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RADIATION-INDUCED DEFECTS FORMATION IN Bi-CONTAINING VITREOUS CHALCOGENIDES

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Processes of formation and annihilation of coordination defects in $As_2Se_3Bi_y$ and $(As_2Se_3)_{1-x}(Bi_2Se_3)_x$ amorphous chalcogenide semiconductors induced by influence of Co^{60} gamma-irradiation (exposure dose rate - over 20 Gy/s, average energy of gamma-flow - 1.25 MeV, exposure doses range for all samples - from 10^5 to 10^7 Gy) are investigated by photoelectric spectroscopy method. It is obtained that radiation-induced changes of photoelectrical properties on bioconcentration of $As_2Se_3Bi_y$ glasses are characterized by anomalous concentration dependence. The nature of this effect is associated with diamagnetic coordination defects formation.

1. INTRODUCTION

The influence of ionizing radiation on physical properties of binary amorphous chalcogenide semiconductors (AChS) such as arsenic trisulphide and triselenide has been studied sufficiently well [1]. However, the analogous radiation induced processes (RIP) in ternary AChS containing heavy-weight metals (thallium, indium, antimony, bismuth etc.) have not been studied yet in details, while in scientific papers [2-7] a new field of solid state physics - the radiation physics of glasses - has been mentioned. At the same time, it has been established in some papers [8-10] that small additions of the above mentioned heavy metals in the arsenic-contained chalcogenides lead to the formation of extraordinary anomalous concentration dependences of their physical properties. We suppose that RIP in such AChS systems will also have the anomalous character.

Our consideration of the RIP in bismuth-containing AChS of the invesigated systems will be based on the coordination defects conception successfully used previously for explanation of photo-, gamma-, and electron-induced effects in the AChS binary systems [1,3,11]. These defects represent themselves as the pairs of over- and undercoordinated atoms in structural host having positive and negative

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electrical charge, respectively [12]. The both defects appear commonly keeping in this way the sample electroneutrality. Their electrical charge state is designated by superscript (plus or minus) and quantity of nearest neighbour atoms with covalent bonds - by subscript. Thus, as it is shown in [13], the known photoconductivity quenching effect in As_2S_3 thin films is determined by four defect pairs: (P_2^-; C_3^+), (P_4^+; C_1^-), (P_2^-; P_4^+) and C_1^-; C_3^+). The process of coordination defects formation takes place due to covalent bonds switching, in other words destruction and polymerization transformations without changing of the average covalent bonding of the amorphous matrix. The statistically possible topological variants of these processes have been presented in several papers [5, 14].

2. EXPERIMENTAL

The parallel plane samples of the $As_2Se_3Bi_y$ as well as $(As_2Se_3)_{1-x}(Bi_2Se_3)_x$ AChS systems (with 0.1 - 0.2 mm thickness) prepared from monolithic ingots, obtained by direct melting in evacuated quartz ampoules, were investigated. Two types of the samples were used for investigations: the samples annealed at the 20-30 K below of softening temperature with the aim of homogenization and elimination of internal stresses appeared during the quenching and non-annealed ones. Amorphism of obtained ingots was determined by typical fracture and absence of inhomogeneity using IR microscope observations and X-ray phase analysis. More detail information concerning samples preparation has been described in our previous papers [1,3.6].

The investigated samples were irradiated by gamma-quanta of Co^{60} source at the power of exposure dose over 20 Gy/s (Gray (Gy) - unit of absorbed ionizing radiation dose). The average energy of gamma-flow was 1.25 MeV and the maximum samples heating at the conditions of continuous irradiation does not exceed 370-380 K.

The spectral dependences of photoconductivity were investigated by traditional method at direct current [15].

3. RESULTS AND DISCUSSION

The investigation of photoelectric properties of bismuth-containing AChS based on arsenic triselenide irradiated by gamma-quanta from Co^{60} source gives the possibility to obtain direct confirmations on existing of some defect centers important in RIP.

The position of the basic photocurrent maximum for the both investigated AChS systems doesn't change after gamma-irradiation (Fig. 1-3).

It is established that the steady-state value of photocurrent in the non-annealed $(As_2Se_3)_{1-x}(Bi_2Se_3)_x$ glasses decreases with increase of the absorbed dose D up to $(3\text{-}5)\cdot 10^6$ Gy (Fig. 1b). This process is accompanied by the broadening of additional

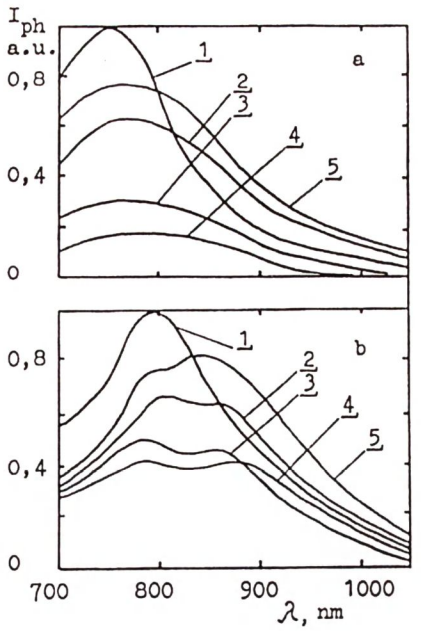

Fig. 1. Spectral dependences of photocurrent of non-annealed glassy As_2Se_3 (a) and $(As_2Se_3)_{0.80}(Bi_2Se_3)_{0.20}$ (b) samples before (curve 1) and after gamma -irradiation with doses of $5 \cdot 10^5$ (curve 2), 10^6 (curve 3), $5 \cdot 10^6$ (curve 4) and 10^7 Gy (curve 5).

band of the photocurrent in longer wavelength region of the spectrum.

The following rise of irradiation dose (up to more than $5 \cdot 10^6$ Gy) causes the increase of photocurrent. As the result the additional maximum of photoconductivity for the samples gamma-irradiated at the dose of 10^7 Gy exceeds considerably the basic maximum situated at 750 nm. The same complicated character of the dose dependences of microhardness and optical properties was observed in these gamma-irradiated glasses previously [16]. We suppose that this complicated behavior of the investigated dose dependences is connected sufficiently with the non-annealed samples inhomogeneity. The processes of coordination defects formation at the boundaries of inhomogeneous fragments are dominant at the low absorbed doses of gamma-radiation (up to $5 \cdot 10^6$ Gy), while at higher doses these fragments disappear due to additional accompanied annealing of the samples in source cavity (up to 370-380 K).

The gamma-irradiation of the annealed chalcogenide glasses of $(As_2Se_3)_{1-x}(Bi_2Se_3)_x$ system causes the increase of the steady-state photocurrent value. This effect is the most evident in arsenic triselenide, *i.e.* in the investigated AChS without Bi content. Therefore we conclude that thermal annealing of the pseudobinary glasses is the necessary condition for appearance of donor-acceptor properties of the heavy metal additions, i.e. ability to decrease the radiation influence on the AChS physical properties. Deviations from this rule are possible only in the $(As_2Se_3)_{1-x}(Bi_2Se_3)_x$ glasses with large Bi content irradiated at the high doses of gamma-quanta (near 10^7 Gy), when the additional weak bend at 800-850 nm corresponding to sufficient coordination defects concentration appears (Fig. 2, curve 5).

The anomalous character of the radiation-stimulated changes of photoelectric properties is expressed more sharply in the ternary AChS of $As_2Se_3Bi_y$ system.

The increasing of the steady state photocurrent may be observed already after gamma-irradiation of $As_2Se_3Bi_{0.005}$ non-annealed glass by the dose of 10^6 Gy (Fig. 3). Comparing the obtained photocurrent spectra before and after irradiation for all investigated samples, we may come to some conclusions on the features of radiation-stimulated changes of photocurrent in this system.

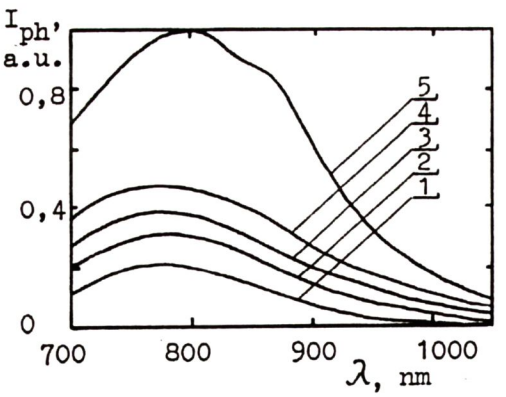

Fig. 2. Spectral dependences of photocurrent of annealed glassy $(As_2Se_3)_{0.90}(Bi_2Se_3)_{0.10}$ samples before (curve 1) and after gamma-irradiation with the doses of $5 \cdot 10^5$ (curve 2), 10^6 (curve 3), $5 \cdot 10^6$ (curve 4) and 10^7 Gy (curve 5).

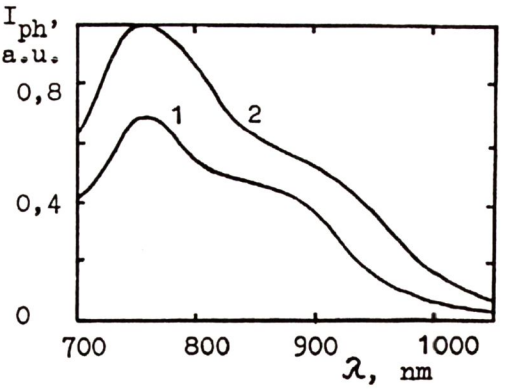

Fig. 3. Spectral dependences of photocurrent of non-annealed glassy $As_2Se_3Bi_{0.005}$ samples before (curve 1) and after gamma-irradiation with the dose of 10^6 Gt (curve 2).

At small Bi concentrations ($y \approx 0.0005$) the gamma-irradiation stimulates the appearing of the additional photocurrent maximum at the $h\nu$ = 1.4-1.5 eV (λ = 830-880 nm) as in the case of As_2Se_3 (Fig. 1a). This energy corresponds to the level depth of positive defect centers playing the most significant role in the steady-state photocurrent forming. In the range of $0.0025 \leq y \leq 0.025$ the value of additional maximum doesn't change essentially with irradiation (Fig. 3), while some tendency to its decreasing takes place. The radiation-stimulated broadening of the investigated spectral characteristics is observed. It must be noted that the small radiation-induced shift of the basic photocurrent maximum (near 10 nm) to the longer wavelength region is revealed in the $As_2Se_3Bi_{0.2}$ glasses characterized by slight liquation processes.

Hence, we conclude, taking into account obtained experimental data, that radiation-stimulated changes of photoelectric properties of bismuth-containing ternary AChS are caused by superposition of several processes connected with not only coordination defects formation, but also radiation annealing. Each of these processes is predominant in certain concentration range and conditions of gamma-irradiation.

We mark out three different concentration ranges of the $As_2Se_3Bi_y$ investigated system at the discussion.

$0 \leq y \leq 0.002$ region. "Clear" radiation defects formation, *i.e.* increasing of defects concentration (Se_3^+ mainly) due to chemical bonds breaking is observed in this region. It may be assumed that at small Bi concentrations the radiation-stimulated transformations of glass structure are carried out near the native defect centers. The latter, commonly with newly appeared defects based on the radiation-destroyed bonds, play an important role in the process of RIP. At the end of this concentration range the additional process of defects annihilation takes place due to donor-acceptor properties of Bi atoms [17].

$0.002 \leq y \leq 0.006$ region. The influence of the additional annealing during radiation treatment of the samples in the Co^{60} source cavity is sufficient in this region. The thermoradiation effects must be considered as the united process of destruction-polymerization transformations which are characterized, from the one side, by the change of distribution between homo- and heteropolar bonds of the glass host, and, from the other side, by the appearing of the new coordination defects and recharging of the existing ones. Radiation heating assists to uniformity of Bi atoms distribution in glassy-like matrix of arsenic triselenide (radiation-stimulated homogenization). Therefore the more effective "healing" of defect centers occurs in this conditions.

$y > 0.006$ region. The decreasing of RIP in this region is explained by local annihilation of coordination defects. This process intensifies at the presence of intermediate links which have effective donor-acceptor properties. Such properties are typical of Bi atoms which promote structural transformations of polymer matrix to the metastable state with normal atomic coordination (double one for Se and triple one for As).

Now, we shall consider shortly the possible mechanism of the above described radiation-stimulated transformations at the microscopic level. Taking into account the established fact of the absence of ESR signal, corresponding to bismuth-containing centers in investigated glasses, we suppose that diamagnetic defects of undercoordination of arsenic (As_2^-) and overcoordination of selenium (Se_3^+) play the main role in the processes of radiation-stimulated defects formation. The creation of such defect pair under the influence of penetrating radiation may be presented as:

$$As_3^0 + Se_2^0 \rightarrow As_2^- + Se_3^+ \tag{1}$$

At the presence of Bi atoms ($y > 0.006$) the balance of (1) equation may reverse. Initially tricoordinated Se atom interacts with As_2^- defect and, being with respect to the last the acceptor of lone-pair of electrons, promotes the transformation $As_2^- \rightarrow As_3^0$:

$$As_2^- + Bi_3^0 \rightarrow As_3^0 + Bi_2^- \tag{2}$$

The defect Bi_2^- is unstable and transforms easy into Bi_3^0 passing the lone-pair of electrons to Se_3^+ center:

$$Se_3^+ + Bi_2^- \rightarrow Se_2^0 + Bi_3^0 \tag{3}$$

As a result both As_2^- and Se_3^+ defects annihilate. Thus, our experimental results show that coordination defects formation processes stimulated by high-energy radiation treatment play an important role in the stabilization of new AChS metastable state with well defined physical properties. As it was obtained previously the same results concern also thin films of investigated ternary system prepared by thermal evaporation [18].

Moreover, on the base of strong correlation between photoelectric properties of the investigated samples and absorbed dose of gamma-irradiation, we conclude that

these materials may be used as radiation-sensitive elements of solid state dosimetric systems of high-energy ionizing radiation [19].

4. CONCLUSIONS

We can conclude that RIP in non-annealed AChS of $(As_2Se_3)_{1-x}(Bi_2Se_3)_x$ system are connected with the processes of coordination defects formation occurring at the boundaries of inhomogeneous fragments. The annealing of the pseudobinary glasses is the necessary condition for appearance of donor-acceptor properties of the heavy metal additions, *i.e.* ability to decrease the radiation influence on the AChS physical properties.

In contrary to these results, the processes of both coordination defects formation and annihilation determine the final metastable state of the ternary Bi-containing glasses. The relative weight of these processes depends on the concentration of Bi additions.

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DEFEKTY PORADIACYJNE W BIZMUTOWYCH CHALKOGENIDACH SZKLISTYCH

Streszczenie

Metodą spektroskopii fotoelektrycznej zastosowano do procesu formowania i anihilacji defektów koordynacyjnych w chalkogenidnych półprzewodnikach amorficznych układów $As_2Se_3Bi_y$ i $(As_2Se_3)_{1-x}(Bi_2Se_3)_x$ pod działaniem promieniowania gamma (moc dawki ekspozycyjnej - ponad 20 Gy/sec, średnia energia strumienia promieni gamma - 1.25 MeV, zakres dawek ekspozycyjnych - od 105 do 107 Gy). Ujawniono, że radiacyjno-indukowane zmiany właściwości fotoelektrycznych szkieł układu $As_2Se_3Bi_y$ charakteryzują się anomalną zależnością od koncentracji Bi. Mechanizm tego efektu wiązany jest z procesem generacji diamagnetycznych defektów koordynacyjnych.