SPECTROSCOPY, INTERACTION WITH RADIATION

Positronics of Radiation-Induced Effects in Chalcogenide Glassy Semiconductors

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Abstract—Using As_2S_3 and AsS_2 glasses as an example, the principal possibility of using positron annihilation spectroscopy methods for studying the evolution of the free volume of hollow nanoobjects in chalcogenide glassy semiconductors exposed to radiation is shown. The results obtained by measurements of the positron annihilation lifetime and Doppler broadening of the annihilation line in reverse chronological order are in full agreement with the optical spectroscopy data in the region of the fundamental absorption edge, being adequately described within coordination defect-formation and physical-aging models.

1. INTRODUCTION

Recently, positronics methods, i.e., positronium and positron annihilation spectroscopy (PAS), based on investigation of the physical features of the electron−positron annihilation phenomenon, have been increasingly applied to identify the atomic and electron−defect structure of semiconductor materials [1]. The experimental implementation of PAS in the modes of the positron annihilation lifetime (PAL), the Doppler broadening of the annihilation line (DBAL) with an energy of 0.511 MeV, and the angular distribution of annihilation photons (ADAP) allows the determination of the nature and quantitative characteristics of extended defect states in various materials, independently on the type of their structural ordering [1−4]. Indeed, the effect of the electronic characteristics of defect states, corresponding free volumes, and the type of the immediate structural environment [1−5] are most significant in PAS. This makes PAS methods especially efficient and informative when analyzing induced effects in semiconductors, caused by the effect of various external factors resulting in significant changes in their atomic−defect structure.

The application of PAS methods to the investigation of radiation-induced effects (RIEs) in elemental semiconductors and various III−V and II−VI semiconductor compounds is considered in a number of papers (see, e.g., study [1] and references therein, and reviews by Grafutin et al. [2−4]). Since the mid-1970s, the PAS methods have also been applied to study disordered semiconductors, in particular, chalcogenide glassy semiconductors (CGSs), i.e., promising materials for optoelectronics and IR (infrared) photonics [5]. The PAL methods were applied to study various positron states in the model chalcogenide binary systems As−S and As−Se, including the stoichiometric compositions As_2S_3 and As_2Se_3 in the amorphous and crystalline states [6, 7], Ge−S and Ge−Se [8, 9], and multicomponent systems of mixed arsenic−germanium glasses As−Ge−S, As−Ge−Se, and As−Ge−Te with metal additions [10, 11]. Since the early 2000s, the PAL methodology has also been used to study post-radiation effects in γ-irradiated CGSs, mostly in glassy arsenic trisulfide and triselenide (As_2S_3 and As_2Se_3) and some of their derivatives, i.e., glasses of pseudobinary systems $As_2S_3–Sb_2S_3$, $As_2S_3–GeS_2$, $As_2S_3–Ge_2S_3$, $Sb_2S_3–Ge_2S_3$, and others [5, 12−16]. In particular, it was found that the dynamic behavior of the relaxation of extensive extended radiation defects is also reflected in the similar decay kinetics of the trapping rates of annihilating positrons, and the partial restoration of the spectral position of the optical-absorption edge of irradiated CGSs [15, 16].

We note that the use of the PAS method requires a very careful and rigorous approach when interpreting the experimental results. For example, in [17], using a

combination of PAL and DBAL methods, an attempt was undertaken to study radiation-induced effects in As_2S_3 and $Ge_{15.8}As_{21}S_{63.2}$ CGSs. However, an analysis of the presented results raises some questions, since the authors of [17] did not give proof of the existence of RIEs in the CGSs under study. The stages of the γ-irradiation of glasses with a dose of 2.41 MGy in 2005 [18] and their experimental testing in 2012 [17] are separated by a rather large time interval of more than 7 years which, taking into account intense RIE reduction after radiation exposure (the so-called dynamic component) [19], does not give grounds to expect significant contributions of residual post-radiation effects. Negligible changes in the experimental shape parameters of the annihilation lines S and W in the DBAL method are given in [17] only as errors in mathematical processing of the experimental data ($\sim 0.0001 - 0.0002$ for parameters S and W), but there are no data on errors in measurement reproducibility which, under the experimental conditions, are no less than $\Delta S = \pm 0.0015$, $\Delta W = \pm 0.0005$ [20−22]. Thus, there are reasons to assume that the value of the "recorded" RIEs in [17] is several times smaller than the instrumental error. Comparing the PAL data for γ-irradiated As_2S_3 glasses with the experiment [15], the authors of [17] came to a conclusion regarding the total absence of RIE. In summary, a misconception can arise that CGS radiation defects which are not reflected in experimental PAL spectra with sufficient reliability can cause changes in DBAL parameters S and W, despite complex correct consideration of the background in this method [1, 20].

Certainly, the reliable identification of RIEs in CGSs by PAS methods is possible only in the case of an adequate measuring cycle, i.e., detection of the parameters of glasses with different prehistories cannot be significantly spread over time, since the activity of sources (as well as the analyzer sensitivity) in the used equipment decreases with time. In particular, if the radiation treatment of CGSs takes a rather long time, e.g., in the case of long-term γ-irradiation which, to achieve the detection level at dose rates of $\sim 200 - 300$ Gy/s, conventionally lasts several months [19], the performance of separate studies before and after irradiation is simply unacceptable. Comparative studies of irradiated and unirradiated samples are also inexpedient, since a difference between CGS samples is highly probable, and additional proof of the identity of the used materials is necessary. Hence, most appropriate are RIE studies in the so-called reverse chronological-order mode [19, 23−25], i.e., when CGS samples are compared right after radiation treatment and after additional annealing or restoration, when all measurements of the same sample are closest in time. Under the same conditions, optical studies should be performed with the purpose of identifying the existence and nature of the RIEs themselves in CGSs in magnitude and sign of the fundamental optical absorption-edge shift [19].

In the present work, we demonstrate the principal possibility of using the PAL and DBAL methods implemented in the measurement procedure in reverse chronological order for studying RIEs in CGSs. Using the example of As_2S_3 and AsS_2 glasses in which various types of radiation-structural transformations (switchings of covalent chemical bonds, accompanied by the possible formation of coordination defects [19] and glass-forming framework shrinkage corresponding to physical aging [25]) dominate, the specificity of the evolution of the free volume of hollow nanoobjects in defect and defect-free transformations of CGSs is determined.

2. EXPERIMANTAL

The As_2S_3 and AsS_2 glass samples under study were prepared by the conventional melt-quenching method as described in [26]. The samples were synthesized in evacuated and sealed quartz cells using corresponding amounts of high-purity elemental components As (Alfa-Aesar, 99.9999%) and S (ASARCO, 99.999%). The molten mixture of the initial components was kept in a heater at 470−520°C for 12−24 hours under continuous stirring. Then the obtained ingots were cooled in air to a glassy state which was verified visually by a characteristic conchoidal fracture and was confirmed by X-ray diffraction. After synthesis, the samples were annealed for several hours at a temperature of 30−40°C below the glass-transition temperature. For studies, the samples were cut into individual plane-parallel plates ~ 1.5 mm thick and polished to obtain a surface corresponding to the roughness class of optical glasses.

Radiation treatment of the CGSs was performed using γ rays under normal conditions in a cylindrical closed-type reactor with concentrically positioned sources (^{60}Co isotope with an average γ-ray energy of 1.25 MeV). Irradiation lasted about 6 months; the accumulated dose was ~ 3 MGy.

PAL measurements were performed using a time-resolved ORTEC spectrometer FWHM = 230 ps (full width at half maximum of the ^{60}Co reference source) at a temperature of 22°C and a relative air humidity of 35%. As the positron source, the ^{22}Na radionuclide with an activity of ~ 50 kBq placed between two identical CGS samples was used. The measured spectrum included $\sim 10^6$ annihilation events distributed over 8000 channels each 6.15 ps wide. In this case, the contribution of the positron source at a level of 10% was taken into account, which was determined by special calibration tests using Ni and kapton films, which allowed almost complete compensation for the contributions by annihilation in the source itself and in the covering kapton film. The correction of the results for the source contribution and spectrometer response function was performed for all CGS samples under study.

The results obtained were processed using the known LT 9.0 software [27] with the known computational procedure of two-component reconstruction of the PAL spectra, in which the positron lifetimes $\tau_{1,2}$ of two spectral components and their corresponding contributions $I_{1,2}$ were determined [1]. The expedience of this approach is based on the almost total lack of long-lived time components (above 1 ns) in the PAL spectra of known CGSs [5–16]. Then the results were optimized by comparing the statistically weighted root-mean-square deviations of the experimental values of the PAL annihilation spectra and the theoretical curve of the superposition of two independent components. The quantitative trapping characteristics (the average positron lifetime τ_{av}, the positron lifetime in the defect-free τ_b and defect τ_d states, and the positron trapping rate in defects κ_d) were calculated as [1, 5]

$$\tau_{av} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2}, \qquad (1)$$

$$\tau_b = \frac{I_1 + I_2}{I_1/\tau_1 + I_2/\tau_2}, \qquad (2)$$

$$\tau_d = \tau_2, \qquad (3)$$

$$\kappa_d = \frac{I_2}{I_1}\left(\frac{1}{\tau_b} - \frac{1}{\tau_2}\right). \qquad (4)$$

The final determination errors for the positron lifetimes $T_{1,2}$, intensities $I_{1,2}$, and trapping rate in the defects κ_d were ±0.005 ns, ±0.01 rel. units, and ±0.01 ns^{-1}, respectively.

The DBAL spectra were measured using a similar setup with a high-purity germanium detector with an energy resolution of 1.54 keV at 511 keV. A multichannel analyzer was calibrated using a set of standard sources with known γ photopeaks on both sides of the fixed annihilation line: ^{214}Pb with γ photopeaks at 241.92 keV (FWHM = 1.54 keV), 295.21 keV (FWHM = 1.53 keV), 351.92 keV (FWHM = 1.52 keV) and ^{214}Bi with a γ photopeak at 609.31 keV (FWHM = 1.54 keV). The shape of the 511-keV annihilation line of the samples under study was analyzed using the so-called Doppler parameters S and W [1]. The parameter S defined as the ratio of the central area of the 511-keV annihilation line to its total area characterizes positron annihilation with valence electrons of atoms (i.e., the parameter S is mainly sensitive to defects associated with the free volume of the medium). The parameter W defined as the ratio of "tail" areas of the 511-keV annihilation line to its total area characterizes positron annihilation with core electrons (i.e., the parameter W is more sensitive to the chemical environment of the annihilation complex). The parameters S and W were determined from the DBAL spectra in the energy range of 502.29–519.71 keV ($\Delta E = 17.42$ keV) corresponding to ~260 measuring channels, thus providing a general energy resolution of 0.067 keV/channel. The reproducibility of the analyzed DBAL spectra was provided by two independent measurements for each sample with the collected statistics of ~2×10^6 elementary annihilation events. The relative errors of ex-situ experimental determination (when the samples were alternately removed from the spectrometer for corresponding annealing, or samples with different prehistories were used) of parameters S and W were 0.3 and 1.5%, respectively [20]. Since the parameter S was chosen close to ~0.50 [1], its determination accuracy under such conditions was ±0.0015.

After studying the γ-irradiated samples, they were additionally annealed for several hours at a temperature of 30–40°C below the glass–transition temperature, and then were restored in a heating–cooling cycle from room temperature to the temperature of the transition to the supercooled liquid state (the annealing and reduction temperatures were chosen based on known results [28]). This allowed us to perform all studies in the mode of so-called reverse chronological order for a rather short time after γ-irradiation, thus having excluded all possible errors caused by spread of the measurements over time. In summary, within the developed methodological approach, it became possible to distinguish three significantly different structural states of CGSs.

(i) State *1* corresponding to γ-irradiated glass (radiation-aged glass).

(ii) State *2* corresponding to γ-irradiated glass subjected to additional annealing (thermally aged glass).

(iii) State *3* corresponding to glass thermally restored after γ-irradiation (newly prepared or unaged glass).

This classification is based on the assumption that the restoration procedure makes it possible to obtain CGSs in a state close enough to newly synthesized glass [29], while annealing of the irradiated CGS samples below the glass-transition temperature transforms them to a thermodynamically more equilibrium structure state [19, 30]. Thus, the evolution of hollow nanoobjects in CGSs was studied for three aforementioned states with combined application of the main positronics methods, i.e., PAL and DBAL spectroscopy.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the typical PAL spectrum and the sequence of its two-component restoration for γ-irradiated As$_2$S$_3$ glass. The bottom of Fig. 1 additionally shows the set of mean-square deviations (MSD) of the PAL reconstructed spectrum from the experimental values; its minimum spread indicates rather high reliability of the used mathematical reconstruction procedure.
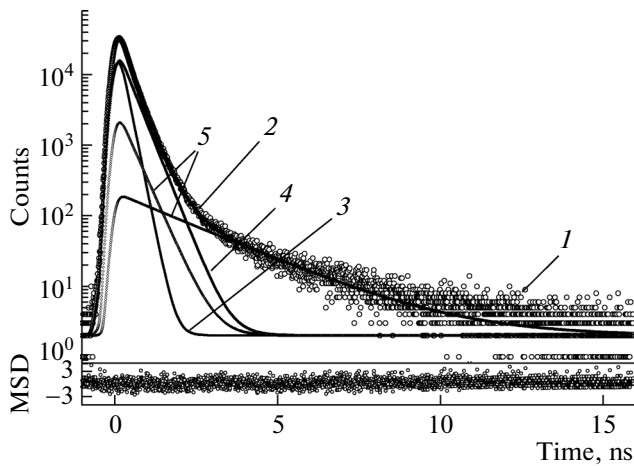
Fig. 1. Experimental PAL spectrum of γ-irradiated As_2S_3 glass and its two-component reconstruction into components with the positron lifetimes τ_1 and τ_2, taking into account the 10% contribution of the source: (*1*) experiment, (*2*) reconstructed spectrum, (*3*) τ_1 component, (*4*) τ_2 component, and (*5*) source contribution.

The parameters of mathematical reconstruction of the experimentally measured PAL spectra and the numerical characteristics of positron trapping, calculated by formulas (1)−(4) within the model with one dominant defect type [1, 5] for the γ-irradiated (state *1*), thermally aged (state *2*), and restored (state *3*) CGS samples As_2S_3 and AsS_2 are listed in Tables 1 and 2.

As follows from the tables, the changes in the positron lifetimes τ_{av}, τ_b, and τ_d in samples with different prehistories are insignificant, and do not exceed the general measurement error. Invariability of the positron lifetime τ_b in the defect-free state is expected, since this parameter is mainly defined by chemical composition of the CGS [1, 5], rather than by structural changes in the irradiated material itself. The constancy of the positron lifetime τ_d in the defect state suggests that hollow CGS volumes which trap

Table 1. Parameters of mathematical reconstruction of the PAL spectra of γ-irradiated, annealed, and restored As_2S_3 and AsS_2 CGSs

CGS prehistory	τ_1, ns	I_1, rel. units	τ_2, ns	I_2, rel. units
		As_2S_3		
γ-irradiated	0.193	0.38	0.378	0.62
Annealed	0.196	0.39	0.380	0.61
Restored	0.194	0.42	0.384	0.58
		AsS_2		
γ-irradiated	0.204	0.44	0.378	0.56
Annealed	0.202	0.44	0.377	0.56
Restored	0.203	0.45	0.380	0.55

positrons are not subjected to significant changes upon exposure to radiation. Similar conclusions are valid for interpretation of the invariability of the average positron lifetime τ_{av}, which indicates the constancy of the statistical average center of mass of all possible annihilation channels.

Nevertheless, the invariability of the positron lifetimes τ_{av}, τ_b, and τ_d is not yet a categorical indication of a lack of structural changes during the γ-irradiation and annealing of CGSs or, as the authors of [17] suppose, insufficient sensitivity of the PAL method to radiation-structural transformations in general, since changes are possible in other positron trapping characteristics. Indeed, as shown in [15, 16], the positron trapping rate in defects κ_d is most sensitive and informative under these conditions. This parameter exhibits a clear trend toward increasing in going from restored to γ-irradiated and annealed samples; the increase in κ_d for the stoichiometric As_2S_3 glass and sulfur-enriched AsS_2 dominates during γ-irradiation and annealing, respectively (see Table 2).

It is reasonable to analyze these results taking into account the different effect of influencing factors on the spectral position of the fundamental optical-absorption edge of the CGSs under study. As optical in-situ studies [25] showed, annealing and restoration of the γ-irradiated As_2S_3 glasses cause a short-wavelength shift of their fundamental optical-absorption edge. But in the case of γ-irradiated AsS_2 glasses, annealing appears inefficient, whereas restoration shifts the fundamental optical-absorption edge to long wavelengths. In this case, for both CGS compositions, annealing causes a short-wavelength shift of the optical-absorption edge in comparison with restored samples.

Thus, the features of the thermally induced effect on the optical properties of γ-irradiated As_2S_3 and AsS_2 CGSs indicate fundamental differences between their structure states. To explain these differences, the concepts of the coordination defect formation and physical aging of CGSs were used in [25], which can also be applied to analyze the PAL results. For example, taking into account that γ-irradiation causes the switching of covalent chemical bonds in the glassy matrix of stoichiometric As_2S_3 followed by the possible production of pairs of charged coordination defects [19], we can explain why γ-irradiated arsenic trisulfide exhibits a long-wavelength shift of the fundamental optical-absorption edge. Indeed, heat treatment of this glass (both annealing and restoration) should certainly cause the decay of γ-induced defect centers, thus restoring the initial distribution of covalent chemical bonds of the matrix [19]. This approach adequately explains the maximum value of the positron trapping rate in defects κ_d in the γ-irradiated stoichiometric As_2S_3 CGS sample, where, according to estimations [19], the defect density is maximum. Since a deviation from stoichiometry decreases the concen-

tration of covalent chemical bonds As—S required for γ-induced defect formation [31]; hence, this process is not determining in sulfur-enriched AsS$_2$ glass, which is confirmed by both the fundamental optical-absorption edge spectroscopy data [25] and the PAL method results (Table 2).

At the same time, it is known that, as the amount of chalcogen (sulfur in this case at hand) is increased, the CGS susceptibility to physical aging (both natural and induced) increases due to efficient "shrinkage" of the structural matrix [23, 28, 32]. In the optical spectra, these processes manifest themselves in a fundamentally different effect, i.e., a short-wavelength shift of the fundamental absorption edge [33]. But if we consider the effect of structural shrinkage on the PAL parameters, an increase in the positron trapping rate κ$_d$ can be expected due to fragmentation of the CGS free volumes [34]. Indeed, as follows from Table 2, the parameter κ$_d$ in AsS$_2$ glass increases in going from the restored sample to the γ-irradiated or annealed sample. Taking into account the optical spectroscopy data [25], we can say with confidence that it is the thermal and γ-induced physical aging processes that are responsible for the increase in the positron trapping rate κ$_d$ in this case.

These conclusions are in good agreement with the DBAL results shown in Fig. 2. Strong effects in the parameters of the annihilation line shape in the S–W diagram should not be expected; however, the accuracy of the above-described experimental setup with an energy resolution of 0.067 keV/channel is quite sufficient for the reliable determination of corresponding changes, even taking into account the spurious effect of the uncompensated background [1, 20]. It should be noted that conclusions about possible changes in DBAL characteristics are made in an aforementioned study [17] at an energy resolution of ~0.23 keV/channel which is clearly insufficient for reliable conclusions.

Figure 2 shows the S–W characteristics of As$_2$S$_3$ and AsS$_2$ CGSs with different prehistories, obtained by the DBAL method. It is easily seen that the experimental values corresponding to restored samples are in the top left corner of the diagram, i.e., these samples are characterized by the smallest parameters W and the largest parameter S for both glasses. The transition to annealed samples is accompanied by a decrease in the parameter S and an increase in W. A significant difference between CGS samples appears only upon going to the γ-irradiated state: the dominant positions corresponding to γ-irradiated As$_2$S$_3$ glass are arranged in the bottom right corner of the S–W diagram (Fig. 2a), whereas they shift to a position intermediate between states 2 and 3 for the sulfur-enriched AsS$_2$ sample (Fig. 2b).

These results correlate with known variations in the parameters S and W, observed in crystalline materials [20—22, 35]. As is known, the defect-free state in them

Table 2. Positron trapping parameters of γ-irradiated, annealed, and restored As$_2$S$_3$ and AsS$_2$ CGSs

CGS prehistory	τ_{av}, ns	τ_b, ns	τ_d, ns	κ_d, ns^{-1}
As$_2$S$_3$				
γ-irradiated	0.308	0.277	0.378	1.57
Annealed	0.307	0.277	0.380	1.50
Restored	0.304	0.272	0.384	1.47
AsS$_2$				
γ-irradiated	0.301	0.275	0.378	1.26
Annealed	0.300	0.273	0.377	1.27
Restored	0.300	0.272	0.380	1.25

is characterized by the largest parameter W and the smallest parameter S, i.e., they are in the bottom right corner of the S–W diagram [20—22, 35]. The formation of defects (first of all those characterized by the
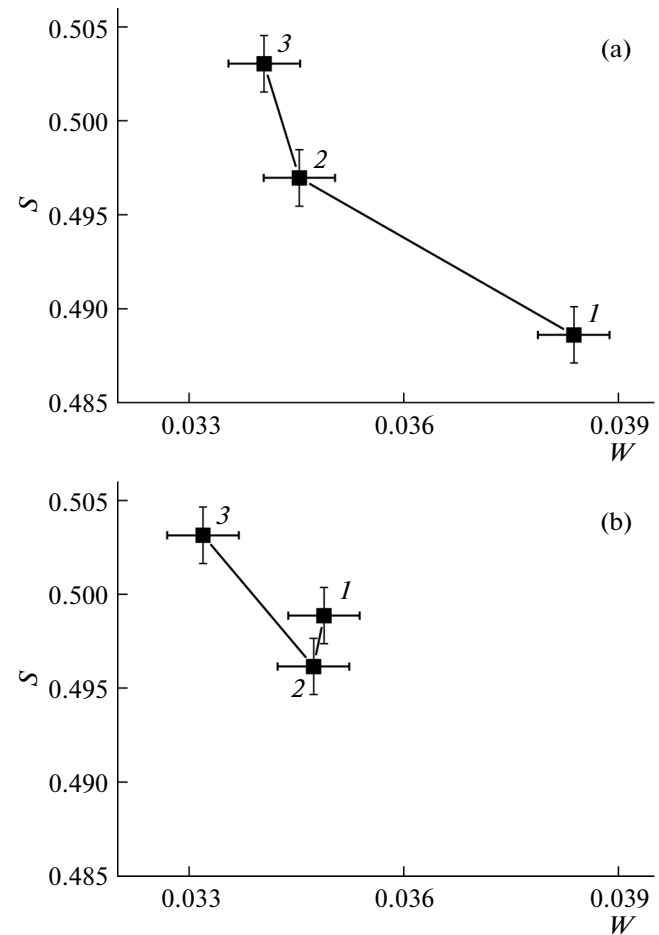

Fig. 2. Experimental S–W characteristics of (a) As$_2$S$_3$ and (b) AsS$_2$ glasses with different prehistories ((1) γ-irradiated, (2) annealed, (3) restored), obtained by DBAL spectroscopy.

presence of free volume) results in an increase in S and a decrease in W; all intermediate values of these parameters describing identical defect states of various concentrations form a straight trajectory [20–22, 35]. In CGSs, the role of such defects (to which the PAS methods are sensitive) is played by regions with excess free volume (both atomic and electronic) with respect to the hypothetically defect-free crystalline state [5, 30]. Thus, in the DBAL methodology, an analogue of a defect-free crystal is a glass in the most equilibrium aged state [30]. Newly synthesized or restored CGSs can be considered as the most imperfect or non-equilibrium ones, since the free volume (as well as the enthalpy and configuration entropy) excess in them is maximum [30]. Exactly such behavior is observed in Fig. 2, when the dominant $S–W$ positions of the restored samples are arranged in the top left corner of the diagram, while annealing (i.e., thermally induced physical aging accompanied by free-volume fragmentation [36]) shifts them toward the bottom right corner.

If we compare the dominant positions in the $S–W$ diagram, corresponding to γ-irradiated As_2S_3 and AsS_2 glasses (Fig. 2), we can conclude that they are principally different. Since points *1* and *2* for AsS_2 glass are rather close to each other (Fig. 2b), it can be assumed that the effect of γ-radiation is similar to the effect of annealing in this case, i.e., γ-induced physical aging of the glass occurs, which is accompanied by glassy matrix shrinkage and a corresponding decrease in the free volume. As is known, such effects in fact well manifest themselves only in chalcogen-enriched CGSs, in particular in the system of As–S glasses as well [28].

The shift of position *1* for the γ-irradiated As_2S_3 glass in the $S–W$ diagram to the bottom right corner (Fig. 2a) suggests that completely different defect states associated with the free volume, e.g., above-mentioned defects of covalent chemical-bond switching [5, 19], are responsible for positron trapping in this case. Let us consider what changes can be expected in the $S–W$ diagram when defects of this type appear in the CGS matrix.

On the one hand, the formation of such defects is accompanied by the formation of additional free volumes due to broken bonds near negatively charged undercoordinated sulfur atoms which can be positron trapping centers [5, 19]. In this case, we move away from the hypothetical "defect-free state" in the $S–W$ diagram. However, on the other hand, the sufficiently high trapping coefficient of positrons by such defects (in comparison with neutral-charged free volumes) causes an appreciable increase in the parameter S with a weak change in parameter W, which, in the case of an insignificant defect density (at the level of several atomic percent as is characteristic of irradiated CGSs [19, 37, 38]) shifts the dominant positions in the $S–W$ diagram almost vertically upwards with respect to the "defect-free state." Finally, the $S–W$ parameters of the γ-irradiated As_2S_3 glass appear in the bottom right corner of the $S–W$ diagram, notably closer to the "defect-free state" in comparison with aged glasses.

Thus, the results of the investigation of induced structural transformations in As_2S_3 and AsS_2 glasses, obtained using the PAL and DBAL methods correlate, confirmed by data of fundamental optical-absorption edge spectroscopy, which shows the principal possibility of using the set of positronics methods implemented in the mode of reverse chronological order for studying radiation-induced effects in CGSs.

4. CONCLUSIONS

The technique of positron annihilation spectroscopy (positronics) in the PAL and DBAL spectroscopy methodology can be efficiently applied to study the evolution of the free volume of hollow nanoobjects in CGSs, caused by radiation, which was demonstrated by the example of As_2S_3 and AsS_2 glasses. It was shown that the positron trapping rate in defects κ_d exhibits a clear trend toward increasing upon going from restored to γ-irradiated or annealed samples. The results obtained are in good agreement with the data of fundamental optical-absorption edge spectroscopy on these glasses and are also complemented by the results of the investigation of the Doppler shape parameters S and W of the annihilation line in the DBAL method.

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