Journal of Optoelectronics and Advanced Materials Vol. 3, No. 2, June 2001, p. 329 - 332

RADIATION DEFECTS IN AMORPHOUS As-Ge-S STUDIED BY POSITRON ANNIHILATION TECHNIQUES

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The nature of coordination defects in chalcogenide vitreous semiconductors of As-Ge-S system have been analysed before and after γ-irradiation using the results of positron lifetime measurements. The correlations between the positron lifetime data, the structural features and the chemical compositions of glasses have been established. The identification of negatively charged point defects has been carried out.

(Received May 25, 2001; accepted June 11, 2001)

Keywords: Positron annihilation, Lifetime, Chalcogenide glasses, γ-irradiation, Defects

1. Introduction

A good sensitivity of positron annihilation method to the changes in local structure of solids, to the presence of point defects, inhomogeneities and phase transitions makes it an important source of information, which allows to verify and to complete the results obtained by various experimental techniques. Sometimes, as in the case of chalcogenide vitreous semiconductors (ChVS), it is one of the exclusive experimental methods, which provides us with the qualitative and quantitative characteristics of the defect configuration [1-3]. ChVS are characterized by the presence in glass matrix of the specific oppositely charged diamagnetic D^+–D^- coordination defects (CD) [4], which usually cannot be identified by the traditional techniques for the defects detection (ESR, luminescence, etc.). Such defects lead to the appearance of localized electronic states lying at the edges or inside of the ChVS band gap [5] that determines their main physical properties. The positron annihilation method was used for the investigation of CD nature practically in all of the known binary ChVS systems (As-S, As-Se, Ge-S, Ge-Se, Ge-Te and others) [1-3,6,7]. As a rule, two positron lifetimes were revealed for these ChVS. The first component (short-lived) was normally associated with the free positron annihilation, and the second (long-lived) one was attributed to the positron annihilation on the negatively charged point defects. At the same time, in some glasses the third component (with even greater lifetime) was observed. The last was connected with positronium formation inside of glass "free volume" [6]. Taking into account these results, positron annihilation studies for some elemental amorphous materials (such as Se [1]) as well as the data of other defect-sensitive methods the proper CD were identified for almost all binary ChVS. However, the ternary ChVS systems, which are more complicated from the structural point of view, are studied insufficiently in this context. The features of radiation-induced effects, intensively studied in last years, are determined by D^+–D^- CD formation processes too [8,9]. Fair identification of these defects in ChVS before and after the radiation treatment is an important step to the understanding of the mechanism of induced changes. However, such investigations were not performed up to now.

In this connection, the positron lifetime measurements were performed for "stoichiometric" $(As_2S_3)_y(GeS_2)_{1-y}$ and "non-stoichiometric" $(As_2S_3)_x(Ge_2S_3)_{1-x}$ ChVS systems before and after γ-irradiation. The analysis of possible CD formation processes was carried out taking into account the γ-induced optical changes in the fundamental absorption edge region.

2. Experimental

The bulk samples of stoichiometric (As_2S_3-GeS_2) and non-stoichiometric (As_2S_3-Ge_2S_3) cross-sections of correspondent glass forming region were prepared by the melt quenching method using the

mixture of high purity (99,9999%) Ge, As and S elements. The initial ingredients were sealed in quartz ampoules (10^{-3} Pa) and heated gradually up to 1200 K. The furnace was rocked for 24 hours to obtain the most homogeneous melt. Then the obtained ingots were quenched on air at the ambient temperature. All ampoules were annealed additionally at the temperature of 20-30 K below softening point (T_g) to remove the mechanical strains. The amorphous state of the obtained materials was controlled by character conch-like fracture, data of X-ray diffraction study and IR microscopy. Finally, all ingots were sliced into 1 mm thick disks and polished for precision optical measurements. The ChVS samples were irradiated by γ-quanta at the power of exposure dose of 20 Gy/sec. The radiation treatment was performed in the normal conditions of the stationary radiation field, created in the closed cylindrical cavity owing to the concentrically established ^{60}Co (E=1.25 MeV) sources. The accumulated dose of 2.82 MGy was chosen taking into account previous investigations of radiation-induced effects in binary chalcogenide glasses [8,9]. The optical absorption coefficient α(hν) was calculated from the transmission characteristics τ(hν) (as described elsewhere [10]) measured before and after γ-irradiation using two-beam "Specord M-40" spectrophotometer (200-900 nm). Measurements of positron lifetimes were carried out using an ORTEC spectrometer of the resolution FWHM (full width at half maximum) = 270 ps. ^{22}Na isotope positron source with 0.74 MBq activity was situated between two identical samples, forming a "sandwich" system.

3. Results and discussion

As it is known [11,12] the exponential character of the fundamental absorption edge (or so-called Urbach tail of absorption) is caused by the stochastic electrical fields of charged defect centers. As it was stated above in ChVS the D^+–D^- CD can play the role of such defects. The typical absorption spectra α(hν) at the region of fundamental absorption edge before and after γ-irradiation for the investigated glasses are shown in Fig. 1. It is clearly seen that after radiation treatment with 2.82 MGy dose the edge shifts towards the low energy values for all studied ChVS. This shift is accompanied with the changes in the edge slope and depends on the chemical composition of the sample. According to [13], the edge slope is directly connected with CD concentration. Thus, we can conclude that γ-irradiation leads to the redistribution of defects in investigated ChVS. It was assumed previously [10] that radiation treatment of As-Ge-S glassy system causes the appearance of new D^+–D^- CD, but the quantitative and qualitative description of this process was not carried out.

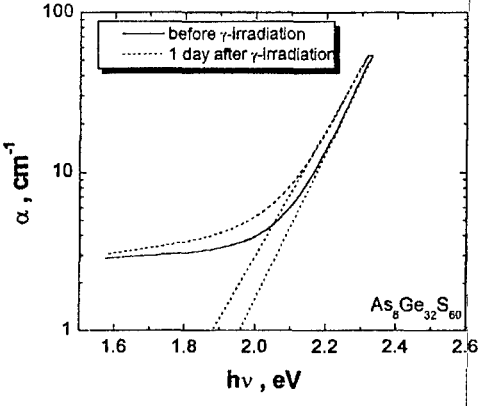

Fig. 1. The typical spectral dependence of absorption coefficient α(hν) before and after γ-irradiation with 2.82 MGy dose for As-Ge-S ChVS system.

Positron annihilation lifetime measurements show that before the γ-irradiation all stoichiometric compositions (data for two of them with the maximal content of As_2S_3 and GeS_2 components are presented in the Table 1) are characterized by the lone mean lifetime of positrons ~0.36 be ns. This usually happens, when the channels of comparable intensities and close lifetimes cannot be resolved by the computer. According to [14,15], the above lifetime value is formed as a superposition of lifetimes corresponded to the free positron annihilation (~0.2 ns), to the annihilation on dangling bonds of Ge_3^- CD (~0.42 ns), of S_1^- CD (~0.32 ns) and of As_2^- CD (~0.37 ns) (the upper index in the defect signature means the electrical charge of atom, and the lower one – the number of nearest covalent-bonded atoms). Because of small concentration of free carriers in most of ChVS (~10^8 cm^{-3} [16]) in comparison to D^+–D^- CD concentration (~10^{16}-10^{19} cm^{-3} [13,16]), the free positron annihilation component should bring a small contribution into the mean lifetime. Therefore, it can be concluded that before the γ-irradiation the amounts of Ge_3^-, S_1^- and

As_2^- CD in stoichiometric ChVS are of the comparable concentration. The changes in optical spectra after the γ-irradiation (Fig. 1) are the evidence of the additional CD formation. The qualitative analysis of measured lifetimes shows the existence of two lifetime components after γ-treatment: short- and long-lived (τ_1 and τ_2, respectively). The first one (τ_1~0.28 ns) seems to be responsible for the annihilation on S_1^- CD. The second lifetime (τ_2~0.39 ns) is attributed to the superposition of the annihilations on dangling bonds of Ge_3^- and As_2^- CD. According to the ratio of short- and long-lived components intensities (see Table 1), it can be concluded that in the case of As_2S_3-enriched compositions the S_1^- γ-induced CD creation is preferred. With the increasing of GeS_2 content in the investigated ChVS the role of Ge_3^- and As_2^- CD in radiation-induced optical effects becomes more essential.

Table 1. Positron lifetime characteristics of the samples from stoichiometric $(As_2S_3)_y(GeS_2)_{1-y}$ ChVS system measured before and after γ-irradiation with 2.82 MGy dose.

Chemical composition	Before γ-irradiation		After γ-irradiation (2.82 MGy)	
	Experimental values	Mean lifetime	Experimental values	Mean lifetime
$As_{28.6}Ge_{9.5}S_{61.9}$ y=0.6	$\tau_1 = 0.3638\pm0.0002$	$\tau = 0.3638\pm0.0002$	$\tau_1 = 0.277\pm0.002$; $I_1=0.67\pm0.01$ $\tau_2 = 0.386\pm0.003$; $I_2=0.33\pm0.01$	$\tau = 0.313\pm0.003$;
$As_{6.25}Ge_{28.125}S_{65.625}$ y=0.1	$\tau_1 = 0.3644\pm0.0004$	$\tau = 0.3644\pm0.0004$	$\tau_1 = 0.282\pm0.009$; $I_1=0.53\pm0.05$ $\tau_2 = 0.397\pm0.010$; $I_2=0.47\pm0.05$	$\tau = 0.336\pm0.010$;

The results of positron lifetimes measurements for two non-stoichiometric ChVS compositions are presented in Table 2. As-enriched glasses are characterized by a lone mean lifetime of positrons (~0.34 ns) before the irradiation. The most probably, this value is a superposition of positron lifetimes connected with the annihilation on dangling bonds of the same CD (S_1^-, Ge_3^- and As_2^-) [14,15] as in the case of stoichiometric samples. The ChVS with greater Ge content are characterized by two lifetimes. The short-lived component (τ_1~0.24 ns) is connected with superposition of positron annihilation on the dangling bonds of S_1^- CD and positron annihilation on the trapping sites formed by the open volume defects such as the As, S or Ge vacancies (~0.25 ns) [17]. Since Ge-enriched samples of non-stoichiometric ChVS system are characterized by an excess of four-fold Ge atoms, we suppose a large number of such vacancies to be formed. The greater open volume, associated with clusters of above vacancies, is also assumed, but it can contribute only into τ_2 (long-lived component of positron lifetimes) according to [17]. Besides it, $\tau_2 \sim 0.39$ ns lifetime component includes the positron annihilation on dangling bonds of Ge_3^- and As_2^- CD [15]. It should be noted, that in the case of stoichiometric samples the contribution into measured lifetime from positron annihilation processes inside of microvoids (vacancies or their clusters) is of less order. The reason is that the stoichiometric ChVS compositions predict the saturation of all chemical bonds due to their main structural units – $AsS_{3/2}$ pyramids and $GeS_{4/2}$ tetrahedra and, as a result, the more compact ChVS structure. In the non-stoichiometric glasses (especially those with high Ge content) the construction of optimal number of such structural units is complicated that favor the formation of open volume defects. Two positron lifetimes were observed after the γ-irradiation of non-stoichiometric ChVS samples. The short-lived component (τ_1~0.27 ns) was connected with positron annihilation on the trapping sites of As, S or Ge atoms and with annihilation on the dangling bonds of S_1^- CD. The long-lived one (τ_2~0.39 ns) was attributed to the positron annihilation processes in the microvoids of a greater volume as well as to the annihilation on dangling bonds of Ge_3^- and As_2^- CD. Owing to the intensities ratio of these lifetime components in the investigated non-stoichiometric ChVS, it can be concluded that the γ-radiation produces the additional number of D^+–D^- defects and favors the microvoids formation.

Table 2. Positron lifetime characteristics of the samples from non-stoichiometric $(As_2S_3)_x(Ge_2S_3)_{1-x}$ ChVS system measured before and after γ-irradiation with 2.82 MGy dose.

Chemical composition	Before γ-irradiation		After γ-irradiation (2.82 MGy)	
	Experimental values	Mean lifetime	Experimental values	Mean lifetime
$As_{16}Ge_{24}S_{60}$ x=0.4	$\tau_1 = 0.3396\pm0.0003$	$\tau = 0.3396\pm0.0003$	$\tau_1 = 0.275\pm0.010$; $I_1=0.55\pm0.06$ $\tau_2 = 0.392\pm0.013$; $I_2=0.45\pm0.06$	$\tau = 0.328\pm0.013$;
$As_8Ge_{32}S_{60}$ x=0.2	$\tau_1 = 0.239\pm0.006$ $I_1=0.43\pm0.02$ $\tau_2 = 0.385\pm0.005$ $I_2=0.57\pm0.02$	$\tau = 0.322\pm0.006$	$\tau_1 = 0.243\pm0.017$; $I_1=0.33\pm0.05$ $\tau_2 = 0.387\pm0.009$; $I_2=0.67\pm0.05$	$\tau = 0.339\pm0.017$;

4. Conclusions

It is established, that γ-irradiation of all investigated samples leads to the low-energetic shift of the fundamental absorption edge. This shift is caused by the additional D^+–D^- defects formation. In the case of stoichiometric $(As_2S_3)_y(GeS_2)_{1-y}$ ChVS compositions, the measured positron lifetimes correspond to the diamagnetic S_1^-, Ge_3^- and As_2^- coordination defects. The additional essential contribution of microvoids into the lifetime characteristics of non-stoichiometric $(As_2S_3)_x(Ge_2S_3)_{1-x}$ ChVS system is assumed.

Acknowledgements

This work was carried out in the framework of Agreement on Scientific-Technical Cooperation between Scientific Research Company "Carat" (Lviv, Ukraine) and Pedagogical University of Czestochowa (Poland), supported by Ukrainian Ministry on Science and Technology and Polish State Committee for Scientific Research. Special thanks to the colleagues from Bulgarian Academy of Sciences and Lutsk State University for samples preparation.

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