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Mass-spectrometric studies of vitreous As_2S_3

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An analyze of vitreous As_2S_3 network structure models and photoinduced change of the structure is done in this paper. Is concluded that the interpretations of the results are not equivocal. Application of mass spectrometry, although it is an indirect method, contribute to the identification of main particles created during the evaporation of As_2S_3 glass in vacuum. As was established, the As_4S_3, As_4S_4, As_4S_5, As_2S_3, As_2S_4, As_2S_5, As_2S_6 molecular units and the $As_3S_4^{\bullet}$, $As_3S_3^{\bullet}$, $As_3S_2^{\bullet}$, $As_3S^{\bullet}$, $As^{\bullet}$, $AsS_2^{\bullet}$, $As_2S^{\bullet}$, $As_3S_2^{\bullet}$, $As_2S_2^{\bullet}$, $S_2^{\bullet}$, $As^{\bullet}$, $As_2^{\bullet}$, $As_3^{\bullet}$ free radicals exist in the gas phase. The clusters like $As_{10}S_{15}$ can be created during the deposition on the substrate. Clusters are characterized by a different spatial structure with the same ratio of As/S atoms of 2:3. This particularity can explain the deposition of thin As_2S_3 films with different optical properties.

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1. Introduction

Unlike semiconductor crystalline state, whose atomic structure is unambiguously determined by well-developed diffraction methods, the vitreous and the amorphous semiconductors have a distorted atomic structure that mainly contains molecular structure units that form the glass network. The X-ray, electron, neutron rays diffraction methods or the EXAFS X-ray absorption method are widely used in order to study the glass structure. However, it's obvious that in the case of the amorphous condensed state, these methods give insufficient information for the reconstruction of the spatial atoms distribution. Therefore, besides the diffraction based methods, complementary methods such as electron spin resonance, nuclear resonance, Mossbauer spectroscopy, etc. have been lately used. Indirect physical methods such as: IR spectroscopy, Raman spectroscopy, and so on are used as well. A bibliographic comparative study reveals that the analysis of the results does not allow a consistent interpretation of the As_2S_3 glass network structure.

We analyze in this paper the existing models of the network structure. Experimental investigation of the As_2S_3 glass is performed for the investigation of gas phase formed during thermal evaporation process using mass spectrometry method. A distinct model for the structure of vitreous chalcogenide As_2S_3 compounds is proposed. The model is based on clusters formation from the elementary components detected in the gaseous phase.

2. Concepts and models regarding the vitreous As_2S_3 structure

The information about the distribution of atoms in the lattice is obtained with the help of X-Ray methods. Planar distribution of atoms in As_2S_3, which in the crystalline state has a monoclinic symmetry, and the transition model to amorphous state are presented in Fig. 1, according to [1].

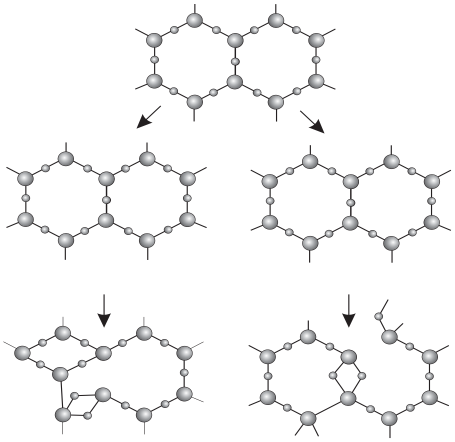

Fig. 1. Planar representation of the redistribution of atoms, which can occur at the transition from the ordered crystalline structure of As_2S_3 to the vitreous structure.

In the first researches on amorphous As_2S_3-based thin films, previously irradiated in open atmosphere with visible light, cubic and orthorhombic As_2O_3 microcrystals of diameter up to 0.2 μm were detected by X-Ray method [2,3]. In order to exclude oxidation, film irradiation was performed in vacuum. The authors of the paper [4], using X-Ray method, have concluded that a redistribution of atoms in As_2S_3-based thin films and change in the first coordination sphere occur due to irradiation. This process may be reversible [5], especially if we consider that the structure of glassy materials consists of atoms arranged without an order in the three-dimensional space [6].

A more detailed study of the As_2S_3 thin films structure, using X-Ray diffraction, proves that this structure consists of densely packed As_4S_6 structural units and that the dominant process, which takes place on irradiation is the polymerization of these molecules [7]. Other papers based on the study of the X-Ray diffraction [8,9] identify that the structure of As_2S_3 fresh thin films consists of As_4S_4 molecules and S_2.

Electron and neutron diffraction methods [10,11] confirmed a multiple-layered structure of As_2S_3 [67]. A decomposition of As_2S_3 during irradiation and As-S bonds redistribution with the formation of homogeneous As-As and S-S bonds were noticed [12]. By EXAFS method, these authors have not observed changes in the first coordination sphere after irradiation of As-S samples and they have concluded that the photostructural reversible changes in amorphous As_2S_3 are produced in the second coordination sphere of atoms.They have explained this result by the existence of a bistable spatial configuration. At the same time, the authors of the paper [13] have detected in glassy As_2S_3 minor changes in the first coordination sphere during the photostructural reversible processes. For to elucidate the nature of the photoinduced reversible processes, the authors [14] have studied As_2S_3 thin films, subjected to three cycles of irradiation-quenching at 220 °C for two hours. As a result, an insignificant increase of As-As bonds and the widening of As-S-As angles in the first order were determined. At the same time, an increase of As-As distances was determined in the intermediate order but no changes in far order were noticed. The experimental results [15] by EXAFS method confirmed changes in the intermediate order in the case of the photostructural reversible changes. These changes are accompanied by the increase of density at irradiation [16]. The authors [17] explain the changes in the intermediate order by the rotation of neighboring AsS_3 pyramids with respect to the common sulfur atom.

Based on IR spectroscopy data, the authors of the paper [18] have proposed the mechanism of irreversible photostructural changes in As_2S_3, which consists in As_4, As_4S_3, As_4S_4, S_8 molecular units condensation for the newly-deposited and irradiated thin films. The changes in IR spectra characteristic for AsS_3 pyramidal structural units [19,20] were found in the case of reversible photoinduced phenomena. From the IR spectroscopic characterizations became clear [21] that the action of light changes also the relationship between the As-S, As-As and S-S bonds in As_2S_3 thin film matrix. A more conclusive result about the photostructural reversible changes at the molecular level was obtained in [22]. According to them, the photostructural reversible changes in the first approximation can be characterized by the following equation:

$$As_2S_3 \rightleftarrows As_2S_{3-X} + S_X$$

The existence of intermediate configuration in glassy materials, that is a positioning of atoms at distances that exceed the local order, allows us to suppose that the size of photostructural changes at the molecular level is comparable with the region of intermediate order in vitreous arsenic sulphide structure. The molecular nature of the structure of freshly-deposited As_2S_3 thin films is determined in all papers. The results differ only in the type of the predominant molecular units.

In one of the first papers [7], the model of densely packed As_4S_6 molecules was proposed, but this molecule was not identified. Further researches showed that freshly-deposited As_2S_3 thin films contain As_4S_4 molecules [23]. Also, As_4S_4 and S_2 molecules have been identified in the films of As_2S_3 obtained on substrates cooled down to a temperature of -170 °C [24]. The authors [12] have also recorded the presence of As_4S_3 molecules in freshly-deposited As_2S_3 thin films using neutron diffraction. As_4S_5 molecules were detected in As_2S_3 thin films by nuclear resonance.

By using a computer modeling technique, M. Popescu [25] obtained the simulation of the structural changes in As_3Se_2 compounds, where As_4Se_4 molecules coexist with disordered layers of As_2Se_x. The proposed model explains the modification of the structure at the level of the intermediate order. O. Shpotyuk [26], based on the concept of coordination defects, developed the model of structural modifications at the atomic level taking into account the topological considerations. Three stages of the process were evidenced, by invoking the excitation of the electronic system in the initial phase.

In other studies, the molecular model of photostructural reversible changes is proposed, based on the switching of certain bonds inside the structure of the molecular units [22]. The model is based on the data provided by EXAFS method [17]. Both papers refer to the model consisting of 11 atoms, which participate to the photostructural reversible changes. According to this model the structure of the sulfur atoms contains a pair of undistributed p-electrons due to which the structure of S-$[As\text{-}[S\text{-}As]]_2$ clusters can be both a bridge and a spiral. These two cluster structures differ in bond energy, so the authors [17] consider this as the main factor in the process of the photostructural reversible changes.

The application of this concept has allowed researchers to explain the multiple aspects of both the structure of these materials and the photoinduced phenomena followed by changes of structure at the atomic level. However, it should be mentioned that the interpretation of the results is not equivocal. Application of mass spectrometry, although it is an indirect method, could contribute, together with the results obtained by the above-mentioned methods to the elucidatation of the vitreous network structure.

3. Study of As_2S_3 gas phase by mass spectrometry

Mass spectrometry is a method which is mainly used for the determination of the high level sensitivity material composition. In a less conventional way, this method can be used to detect the molecular forms which occur during the evaporation in vacuum of bulk arsenic sulphide. The condensed matter structure created during the condensation of these molecular units on substrate can be rebuilt from these data and the use of an appropriate model. The process is nothing more than the deposition of thin films by thermal evaporation of bulk As_2S_3. It is easy to assume that the gas phase will also include other elementary forms besides the atomic arsenic and the sulfur. So, a detailed investigation of gas phase is required.

The composition of the gaseous state above the auripigment (crystalline As_2S_3) was studied for the first time in paper [27]. Studies [28] have clearly demonstrated the existence of As_4S_6 molecule, contested in the case of the application of other methods. However, in this paper the authors have not reached a unique conclusion regarding all the particles contained in the gas phase.

The results of mass-spectrometric measurements which we presented in this paper were performed for various ionization energies, including very low energies, in order to preserve and identify all products formed during evaporation.

The researches were conducted on arsenic sulphide bulk material obtained by direct synthesis of pure arsenic and sulfur elements. Vitreous state is obtained by quenching in water the ampoule with the melt As_2S_3 after a process of synthesis that lasted 24 hours. Subsequently, the material was heated till the glass softening temperature in order to remove tensions. The mass spectrometry measurements are obtained by thermal evaporation of the material deposited on glass capillaries. The initial material subjected to evaporation was crushed and placed in a tantalum basket. Mass spectra of the samples are recorded using the mass spectrometer MX-1320. The temperature evaporator is fixed and remains stable within the range 373-573 K, being controlled with a thermocouple Pt-Rh. Ionization energy ranges from 10 to 70 eV. Spectra were recorded in the range of m/z = 20-800 atomic mass units. Based on mass spectra, chemical formulas of the registered ions were identified.

It is known that the ionic currents consist of molecular ionic currents (when the ions are formed as a result of ionization of molecules) and dissociative ionic currents (when ions are formed in the dissociation of molecules). Mass spectra recorded at low energies of ionization show that As_4S_5, As_4S_4, As_2S_3 and As_2S_4 particles are of molecular nature and therefore, the basic components in the gas phase arsenic sulfide are the molecules As_4S_5, As_4S_4, As_2S_3 and As_2S_4 [29]. However, it should be mentioned that in the gas phase ions ($As_3S_4^+$, $As_3S_3^+$, $As_3S_2^+$, As_3S^+, AsS^+, As_2S^+, $As_2S_2^+$, S_2^+, As_2^+) were detected that could not be attributed to molecules that correspond to all valence bonds saturated. A typical spectrum of the recorded mass units is shown in Fig. 2. Results of basic ionic current intensity measurement recorded in mass spectra of arsenic sulfide films obtained at temperatures of 423, 463, 548 K are shown in Tables 1 and 2 [30]. As a basis for calculating the mass spectra, the AsS^+ ion intensity was taken as 100%. As a comparison, the results obtained by the authors of papers [27, 28] are also presented in the tables.

The results presented in Table 1 show that the concentration of particles in the gas phase of arsenic sulphide depends on the temperature of evaporation and the previous heat treatment conditions of the samples. The predominance of one or other components is determined by the evaporation temperature of the sample.

Table 2 shows that the evaporation of arsenic sulphide at a temperature of T = 423 K, which is lower than the softening temperature T_g = 453 K, takes place with the ratio of As_2S_3/As_4S_4 molecular units of 1.8. Therefore, we can consider that at low temperatures, arsenic sulphide sublimes with predominant formation of As_2S_3 molecules.

At the increase of the evaporation temperature to the values higher than the vitreous arsenic sulphide softening temperature, the As_2S_3/As_4S_4 ratio becomes smaller than one and it is 0.33 at the temperature of T = 548 K. This means that at high evaporation temperatures the As_4S_4 molecules prevail in the gas phase. The obtained results allow us to explain the shift of arsenic sulphide thin film absorption edge, discussed in [31]. Films obtained by high evaporation temperatures are characterized by predominant formation of As_4S_4 structural units, for which it is known that the absorption edge is shifted to higher wavelength region of the spectrum in respect to the absorption edge of As_2S_3.

The results of mass spectrometry data analysis for arsenic sulphide in Table 2 prove that at high temperatures, As_4S_4 molecules are more stable than those of As_2S_3. To confirm the high content of As_4S_4 molecular units in the initial material, the ratio of As_2S_3/As_4S_4 ionic currents were analyzed. From this analysis it results that at high temperatures, there is a lower value of As_2S_3/As_4S_4 ratio of 0.16 as compared to the data from the paper [30].

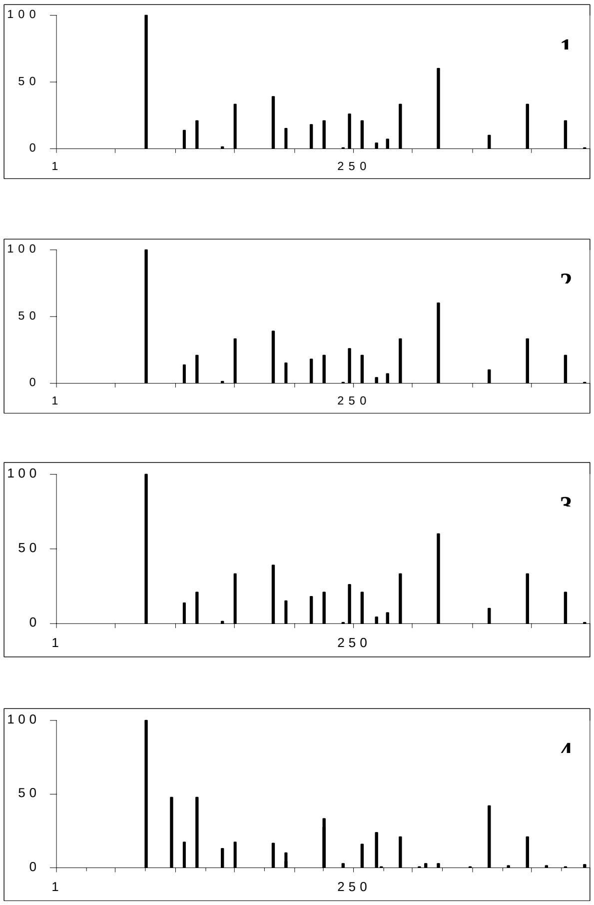

Fig. 2. Normalized mass spectra of vitreous compound As40% S60% at 70 eV ionization energy and 453 K vaporization temperature for: 1 - bulk, 2 - residue, 3-freshly deposed film, 4 - film after argon laser irradiation

Table 1. Changes of mass spectra of arsenic sulphide for different temperatures and processing procedures

Ion$^+$	m/z	423K	463K	548K	463K [29]	573K [30]	463K hardened	463K hardened
S_2	64	33	20	42	14	11,2	25	34
AsS	107	100	100	100	100	100	100	100
As_2	150	33	50	64	6	65	16	13
As_2S	182	76	62	57	12	14,6	25	23
As_2S_2	214	90	87	71	27	36,8	37	39
As_2S_3	246	90	22	90	9	8,4	8	10
As_2S_4	278	50	32	14	15	24	16	21
As_3S	257	80	15	36	5	11,4	33	21
As_3S_2	289	19	25	93	6	12,3	16	21
As_3S_3	321	40	27	107	11	30,2	60	50
As_3S_4	353	33	50	86	19	40,8	45	49
As_4S_3	396	17	4	100	2	5,7	20	5
As_4S_4	428	50	25	270	10	30	50	70
As_4S_5	460	12	25	43	5	12	15	48

Tabel 2. Ionic current intensity recorded in mass spectra of the vitreous compound As40%S60%.

Ion^+	m/z	Ionic current intensity at $U_{ioniz.}$=15 eV for different evaporation temperatures				
		413 K	433 K	453 K	473 K	493 K
As_2S_3	246	100	32,5	20	15	10
As_3S	257	-	-	-	-	-
As_2S_4	278	90	50	85	100	100
As_3S_2	289	-	-	-	-	-
As_4	300	-	-	-	-	-
As_2S_5	310	40	22,5	55	75	68
As_3S_3	321	-	-	-	-	-
As_2S_6	342	4,0	3,3	2,0	1,0	1,3
As_3S_4	396	-	-	-	-	-
As_4S_3	396	70	3,8	5,0	4,0	3,8
As_4S_4	428	90	100	100	100	100
As_4S_5	460	80	70	66	64	81

4. Discussions

As shown in the tables, the conditions of the experiments such as the evaporation temperature and the ionization energy influence the relative intensity of ionic currents. High ionization energy allows the ionization of all particles of gas phase, but in this case, the proportion of the ionic currents resulting from dissociation of molecules is high. Therefore, mass spectra recorded at high ionization energies do not match with the corresponding particles which constitute the gas phase above the material. At low ionization energies not all the molecules are ionized, and therefore they are not even identified. From the above-mentioned aspects, it results that for the correct interpretation of mass spectra we must take into accout the experimental conditions.

The 40% S60% vitreous compound has been widely studied and it is used as reference material for the modeling of the properties of chalcogenide glasses. It is known also the chemical compound As_2S_3, which corresponds to this composition. The mass spectra of these compounds studied by the authors of [30] at ionization energy of 70 eV confirm the overall results of our measurements. Note, however, that the peak identified as belonging to the As_4S_6 molecule was not recorded. At the same time, it was recorded for the first time the peak of $As_2S_6^+$ ion, which is formed from the ionization of the As_4S_6 molecules. The absence of $As_4S_6^+$ ion peak results from the instability of As_4S_6 molecules in the gas phase.

The analysis of As40% S60% mass spectra at low ionization energies allowed the identification of the basic molecular units: As_4S_3, As_4S_4, As_4S_5, As_2S_3, As_2S_4, As_2S_5, As_2S_6. As shown in Table. 2, the gas phase molecular composition in vitreous As_2S_3 compound depends on the temperature at which evaporation is carried out.

The results obtained in this paper by the use of the mass spectrometry method at low ionization energies show that in the As-S system, evaporation reactions with participation of other molecular forms can be identified:

$$\begin{array}{rl} & \nearrow As_4S_5 + As_2S_4 \\ As40\%S60\% \rightarrow 3As_2S_3 & \rightarrow As_4S_4 + As_2S_5 \\ & \searrow As_4S_3 + As_2S_6 \end{array}$$

Besides this, there have been identified ions that do not correspond to molecular forms. In the gas phase, the following particles were found: $As_3S_4^\bullet$, $As_3S_3^\bullet$, $As_3S_2^\bullet$, $As_3S^\bullet$, $AsS^\bullet$, $AsS_2^\bullet$, $As_2S^\bullet$, $As_3S_2^\bullet$, $As_2S_2^\bullet$, $S_2^\bullet$, $As^\bullet$, $As_2^\bullet$, $As_3^\bullet$. They are positive charge free radicals that are particularly active in the formation of condensed state network.

It has been experimentally established that during the evaporation process, the ratio between the arsenic atoms and the sulfur atoms in the gas phase remains unchanged. The ionic current spectrum for different temperatures of evaporation, recorded at the beginning of the sample evaporation and after a period of time, remained unchanged. However, differences in thermodynamic constants of different reactions lead to the different gas phase compositions as well. Thus, the thin films physicochemical properties depend on the temperature at which evaporation occurs.

$$\begin{array}{l} As_4S_4 + As_3S_3^\bullet + As_2S_5 + AsS_3^\bullet \rightarrow As_{10}S_{15} \\ As_4S_5 + As_3S_4^\bullet + As_2S_4 + AsS_2^\bullet \rightarrow As_{10}S_{15} \\ As_4S_3 + As_3S^\bullet + As_2S_6^\bullet + AsS_2^\bullet + S_3 \rightarrow As_{10}S_{15} \end{array}$$

Fig. 3. Possible evaporation and amorphous network formation mechanisms with the participation of molecules and free radicals. $As_{10}S_{15}$ cluster can have different structures.

Using quantum chemistry modeling, the spatial structures of molecules and free radicals composed from sulfur and arsenic atoms can be determined. A network forming mechanism that occurs during condensation on substrate is proposed in Fig. 3. It involves the identified particles in the gas phase and can be designed as $As_{10}S_{15}$ cluster. This configuration satisfies the arsenic/sulfur 2:3

percentage ratio, which has different spatial structure in accordance with its elementary forms. The contents of the elementary particles, as shown by mass spectrometry, depend on the temperature. This mechanism explains the feasibility of As_2S_3 films with different refractive index by varying the evaporation temperature [32]. The diversity of vitreous As_2S_3 compound properties can be explained by structural differences in the second coordination sphere. Photoinduced reversible phenomena [33,34] can also be interpreted as changes in the intermediate order (the second coordinate sphere) as a result of cluster formation with the same $A_{10}S_{15}$ composition, but with a different structure. These clusters are not so stable in order that be identified by mass spectrometric mesurements. They form the glass matrix in the second coordination sphere. The energy barrier between clusters with different structures is insignificant and therefore, the thermal fluctuations restore quickly the state with lower energy as the temperature is higher.

5. Conclusions

By the analysis of existing literature, we can see that several models of the As_2S_3 chalcogenide vitreous glass network were proposed, which are not equivocal. The application of mass spectrometry, as a complementary method of study, allows us to highlighten the formation of clusters such as $As_{10}S_{15}$, characterized by a different spatial structure. Subsequent thermal treatment of films or their illumination can stimulate easy transitions from one structure to another, which explain changes in optical properties.

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