Journal of Optoelectronics and Advanced Materials Vol. 4, No. 1, March 2002, p. 45 - 50

STRUCTURAL–TECHNOLOGICAL MODIFICATION OF As_2S_3 GLASSES

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As_2S_3 glasses prepared in different technological modes were investigated by direct methods of transmission electron microscopy and electron diffraction. As samples we took thin slices with 0.08 – 0.1μm thickness got by cutting the initial bulk glasses. All the investigated glasses, according to their microstructure, were divided into two categories: samples got at melt temperature T = 870 – 1120 K and melt cooling speed v = 0.01 – 1.3 K/s have homogenous microstructure while glasses got at melt temperature T > 1200 K and melt cooling speed v = 1.5 – 150 K/s exhibit a heterogenous microstructure. Different structural models of near and middle range order for each type of As_2S_3 glasses got under different technological conditions were discussed.

(Received June 28, 2001; accepted March 3, 2002)

Keywords: As_2S_3 glass, Microstructure, Electron microscopy, X-ray diffraction

1. Introduction

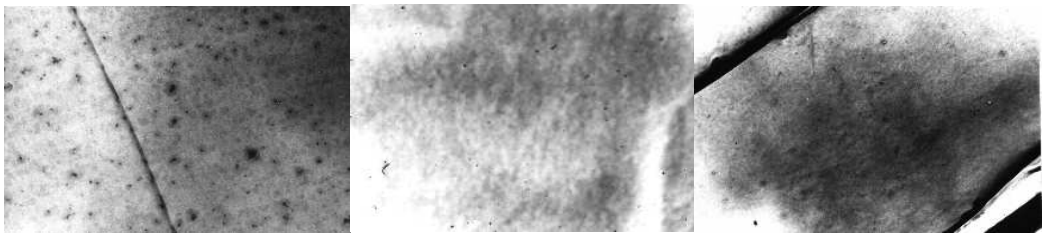
The possibility of structural and technological modification of chalcogenide vitreous semiconductors are important for the control of the physical properties of glassy materials. Detailed experiments and structural investigations and models are necessary in order to clarify the relation technological parameters – physical properties. This paper is dedicated to the influence of the synthesis conditions on the microstructure and short-range order of glassy As_2S_3, obtained and different temperatures of isothermal exposure $T_1 = 870$ K, $T_2 = 1120$ K, $T_3 = 1370$ K and melt cooling velocity $v_1 = 10^{-2}$ K/s, $v_2 = 1.5$ K/s, $v_3 = 1.5 \cdot 10^2$ K/s.

2. Experimental

The samples for structural investigations by the methods of electron microscopy and electron diffraction were prepared in the form of thin slices of 50-70 nm thickness got on ultramicrotome UMTP-4. Using the data of electron diffraction investigation the radial distribution functions (RDF) were calculated.

3. Results

The electron microscopy images of the microstructure of glassy sample, obtained in different technological conditions are given in Fig. 1, 2, 3. On the basis of microstructure analysis of temperature-velocity T-V diagram of As_2S_3 glass synthesis was built (Fig. 4). The diagram is divided into two regions: A – region characterized by homogenous microstructure and B – region characterized by heterogeneous type of microstructure.



a b c

Fig. 1. Electron microscopy images of As_2S_3 glass cuts got in different technological conditions: a – T_1v_1; b – T_1v_2; c – T_1v_3.

A region is characterized by weak microdisperse microstructure of the glasses. It includes subregion *a* with small v and T where microstructure of homogenous matrix glass is realized and crystallization processes take place. On the border with B region the level of glass microdispersion increases. The increase of melt temperature or hardening velocity of glasses in A region leads to the increase of their microdispersion level, too.

B region with heterogeneous type of microstructure is characterized by strong level of microdispersion. It embraces glass synthesis regimes with maximum temperature of melt exposure. Hardening velocity increases in B region, which is connected, by the increase of structural relaxation time at sharp decrease of the temperature. The character of the glass microstructure in this region is defined by dissociation of As_2S_3 melt at $T_2 = 1370$ K.

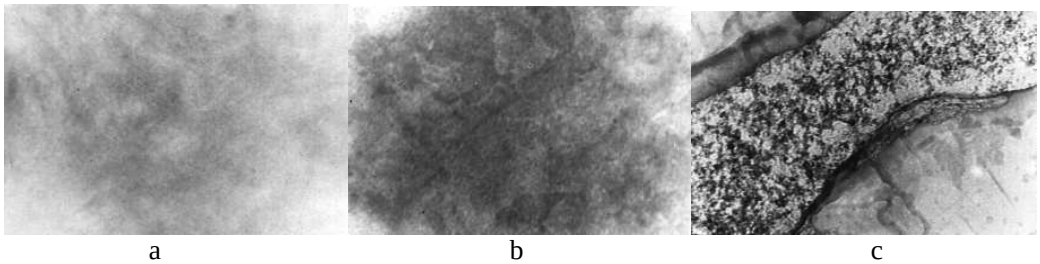


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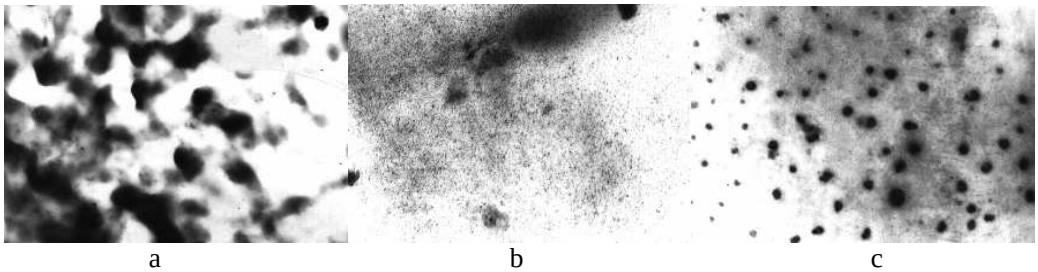
Fig. 2. Electron microscopy images of As_2S_3 glass cuts got in different technological conditions: a – T_2v_1; b – T_2v_2; c – T_2v_3.



a b c

Fig. 3. Electron microscopy images of As_2S_3 glass cuts got in different technological conditions: a – T_3v_1; b – T_3v_2; c – T_3v_2.

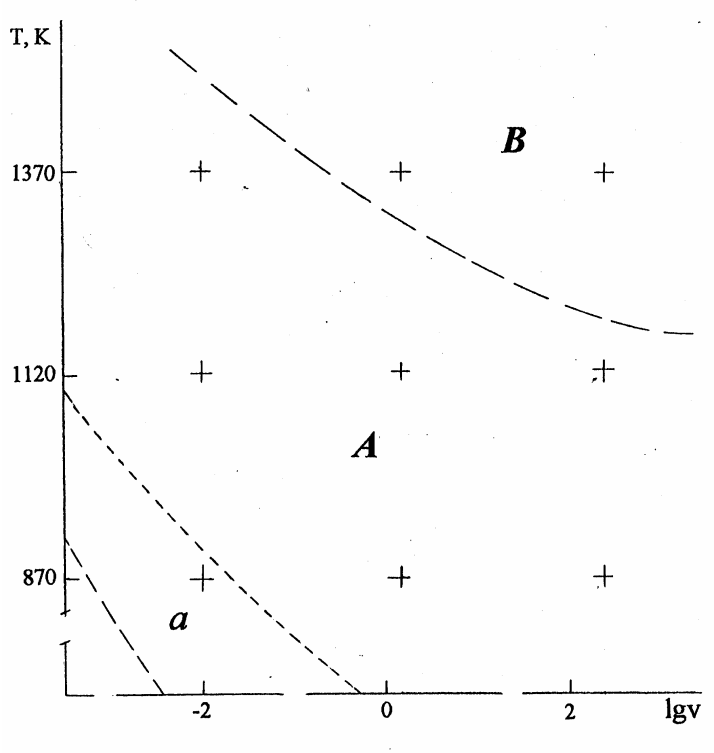
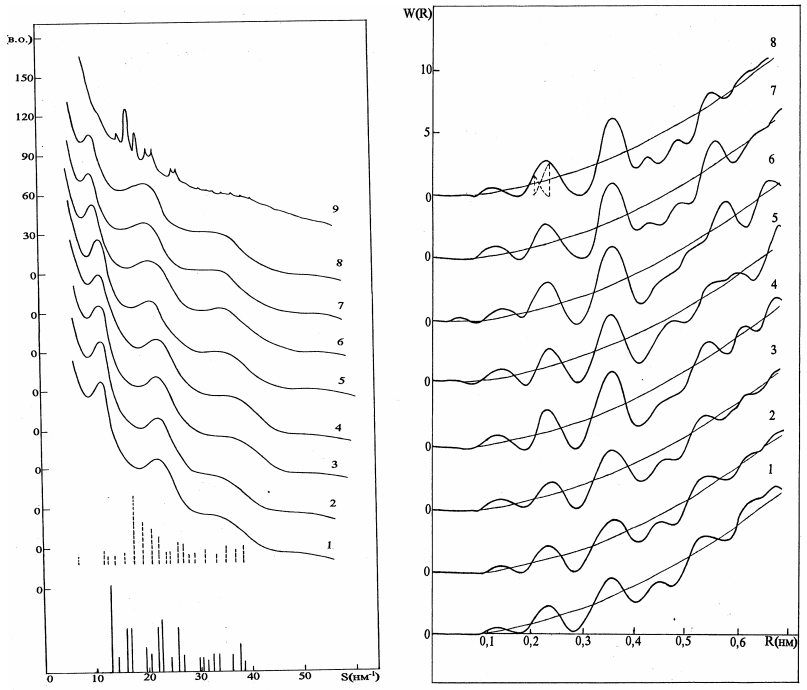


Fig. 4. Temperature – velocity diagram of As_2S_3 glass synthesis.

On the basis of T-v diagram peculiarities, type and level of microdispersion and size of preudograins we defined the order of microstructure connectivity growth depending on technological conditions of As_2S_3 glass synthesis: T_3v_1, T_1v_2, T_2v_1, T_1v_3, T_3v_1, T_2v_2. The meanings of glass physical parameters (density, temperature of softening, self-absorption edge, and refractive index) smoothly change along the said row. Their magnitude is known to be defined by peculiarities of glass structure.

Electron diffraction maxima of the T_1v_1 samples correspond to Debye lines of orpiment (continuous lines in Fig. 5a). That is why we assume similarity of structure in this sample and crystal. The first coordination radius of glass r_1 = 0.24 nm (Fig. 5b) practically equals the smallest interatoms distances in orpiment (0.235 nm). The first coordination numbers were calculated according the magnitude of the area under the first maximum of the radial atomic distribution curve. These meanings are $z_S(As)$ = 3.8 and $z_{As}(S)$ = 2.3 and are somewhat larger than the values corresponding to are for As_2S_3 crystal [1, 2]. It is natural to accept that the main structural unit in glass is the trigonal pyramid As_2S_3. The values of coordination numbers can be explained by the presence in glass of disordered flat areas created as well as in crystal by the closed heteroatomic chains but with the less amount of atoms. Such flat areas are oriented approximately parallel to each other and they form locally ordered microregions. According to this model the position of RDF peak with r = 0.52 nm is situated at distances that are 8% larger than those in crystalline As_2S_3 (0.48 nm).

This structural difference is reflected in the density difference in crystalline and glassy As_2S_3. The difference is 8% (ρ_{cr} = 3.46 g/cm^3 and ρ_{glass} = 3.201 g/cm^3, respectively). One more argument in favor of the proposed model is the distinct maximum on the diffraction curve around s = 12.5 nm^{-1}. The appearance of this maximum is explained by the intermediate-range order in amorphous structure. In our model MRO is given by the ordered arrangement of flat configurations.



a b

Fig. 5. Diffractograms (a) and RDF (b) of As_2S_3 glass got in different technological regimes: 1 – T_1v_1; 2 – T_1v_2; 3 – T_1v_3; 4 – T_2v_1; 5 – T_2v_2; 6 – T_2v_3; 7 – T_3v_1; 8 – T_3v_2; 9 – T_3v_3 (Stroke diagram from continuous lines corresponds to crystalline S).

As well as in As_2S_3 glasses (T_1V_1), the groups of Debye lines of orpiment (Fig. 5a) correspond to electron diffraction maximums in A region. For all the samples the position of the first coordination radius r_1 = 0.24 nm remains unchanged. But the area under the first and the second maximum of RDF increase from 24 to 30 relative units and from 51 to 61 relative units (Fig. 5b).

Table 1. Microstructure types and parameters of short-range order in As_2S_3 glasses.

Glass synthesis regime	Microstructure type	Micro-dispersion level	Coordination sphere radii, nm			Areas under peaks (relative units)	
			r_1	r_2	r_3	A_1	A_2
T_1v_1	homogeneous	null	0.23	0.36	0.44	21.5	51
T_1v_2	homogeneous	very small	0.23	0.36	0.45	23.5	54
T_2v_1	homogeneous	very small	0.23	0.36	0.46	23.6	54
T_1v_3	homogeneous	small	0.23	0.36	0.46	26.5	55
T_3v_1	homogeneous	small	0.23	0.36	0.48	27.4	55
T_2v_2	homogeneous	small	0.23	0.36	0.47	28.6	57
T_2v_3	homogeneous	middle	0.23	0.36	0.48 0.51	29.1	60
T_3v_2	heterogeneous	strong	0.23	0.36	0.43 0.51	29.9	62
T_3v_3	heterogeneous	very strong	–	–	–	–	–

4. Discussion

Unchangeability of the first coordination radii means that in all glasses the nearest neighbors are atoms of different type. The As and S atoms preserve their own valency and form three and two bonds, respectively. Thus the main structural unit in the glasses of this group is As_2S_3 pyramid. The coordination numbers can be explained by the influence of neighboring structural units. According to Raman scattering (RS) spectra, the glasses of the given region are formed from the molecular clusters with different polymerization level characteristic to glassy As_2S_3: from clusters weakly interconnected by Van-der-Waals forces to a continuous spatial structure [1]. The basical unit is $AsS_{3/2}$. The structure differs by the dihedral angles. Structural model of glassy As_2S_3 in A region of the diagram can explain the change in glass properties on the basis of microstructural changes induced by technological factors during synthesis. The main difficulty is to explain the growth of coordination numbers which is accompanied by a decrease of glass density at transition from layered to less connected molecular-like structures.

The decrease of glass density is, as a rule, connected with the creation of more disordered structures as free volume increases relative to the occupied volume [2]. In the papers [3, 4] the disordering process is related to the formation of cyclic clusters. Their accumulation violates the continuity of glass polymeric structure and leads to the decrease of microhardness and T_g. Appearance of cyclic clusters in polymeric glass structure may accompany the process of appearence of structural units with mutual cis-orientation. Around them can be formed closed configurations which consist of structural $AsS_{3/2}$ units with different orientation and package. Such model permits to obtain higher coordination numbers keeping unchanged the coordination radii and allows for the decrease in density at the expense of micropores formation.

Glasses in B region are characterized by a heterogeneous type of microstructure. That is why the results of electronographic investigations must be interpreted considering share and composition of structural units. Glasses in this region contain pseudograins with the darker diffraction contrasts in the electron-microscopic pictures and their share coincides within the accuracy of 5%. Thus we can assume identity of chemical compositions of the said structural units in both glasses. Their identification in RDF is complicated by statistic character of the latter. On the intensity curve of As_2S_3 (T_3v_3) glass we see crystalline peaks (Fig. 5a) whose positions coincide with the positions of the peaks in S_λ-rombic sulphur (dashed part in Fig. 5a). Crystallizatin of sulphur microparts of 50 nm in diameter takes place in the process of annealing and storage. As_2S_3 (T_3v_2) glass structure is characterized by the mutual penetration of two types of structures. As a result, the size of pseudograins decreases and crystallization process becomes slower. The share of sulphur is 20% of the total glass volume and the remained can be presented as chemical composition As_2S_3. The sharp bands on the background of continuous glass spectrum of As_2S_3 (T_3v_3) show the presence of molecular complexes. Taking into consideration dissociation of the overheated As_2S_3 [5,6], we are led to the conclusion that in glasses of B region the most characteristic feature is clustering. The main elements of clusters are homogeneous S atoms and molecular dissociation products of the type As_4S_5, As_4S_4, As_4S_3. Thus, the first maximum on RDF in As_2S_3 (T_3v_2) glass is the sum of the two bell-like curves (Fig. 6b). The right part is the direct reflection of the left branch of the first maximum of RDF as to the normal. The normal passes across r_1'' = 0.21 nm which is equal to the shortest inter-atomic distance in S_2 molecule. The second bell-like curve is got by extraction of the first curve from the first peak. Its maximum is situated at r_1'' = 0.23 nm. It includes the distances between the nearest neighbours in all the clusters As_xS_y with molecular structure. The identification of the exact type of molecular units (As_4S_5, As_4S_4, As_4S_3) within the frame of RDF is not simple as well as the interpretation of Raman scattering spectra.

5. Conclusions

The structure of thin slices with 0.08 – 0.1 μ thickness got by cutting bulk As_2S_3 glasses has been investigated. The glasses were obtained in different technological conditions. All the investigated glasses were divided, according to their microstructure in two types: samples got at melt

temperature T = 870 – 1120 K and melt cooling speed v = 0.01 – 1.3 K/s have homogeneous microstructure and glasses got at melt temperature T > 1200 K and melt cooling speed v = 1.5 – 150 K/s have a heterogeneous microstructure.

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