e. promote the formation of the impurity level, that allows to observe the impurity conductivity. As the impurity conductivity and a reduction of the forbidden band occurred on account of the same atoms, differ only in the nearest surroundings, the level should be attached to those permitted bands owing to which the E_g decreases. For the final confirmation of the presence of the impurity conductivity in the glasses with Au doping it is necessary to measure the optical width of the forbidden gap. A difference between measured optical width of the forbidden gap (E_g) and activation energy of the conductivity should be constant, which must testify about the formation of the impurity level hardly attached the edge of a permitted band.

Acknowledgement

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