

Mass-Spectra Of As-S Glasses Evaporation

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Abstract—The complicated complex nature of vapour flows of these glasses which contain about three tens of different As_mS_n atomic complexes ($m = 0 - 4$, $n = 0 - 8 \dots$) has been revealed. By increasing the flow density of an ionizing electron beam of the mass-spectrometer the coincidence of the total mass-spectrometric composition of the vapour phase with the chemical composition of glasses before evaporation has been ensured. The presence of three types of concentration dependences for different As_mS_n clusters versus the chemical composition of initial glasses: growing, decreasing, dome-shaped ones has been established. The influence of technological conditions of synthesis for As-S glasses on their mass-spectra has been revealed.

Keywords—mass-spectrometry; arsenic-sulfur clusters; evaporation of chalcogenides

I. INTRODUCTION

For mass-spectra of As-S glasses a considerable content of As_mS_n polyatomic complexes is typical, where m changes from zero to four, and n - from zero to eight [1, 2]. These various vapour components are adsorbed on the surface of the growing film under condensation and involved into the processes of chemical self-collecting of its atomic grid. The formation of different structural and phase states of As-S amorphous films is conditioned by the chemical composition and structure of these particles, their quantitative ratios, kinetic, energy and chemical characteristics, combined with a certain set of other parameters of the condensation process.

The analysis of mass-spectra of As-S materials, studied by different authors [3 - 9] shows that in most cases the total mass-spectrometric composition of the vapour phase does not correspond to the chemical composition of initial materials. In this case, the chemical composition of the vapour flow is generally substantially enriched with arsenic compared with the composition of initial materials (differences reach 20 at.%). Such large deviations can be caused by several reasons: deviations from the preset chemical compositions of initial materials; differences in their structure; prolonged exposure of the substance at elevated temperatures of an effusion cell prior to the registration of the mass-spectrum, as a result of which volatile particles have time to sublime from the batch; improper conducting of mass-spectrometric measurements and processing of their results and so on. In particular, the ratio of concentrations of different vapour particles greatly differs at the initial, basic and final stages of evaporation. Therefore, our work analyzes the given problem, too.

II. METHODOLOGY OF RESEARCH

Mass-spectrometric studies were conducted by Knudsen method on MH-1201 devices. The effusion cell was made from tantalum foil and had a small diameter of a hole equal to 0.5 - 0.7 mm. Around the cell a radiation screen from tantalum foil was also placed. The ratio of the area of Knudsen cell hole to the area of its section made up 1: 200. The evaporation temperature of the cell batch was measured by the differential W-Re thermocouple. Before each new experiment the effusion cells were heated up to 1000 - 1200 K.

The experiments were conducted in vacuo of $\sim 10^{-5}$ Pa, which was created by a lamellar-rotary pump Pfeiffer Vacuum DUO 2.5 and turbo-molecular pump TMH-150. The devices were calibrated according to atomic particles of aluminum vapours.

According to the data [10], the maximum ionization efficiency of As_mS_n clusters is typical for exciting electrons with energies of 30 - 60 eV. That is why the flow of ionizing electrons was formed just in this energy range. The effective cross section of ionization process of various atoms and molecules by the electrons of low energies is on the average directly proportional to their sizes. The sizes of arsenic atoms are by 30% greater than those of sulfur atoms. Thus enriched with As the As_mS_n clusters will have much larger geometric sizes and therefore significantly greater cross sections of electron scattering. Thus, these clusters will be much more effectively ionized by the flow of exciting electrons of the mass-spectrometer and their ionic currents will prevail in experimental mass-spectra. In our opinion, just by this a significant enrichment with arsenic of the total chemical composition of the ionized flow in the mass-spectrometer is determined (see papers [3 - 9]). Therefore, these effects should be taken into account while obtaining reliable experimental mass-spectrometric data for evaporation of As-S materials. One way of making this effect slacken is to increase the efficiency of vapour flow ionization by an electronic gun.

For evaporation small pieces of glasses of As-S system with the chemical composition of $As_{10}S_{90}$, $As_{20}S_{80}$, $As_{25}S_{75}$, $As_{33}S_{67}$, $As_{40}S_{60}$ та $As_{44}S_{56}$ were taken. The glasses were synthesized by cooling of the ampoules with melt in cold water. The evaporation temperatures T_e of glasses of all chemical compositions were chosen to be such ones, as to ensure optimal densities of vapour flows in the mass-spectrometer. It was found that values T_e , which were 30 - 80 K greater than the glass transition temperature of glasses and

the same 30 - 80 K lower than the corresponding liquidus temperatures of As-S state diagram, correspond to such conditions. During studies the mass-spectra were recorded only during the base average period of the experiment and unstable initial and final stages of the evaporation process of glasses were not considered.

III. RESULTS AND THEIR ANALYSIS

A. Clusters with high content of Sulfur atoms

Mass-spectra of sulfur-rich glasses of As-S system obtained by us contain all atomic complexes of S_n from S to S_8 . But, unlike the elementary sulfur, the mass-spectra lines of all S_n particles are quite intense and lie in the range from 10 to 100 a. u. At this, for the composition of $As_{10}S_{90}$ glasses the most intense mass-spectrum line corresponds to the particle S_4 . With the growth of arsenic part in the composition of glasses the intensities of these lines naturally reduce gradually and for As-rich samples in the vapour phase a small quantity of only S_2 , S_3 and S_7 particles appears.

The averaged data of other researchers correlate quite well with our results. But there are a few features in them that are difficult to explain. 1. The concentration of all S_n complexes changes nonmonotonously with changing the chemical composition of glasses. 2. The intensity of lines of S_7 clusters is practically identical for all investigated glasses from $As_{20}S_{80}$ to $As_{45}S_{55}$, the concentration of sulfur atoms of which is reduced more than twice. 3. The intensity of S_8 cluster lines even increases by four times at the indicated changes in the chemical composition of glasses.

Quite a different behavior with changing the chemical composition of evaporated glasses is typical for AsS_n particles of the second type. In particular, AsS_3 and AsS_4 complexes have not been reported in most previous studies on evaporation processes of As_xS_{100-x} glasses. In our own experiments only AsS_3 particles were fixed in the vapour phase during evaporation of $As_{10}S_{90}$ glasses exclusively.

The lines of AsS_3 and AsS_4 clusters are presented in the mass-spectra more extensively. In our experiments these atomic complexes are found in all investigated glasses of As-S system, except $As_{44}S_{56}$. At this the intensities of lines of the given clusters in mass-spectra of glasses having different chemical compositions are quite similar and lie within 4 - 12 a. u. Previous mass-spectra of other authors point to the presence of AsS_3 and AsS_4 clusters only in vapours of As_xS_{100-x} glasses with $25 \leq x \leq 40$ at.%. A substantial concentration of such clusters was revealed only in vapours of glasses with compositions in the vicinity of $As_{33}S_{67}$.

In a wide range of compositions of As-S glasses from 20 to 33 at.% the lines of As_2S_4 particles have the maximum intensity in the mass-spectra investigated by us. The concentration of such clusters is also quite high in vapour flows of glasses with other chemical compositions. Previous experiments also revealed a significant contribution of the given atomic complexes in the mass-spectra of all investigated As-S glasses. This indicates to the fact that As_2S_4 clusters are one of the main components of vapour flows of all As_xS_{100-x} glasses.

Our experiments also revealed As_2S_3 clusters in vapour flows of glasses with $20 \leq x \leq 40$ at.%. Especially intense lines of these particles are seen in mass-spectra of $As_{33}S_{67}$ and $As_{40}S_{60}$ glasses. In contrast to our data, previous studies by other authors found such complexes mainly in vapours of glasses only in the vicinity of $As_{33}S_{67}$ compositions.

It should be noted that in mass-spectra of vapour flows of $As_{33}S_{67}$ glasses we also constantly recorded a weak line (~ 5 a. u.) of As_3S_5 atomic particles. In all other studies this particle was not detected.

B. Clusters with commensurable content of arsenic and Sulfur atoms

Quite a large number of mass-spectra lines of As_xS_{100-x} glasses corresponds to the complexes in which quantities of sulfur and arsenic atoms are equal or differ by one. One of such AsS clusters is the second main part of vapour flows of the investigated glasses. The intensity of lines of this cluster is high for all glasses and it is maximum for mass-spectra of glasses with a high content of arsenic both for our experiments and other articles.

According to our data the concentration of AsS_2 complexes is high enough only for vapours of $As_{10}S_{90}$ glasses (the line intensity is 87 a. u.). With the growth of As content in glasses the number of clusters is rapidly declining and they are already absent for samples with $x \geq 40$ at.%. According to other researchers AsS_2 atomic particles significantly contribute only into mass-spectra of $As_{33}S_{67}$ glasses.

In previous papers in mass-spectra of almost all glasses of As-S systems there were recorded quite noticeable lines of As_2S_2 , As_2S_3 and As_2S_4 clusters (the intensity of lines was within the limits from 10 to 60 a. u.). But our research revealed such clusters only in vapour flows of glasses rich in arsenic (mainly for compositions with $x \geq 33$ at.%). The intensities of lines of the given particles in our mass-spectra are much smaller (2 - 25 a. u.).

Quite unexpected are the averaged results of previous research as to the content of As_xS_{100-x} clusters with a large number of arsenic atoms: As_3S_2 , As_3S_3 , As_4S_3 and As_4S_4 in the vapours of glasses. These atomic particles were found in the samples of all chemical compositions, beginning with $As_{20}S_{80}$. The intensities of their lines in mass-spectra naturally grow with the increase of x, beginning from 1 a. u. and reaching 20 - 40 a. u. In our experiments such clusters are found in vapours of glasses only for $x \geq 40$ at.%. At this the concentrations of As_4S_3 and As_4S_4 clusters are commensurable with the data from previous studies, and the concentrations of As_3S_2 and As_3S_3 clusters are almost by an order of magnitude less in comparison with previous studies.

For As_3S_4 and As_4S_5 clusters the results of mass-spectrometric experiments are very close both by the intensities of lines and by their change with variations in the chemical composition. The given atomic complexes are revealed only in vapour flows of As_xS_{100-x} glasses for $x \geq 40$ at.%.

C. Clusters with high content of Arsenic atoms

Atomic particles with a large number of As atoms in vapours of As-S system are mainly presented near As_n , where n varies from 1 to 4. But only As and As_2 lines have significant intensities in mass-spectra. In previous studies a great decrease in the intensity of As lines (from 90 to 17 a. u.) with increasing the arsenic concentration in glasses (from 20 to 45 at.%) is unclear. However, in our experiments, the intensities of As lines in mass-spectra of glasses with the same range of compositions are much lower and change very little within 3 - 10 a. u. Researchers usually indicate [1 - 3], that lines of single arsenic atoms in mass-spectra of As-S glasses appear largely due to dissociation of AsS particles under the influence of an ionizing electron beam. But in this case, mass-spectra must have the appropriate intensity of lines of single sulfur atoms. Moreover, the intensities of S, As and AsS lines should correlate with each other, which is not observed in the mass-spectra presented by previous researchers.

At the same time, these distinct patterns of lines are typical for the lines of these particles in our mass-spectra of all investigated As-S glasses. In particular, the intensities of sulfur and arsenic lines in them are very close, and the intensities of AsS lines by 5-10 times higher than S and As lines. In addition, a strong increase in the intensity of AsS lines (to 100 a. u.) for the glasses with $x \geq 40$ at.% is accompanied by the decrease in the intensity of As and S lines to ~ 3 a. u. This indicates to the fact that if dissociation of AsS dimers does occur when the ionization of ionic flow takes place, it does not play a significant role in our experiments.

Regarding As_2 clusters, the results of our research, mainly, coincide with previous data. The intensity of their lines naturally increases with increasing the arsenic content in the composition of glasses. However, the concentration of these clusters in vapour flows investigated by us is twice as low as compared with other scientific works of researchers.

The concentration of As_3 clusters in vapour flows of As-S materials is very low. A weak line of these particles was detected by us only in mass-spectra of glasses in the vicinity of $As_{40}S_{60}$ composition. However, in previous studies this line was mainly observed in mass-spectra of glasses rich in sulfur ($As_{25}S_{75}$ and $As_{33}S_{67}$ compositions), while in the glasses with high arsenic content, this line was missing.

Close are the results of all studies as to availability of As_4 and As_4S_2 clusters in vapour flows of As-S materials. At this the lines of As_4 particles are clearly revealed only in mass-spectra of glasses with the compositions in the vicinity of $As_{44}S_{56}$. However, in our studies, the intensity of these lines was at the level of 2 - 4 a. u., whereas in previous studies it exceeded 60 a. u.

As_4S_2 clusters are present in vapours of all investigated $As_{100-x}S_x$ glasses of compositions with $33 \leq x \leq 40$ at.% (with intensity of lines from 3 to 5 a. u.). But in previous studies a significant concentration of such atomic particles was also revealed in the glasses rich in sulfur (the range of x is from 20 to 25 at.%).

The results also shows a comparison of the initial chemical composition of glasses before evaporation and the

total chemical composition of the vapour flow. As follows from these data, for many previous experiments [3 - 9] the total mass-spectrometric composition of the vapour phase of glasses does not correspond to the chemical composition of initial materials. This averaged vapour flow contains 4 - 8 at.% of arsenic atoms more than compared with the initial glasses. Exceptions are only $As_{33}S_{67}$ glasses, for which such deviation does not exceed 1 at.%. Unfortunately, the authors of papers indicated above do not give a detailed description of mass-spectrometric experiments by which one could analyze the detected deviations.

In our mass-spectrometric studies within the experimental error the total mass-spectrometric composition of the vapour phase coincides with the chemical composition of glasses before evaporation. We believe this is due to a correct choice of conditions of both the evaporation of glasses from Knudsen cells and the ionization of the vapour flow formed. In particular, the 5-fold increase in the value of flow of ionizing electrons provided much greater probability of ionization of all vapour particles, regardless of their sizes. As a result the conditions for effective ionization of overwhelming majority of vapour flow particles were created in the mass-spectrometer and, accordingly, they all gave contribution to the ionic current of the mass-analyzer.

It should also be noted that mass-spectra of As-S glasses under evaporation rather strongly vary depending on the preparation conditions of the initial material. This is evidenced by the experimental data obtained both by us and other researchers [1, 2]. However, in all these spectra relatively "stable" vapour particles appear whose parts in mass-spectra are little dependent on the conditions of synthesis of the initial material. These include S, S_2 , S_3 , As_2S_3 , AsS_3 , AsS_6 , As_2S_4 , As_3S_4 , As_4S_4 clusters. At the same time, the parts of many atomic complexes vary greatly during the transition from one sample of glasses to another. Among them are AsS, As_2S , S_7 , S_8 , As_3S_2 , As_4S_2 , As_4S_3 . Such behavior of different parts of the vapour is caused by both the differences in the structure of initial glasses synthesized under different technological conditions and the differences in the conditions of conducting mass-spectrometric studies. In addition, atomic complexes in these lists can also vary by their stability in the vapor phase.

The analyzed mass-spectra of As-S glasses are prepared at evaporation temperatures of initial materials from 400 to 600 K, which are by ~ 80 K lower than the melting temperature of appropriate substances. In actual manufacturing condensation processes of amorphous films the evaporation of initial materials is carried out at higher temperatures of the evaporator (500 - 900 K). It is clear that in such circumstances of evaporation mass-spectra of glasses can sufficiently differ from the considered above. But methodically to investigate them by traditional mass-spectrometry methods is much more difficult.

IV. CONCLUSIONS

The results of mass-spectrometric studies of evaporation processes of As-S glasses within the range of chemical compositions from $As_{10}S_{90}$ to $As_{44}S_{56}$ have been analyzed. It has been revealed that mass-spectra of vapour flows of these glasses have a complicated complex character and contain

about three tens of different atomic complexes. But the total mass-spectrometric composition of the vapour phase in the majority of mass-spectroscopic studies does not correspond to the chemical composition of initial materials and is significantly rich in arsenic atoms. This fact is explained by the dependence of the ionization probability of vapour particles by an electron beam of the mass-spectrometer on the size of these particles. With significant increase in the flow density of ionizing electrons the ionization probabilities of different vapour clusters are aligned. Under such circumstances within the experimental error the total mass-spectrometric composition of the vapour phase of As-S glasses coincides with the chemical composition of glasses before evaporation.

The dependences of concentrations of different As_mS_n clusters in the vapour flow on the chemical composition of initial As_xS_{100-x} glasses have been studied. The presence of clear correlations in the behavior of these two parameters has been established. Three types of dependencies have been revealed: a) the concentration of some vapour particles decreases with the growth of x ; b) the concentration of other particles increases in this case; c) the dependence of concentration of some vapour particles on the parameter x has a dome-like shape.

It has been found that the change in the structural state of initial As-S glasses by changing the technological conditions of their synthesis can cause significant changes in the concentrations of various complexes in mass-spectra.

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