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CHEMICAL INTERACTION OF CHALCOGENIDE VITREOUS SEMICONDUCTORS WITH ABSORBED IMPURITIES INDUCED BY γ-IRRADIATION

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The chemical interaction of chalcogenide vitreous semiconductors (ChVS) with absorbed impurities induced by high-energetic (*E*>1 MeV) γ-irradiation has been investigated at the example of vitreous v-As_2S_3. Radiation-induced processes of oxidation, hydrogenization, hydratation, carbonization and hydrocarbonization have been observed in this material after prolonged γ-irradiation and studied using IR spectroscopy (4000-400 cm^{-1}), laser mass-spectroscopy methods and electron microprobe analysis.

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1. Introduction

To date, the problem of chemical interaction of chalcogenide vitreous semiconductors (ChVS) with absorbed impurities induced by external influences becomes more and more important from the practical viewpoint, especially taking into consideration the potential application of ChVS in IR optical devices [1]. So, we have reported the investigation of chemical interaction of ChVS with absorbed impurities induced by high-energetic (*E*>1 MeV) γ-irradiation at the example of vitreous v-As_2S_3 [2].

2. Experimental

The ChVS samples of v-As_2S_3 were prepared by the conventional melt-quenching method [3]. The obtained ingots were air-quenched at the ambient temperature. All samples were annealed additionally at the temperature of 20-30 K below softening point T_g to remove the appeared mechanical strains.

The investigated ChVS samples were irradiated by γ-quanta at the normal conditions of stationary radiation field, created in the closed cylindrical cavity owing to concentrically established ^{60}Co (*E*=1.25 MeV) sources [4]. The maximum temperature in the irradiating camera did not exceed 320-330 K during the whole period of irradiation. The total accumulated dose of γ-irradiation varied in the range of $\Phi=5\div10$ MGy.

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IR spectroscopy ("Specord 75 IR" (4000-400 cm^{-1}) double beam spectrometer), laser mass-spectroscopy (LAMMA-1000 "Leybold-Herraeus" spectrometer) methods and electron microprobe analysis ("CAMEBAX" microanalyser) were used for characterization of radiation-induced impurity processes in ChVS.

3. Results and discussion

The radiation-induced oxidation of v-As_2S_3 is sharply expressed at the absorbed doses of γ-irradiation more than 5 MGy [5]. This conclusion has been proved by experimental results of IR spectroscopy in 4000-400 cm^{-1} region shown in Fig. 1. It is obvious that intensities of all impurity bands associated with oxygen-contained complexes such as molecular As_4O_6 (1340, 1265, 1050 and 785 cm^{-1}) and SO_2 (1150 and 1000 cm^{-1}) increase after γ-irradiation with Φ=10 MGy dose (P=25 Gy/s). This oxidation process is visible as white layer of molecular As_4O_6 at the sample's surface.

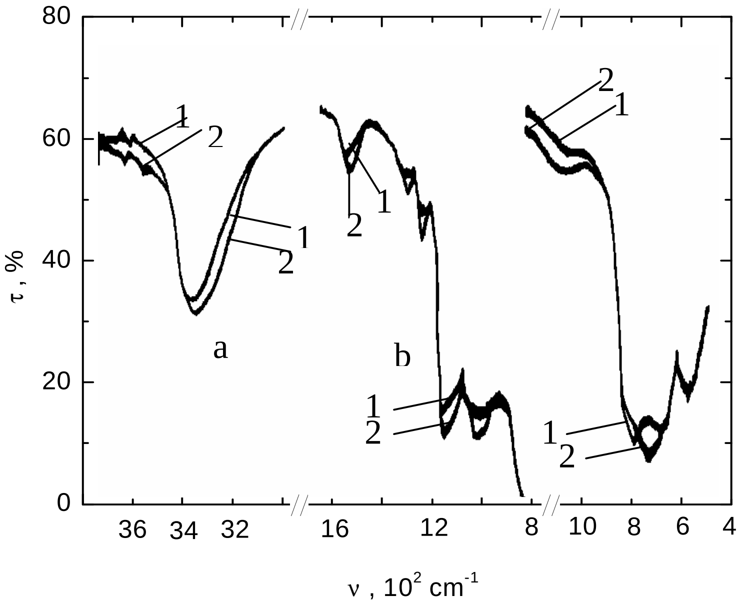

Fig. 1. IR transmission spectra of the v-As_2S_3 before (curve 1) and after (curve 2) γ-irradiation (Φ=10 MGy, P=25 Gy/s) with sample thickness of 12 (a, b) and 1.5 mm (c) [5].

According to the results of electron microprobe analysis, the As:S ratio at the surface of non-irradiated v-As_2S_3 glasses is near 1.56. After γ-irradiation (Φ>5 MGy) this parameter increases in the near-surface layer by ~ 4 %, but it is not changed essentially in the depth of the bulk sample. By grinding of the created oxygen-enriched layer from the surface of the investigated ChVS, we can completely restore the intensities of 1340, 1265, 1050 and 785 cm^{-1} vibrational bands (see Fig. 1) and partially – the intensities of 1125 and 640 cm^{-1} bands, which correspond to =As–O–As= structural groups.

The γ-induced oxidation of v-As_2S_3 is evidently due to the chemical interaction of air-absorbed oxygen with intrinsic structural units, destroyed by a high-energetic γ-irradiation. It is established that this interaction can be sufficiently blocked, when one of the following conditions is fulfilled:

- the investigated v-As_2S_3 samples are placed into evacuated (10^{-1}-10^{-2} Pa) quartz ampoules and then put in ^{60}Co γ-irradiating cavity;
- the total γ-irradiation dose Φ accumulated at the normal conditions of stationary radiation field (without evacuation) does not exceed 1 MGy;
- the dose power P of γ-irradiation (without evacuation) is less than 5-10 Gy/s.

The first condition limits an additional source of oxygen access needed for radiation-induced oxidation, while the next two concern the necessary technical parameters correspondent to molecular As_4O_6 formation.

At the microstructural level of v-As_2S_3, the process of radiation-induced oxidation can be divided into three subsequent elementary stages. Firstly, the metallic arsenic recovers from paramagnetic =As· states by joining some radiolysis products of absorbed moisture (atomic hydrogen, hydrostatic electrons, etc.). Owing to a high pressure of gas phase, this metallic As is extracted from the sample interior onto its surface during the second stage. Then the direct chemical interaction with atmospheric oxygen produces the observable As_4O_6 layer on the surface. So the oxidation process should be enhanced by accompanied thermal annealing during γ-irradiation of v-As_2S_3 samples with high absorbed doses and dose powers, or, alternatively, by additional thermal annealing at the temperatures near T_g performed just after radiation treatment.

The air-absorbed oxygen can be implanted in a glassy-like network through a simple substitution reaction in bridge =As–S–As= structural fragments. This reaction is quite possible as in the sample interior as on its surface. However, the surface-laid =As–O–As= complexes possess an additional ability to chemical interactions and, consequently, can be easily transformed into the molecular As_4O_6 ones.

The similar considerations are proper to the processes of SO_2 formation in γ-irradiated v-As_2S_3.

The *radiation-induced hydrogenization* is a process of chemical interaction of atomic hydrogen (created owing to radiolysis of absorbed moisture and air) with destructed intrinsic complexes. The hydrogen atoms easily join the dangling bonds, created in ChVS by γ-irradiation, leading to their saturation. The molecular H_2S is the main product of hydrogenization. Its appearance in γ-irradiated v-As_2S_3 is clearly evident from the increase in IR spectra (Fig. 1) of vibrational bands intensity at 2470 cm^{-1}. The same conclusion results from low-temperature ESR measurements: the doublet signal 2-8 with resonance splitting A=502 Gs in Fig. 2 is attributed to the ESR signal of hydrogen atoms [6]. The results of laser mass-spectrometry of γ-irradiated v-As_2S_3 samples (Fig. 3) [7] show an increase of the intensities of positively charged HS^+ (33 amu) and H_2S^+ (34 amu) responses that is an additional confirmation for the process of radiation-induced hydrogenization.

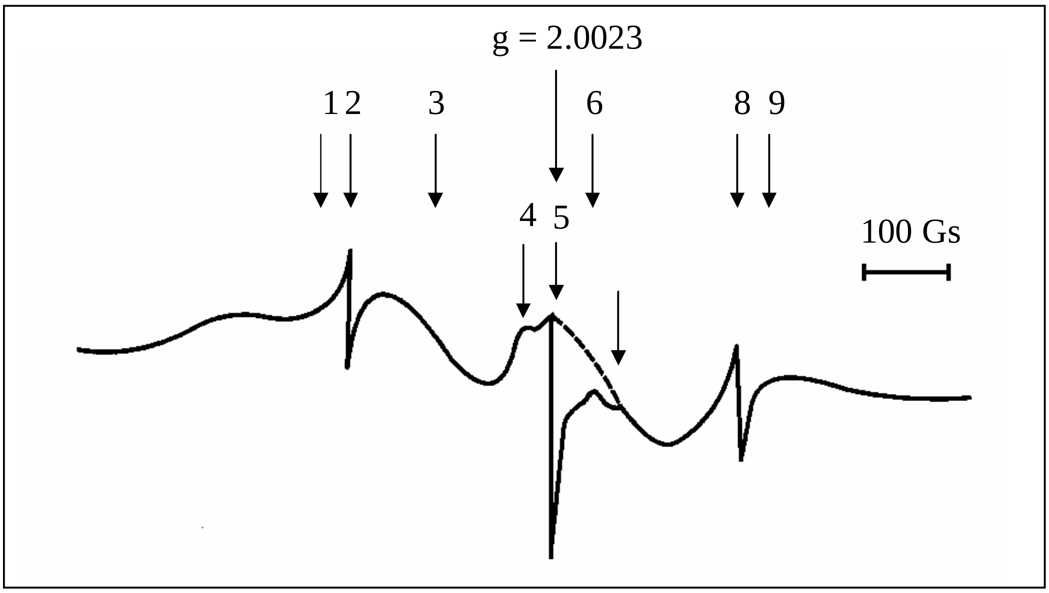

Fig. 2. ESR spectrum of the v-As_2S_3 γ-irradiated with Φ=0.5 MGy dose [6].

The increase of the amount of impurity hydroxide O_nH_m groups linked with intrinsic structural units in γ-irradiated v-As_2S_3 samples is the matter of the irreversible *radiation-induced hydratation* process. In [8] it was firstly pointed out that ^{60}Co γ-irradiation sufficiently affected the spectrum of stretch and bend vibrations of these groups owing to their stronger interaction with radiation-modified glassy-like network. Similar experimental results have been obtained by us [5], but we have put forward their another interpretation, using a more detailed analysis of vibrational OH-group spectrum in ChVS [9]. We believe, in particular, that the 3450 cm^{-1} band in v-As_2S_3 is attributed to =As–OH structural fragments, while the 3420 cm^{-1} band – to –S–OH ones. Therefore, the observed increase in the intensity of 3600-3300 cm^{-1} vibrational band with simultaneous long-wave shift of its maximum (see Fig. 1) testify not only in a favour of radiation-induced absorption of molecular water, but also on its radiolysis with a subsequent joining of the created products to the intrinsic structural units of a glassy-like network. So the =As–OH complexes are dominant among impurity products of radiation-induced hydratation in γ-irradiated v-As_2S_3.

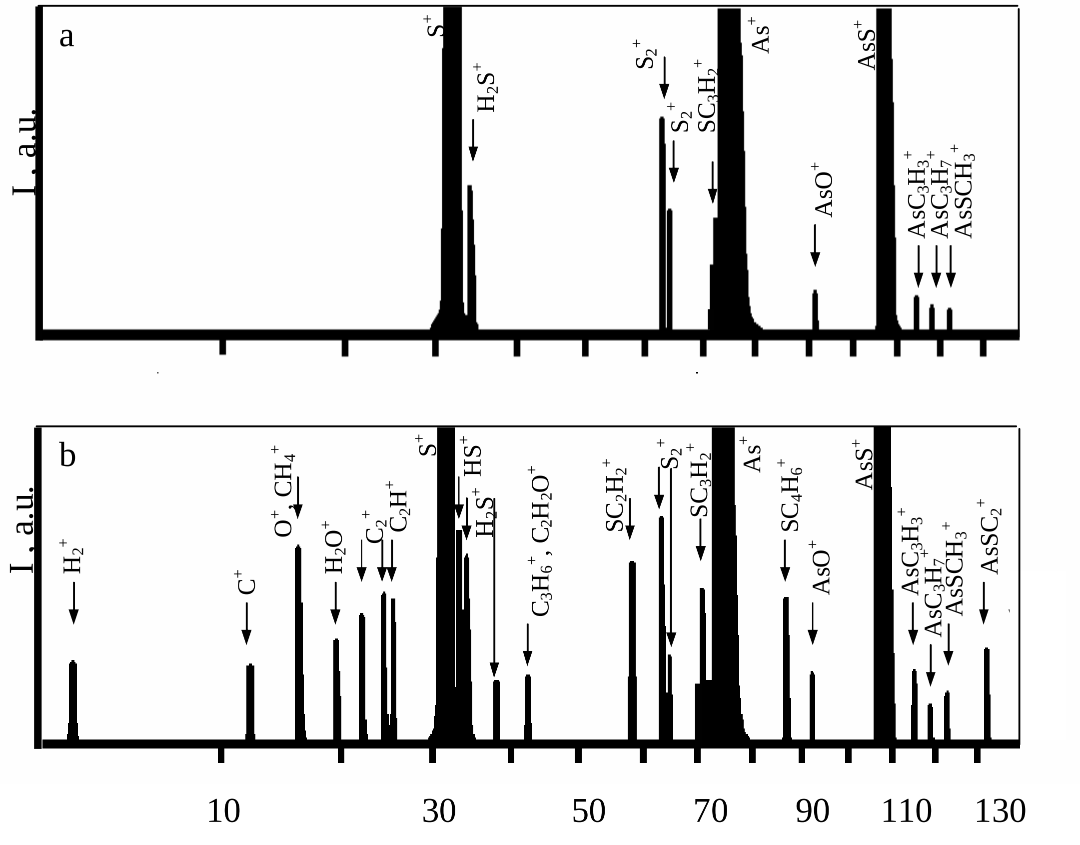

Fig. 3. Fragment of mass-spectrum obtained from the surface of non-irradiated (a) and γ-irradiated (Φ=10.0 MGy, P=25 Gy/s) in the third cycle v-As_2S_3 (b) [7].

If the cycle of radiation-thermal treatment (annealing temperature is near T_g) of ChVSs is performed multiply at high doses of γ-irradiation (Φ~10 MGy) the new kinds of irreversible impurity processes are revealed. The first one is the *radiation-induced carbonization* (chemical interaction of γ-destructed intrinsic structural units with absorbed carbon atoms), and the second one - the *radiation-induced hydrocarbonization* (chemical interaction of γ-destructed intrinsic structural units with absorbed hydrocarbon C_nH_m groups). Their main products in γ-irradiated v-As_2S_3 can be identified with mass-spectrometry technique in the form of positively charged C^+ (12 amu), CH_4^+ (16 amu), C_2^+ (24 amu), C_2H^+ (25 amu), $C_3H_6^+$ (42 amu), $SC_2H_2^+$ (58 amu), $SC_3H_2^+$ (70 amu), $SC_4H_6^+$ (86 amu), $AsC_3H_3^+$ (114 amu), $AsC_3H_7^+$ (118 amu), $AsSCH_3^+$ (122 amu), and $AsSC_2^+$ (131 amu).

The ChVS containing organic components were synthesized firstly by D. Hermann et al. [10,11]. It was shown that organic polymeric chains were linked to inorganic ones in the synthesized mixed glasses through bridge arsenic-carbon and sulphur-carbon units, the double-fold and triple-fold chemical bonds being accepted as quite possible ones.

The similar linked fragments (≡C–As=C≡, =As–C≡, S=C=, –S–C≡, etc.) can be formed during multiple cycles of radiation-thermal treatment of ChVS. So these glasses can be conditionally presented by v-As_2S_3-C_nH_m chemical formula.

It is established that the above irreversible γ-induced impurity transformations decay with concentration of chemical elements having a high level of bond saturation (chemical prototype of As – Sb, Bi) in the framework of quasi-binary $As_2S(Se)_3$-$Sb(Bi)_2S(Se)_3$ cross-sections [7].

4. Conclusions

At least five irreversible radiation-induced impurity processes such as radiation-induced oxidation, hydrogenization, hydratation, carbonization and hydrocarbonization can be distinguished in ChVS after prolonged γ-irradiation.

By the example of v-As_2S_3, it has been shown that the radiation-induced oxidation process is revealed through the increase after γ-irradiation of oxygen-containing complexes, such as molecular As_4O_6 and =As–O–As= structural groups. The radiation-induced hydrogenization process is based on the chemical interaction of atomic hydrogen with intrinsic γ-destructed complexes. The increase of molecular H_2S content in γ-irradiated samples should be interpreted as a result of this process. The radiation-induced hydratation process is connected with formation of OH-containing complexes. In the case of v-As_2S_3 the dominant OH-containing impurity products are =As–OH. The radiation-induced carbonization and hydrocarbonization processes are revealed through the chemical interaction of γ-destructed intrinsic structural units with absorbed carbon atoms and hydrocarbon C_nH_m groups.

The above irreversible radiation-induced impurity processes should be taken into consideration from the viewpoint of application of ChVS-based materials in IR optics.

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