

The evaporation mechanism and mass-spectra of As-S materials

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A simplified two-stage evaporation mechanism of As-S materials has been proposed. During the first stage individual As_nS_m clusters self-organized into different structural forms are formed on the evaporation surface. During the second stage there is a transition into the vapor of clusters which have low total binding energy with the surface. Based on this model and of first principle quantum-mechanical calculations the probabilities of existence of different As_nS_m clusters in the vapor have been defined. It is shown that the concentration of only As_nS_m clusters whose formation energy per one atom exceeds 1.8 eV/at. will be significant in the vapor.

(Received February 26, 2018; accepted October 10, 2018)

Keywords: Evaporation mechanism, Chalcogenide clusters, Chalcogenide vapour

1. Introduction

In the process of preparing amorphous chalcogenide films by thermal evaporation in vacuum there may be distinguished several main stages [1]: a) forming different activated atomic particles on the evaporation surface and their transition into the gas-vapour phase; b) flying away of particles from the evaporation surface into vacuum; c) the evolution of their proper spatial structure and atomic structure by polyatomic particles of the vapor that is equivalent to their self-organization into separate clusters of one or other isomorphous form. However, taking into account the very low concentration of vapour phase particles under standard conditions of evaporation into vacuum the processes of their interaction with each other during movement of the vapour flow from the evaporation surface can be considered insignificant.

To our mind, the determining factor is just the first stage of evaporation, which sets the peculiarities of all subsequent stages. For this stage, there are two limiting mechanisms of forming the activated atomic particles possible. According to the first of these mechanisms the formation of such atomic particles occurs through gradual adjunction to the centre of nucleation of new individual atoms. This mechanism is very complicated to be analyzed. One should take into account the fact that the adjunction of each new atom may be accompanied by a complete restructuring of already existing activated complex into the new formation (including the collapse of the already existing nucleus) on the evaporation surface. The second limiting mechanism is much simpler: a certain activated cluster of corresponding chemical composition is formed in one physical act with a certain number of atoms on the surface. For As-S materials this fact is responsible for the appearance on the evaporation surface of a certain

localized atomic formation with As_nS_m chemical composition. These clusters will be weakly bound to the evaporation surface and to some extent they will be isolated from the bulk of the substance.

Taking into account the nature of the investigated mass-spectra [2] and calculated structures of the vapour phase clusters [3], we believe that the first phase of evaporation of As-S materials follows the second mechanism. Here are the main reasons for this conclusion.

1. The composition of the vapour phase of As-S materials is very complicated because it includes about three dozen of different As_nS_m clusters according to their chemical composition. To form such a broad spectrum of different activated particles by a step-by-step assembly from separate atoms the considerable time intervals are required that do not correspond to the real high rate of evaporation of As-S materials at a relatively low evaporation temperatures from 400 to 800 K.

2. For As_nS_m clusters the formations, quite large by the absolute value of formation energy, are typical that presets the high probabilities of their self-organization into separate atomic formations on the evaporation surface.

3. Strong covalent bonds are acting between atoms in the clusters formed on the surface. It defines small probabilities of their disintegration into separate fragments and, accordingly, sufficiently long lifetimes. Thus the formed clusters have significant probabilities of evaporation in the already finished form.

4. First principle calculations show that the lowest energies of formation are typical for those As_nS_m clusters, which do not have free valences. Others, quite stable clusters, have only one or, exceptionally, two unsaturated chemical bonds. These clusters interact weakly with the evaporation surface and can easily leave it while obtaining small activation energies of the evaporation process.

Thus, the evaporation mechanism of As-S materials and composition of their mass-spectra will much depend on the probability of realization of different atomic complexes in the vapour flow. However, theoretical calculations and experimental studies of probabilities (frequency) of occurrence of different isomers of clusters in the vapour are very small in number. In addition, they mainly concern metal clusters [4 - 7].

The calculations of probabilities of occurrence of different clusters in the vapour are carried out mainly by two methods. The first of them is Monte Carlo method, for which a simple algorithm is realized. 1. The coordinates of the atoms of the cluster are randomly set and the procedure of minimization of the distance between them at a temperature of absolute zero is carried out. 2. The atoms are given the rate according to the Maxwell distribution at temperatures of several tens of Kelvin degrees. 3. At the given temperature the time relaxation (hundreds of thousands of iterations) in the received NVT-ensemble of atoms is held. The system is kept in a thermostatic regulator (e.g. The Nose-Hoover thermostat [8]). During relaxation the solution of equations of motion for all atoms is found by the corresponding mathematical method in a "speedy" form using a certain chosen potential of the interatomic interaction. As a result a certain isomorphic spatial form of the set cluster is obtained.

Another method of investigation of probabilities of forming different isomorphic forms of clusters is first principle DFT method by using molecular-dynamic calculations of Lindeman index dependence on the temperature of a given cluster [9]. In work [10] a slightly modified DFT method for the study of small clusters of gases was proposed. Thus, for different isomorphic forms of clusters the probabilities of their decay or seizure of additional monomers by them have been calculated.

From these examples it follows that the determination of probability of existence of one fixed chemical composition in the gas-vapour phase of different isomorphic forms of clusters requires quite large and lengthy calculations. For materials of As-S system the solution of this problem by mentioned above methods today is unrealistic because it requires modeling studies of more than two dozen of As_nS_m clusters. For each of them one should conduct at least several hundreds of calculations during a period of several hours. Therefore, in this paper we propose a much simpler method for determining the probabilities of realizing different isomorphic forms of As_nS_m clusters in the vapour phase, which is based on the peculiarities of evaporation processes of As-S materials. The theoretical data obtained by this method are compared with the results of mass-spectrometric studies of the evaporation process of As-S glasses.

2. Experimental

Let us consider the process of forming a certain local atomic As_nS_m formation on the evaporation surface. The probability of its occurrence will be determined by the

magnitude of the energy barrier that must be overcome by such a system being self-organized into an activated cluster, weakly bound to the evaporation surface. To calculate such energy barriers is rather difficult, because you need to simulate the evolution of the system from several dozen of atoms by first principle methods. So we make an assumption that the magnitude of this barrier is about the same for all atomic As_nS_m formations. That is, we consider to be roughly similar probabilities of formation on the evaporation surface of different activated atomic formations that can be evaporated further on.

Each formed local activated cluster may exist for some time on the evaporation surface. During its lifetime it can either break up (dissociate) into other structural particles or evaporate. In the first approximation the probability of dissociation P_d of surface activated As_nS_m cluster at the evaporation temperature of the material T_e will be determined by the energy of its formation E_f , taken in terms of a single atom, that is by the value $E_1 = E_f/(m + n)$. Then, according to the statistical laws

$$P_d = A_d \exp(-E_1/kT_e),$$

where A_d is a certain constant.

As a result, the probability that a local activated cluster will be formed and will remain on the evaporation surface in the established form can be found from the relation

$$P_c = [1 - P_d] = [1 - A_d \exp(-E_1/kT_e)].$$

In its turn, the probability of evaporation P_e of the formed activated cluster depends on the energy of its binding with the evaporation surface E_s by a simple functional relation:

$$P_e = A_1 \exp(-E_s/kT_e),$$

where A_1 is also a certain constant.

The cluster activated on the surface will go into the vapor phase if during its life it does not decay and has time to evaporate. Therefore, the probability P of such a complex process for each As_nS_m cluster will be determined by multiplying the values P_c and P_e mentioned above:

$$P = P_c \cdot P_e = A_1 [1 - A_d \exp(-E_1/kT_e)] \exp(-E_s/kT_e).$$

Two unknown constants A_1 and A_d , which act as normalizing factors are included into the resulting relation for the probability of occurrence of a certain atomic As_nS_m cluster in the vapor phase. Their numerical values are important if you want to calculate the probabilities of the mentioned above processes in absolute units. But we expect these probabilities rather in relative units. Then the two constants A_1 and A_d can be taken equal to a unit.

Also note that in case of the evaporation of some sulfur or arsenic atoms the formation of the activated cluster fails and the probability of their evaporation $P = P_e$.

While considering the probability of the formation on the evaporation surface of a certain activated As_nS_m cluster

a statistical and combinational (or entropy) contribution should be considered. It is conditioned by the fact that the possibility of formation of a local atomic formation of a certain complex chemical composition depends on the concentration of various chemical elements in the system, that is on the chemical composition of the evaporated material. Due to this we take into account the collectiveness of the process of formation of that or other cluster from separate atoms with the formation of those or other chemical bonds.

The formation on the evaporation surface of activated As_nS_m cluster requires the simultaneous presence in the given local area of the system of n arsenic atoms and m sulfur atoms. If we consider the process of evaporation of a specific As_xS_{1-x} material, then the probability of realization of the given event on its surface will be proportional to $x^n(1-x)^m$.

Taking into consideration the combination contribution, the probability of evaporation P can be recorded for any evaporated material of A-S system in more general terms, using the function $P(x)$. It defines the dependence of the probability of occurrence in the vapour of a particular As_nS_m cluster on the chemical composition of the evaporated material. At this

$$P(x) = x^n(1-x)^m[1 - \exp(-E_1/kT_e)]\exp(-E_s/kT_e).$$

The resulting relation, of course, ignores many other factors that affect the evaporation processes of chalcogenides. But it allows to carry out the approximate theoretical calculations of relative probabilities of occurrence of different As_nS_m clusters in the vapor phase of As-S materials and to compare these probabilities with intensities of corresponding lines of experimental mass-spectra. Quantitative parameters E_1 and E_s necessary for such calculations can be determined from the results of quantum-mechanical simulation of As_xS_{1-x} clusters [3].

If for As_nS_m cluster with the preset chemical composition there are several isomorphous forms, then for each of them it is necessary to consider its own function of probabilities $P(x)$. The general probability of the existence of As_nS_m clusters in the vapour of the given material will be determined by the sum of the probabilities of occurrence of all identified isomorphous forms for it in the vapour flow.

3. Results

The results of quantum-mechanical first principle calculations of the atomic structure and formation energies of As_nS_m clusters are taken by us from [3]. To calculate the probabilities of existence of different As_nS_m clusters in the vapor phase of As_xS_{1-x} material one should determine two energy parameters for each of them: the formation energy of the cluster per one atom E_1 and the activation energy of its evaporation E_s . It is very easy to find the value of E_1 simply by dividing the formation energy of the cluster E_f by the number of atoms in it. And for finding E_s we used some simple approximations.

1. The value of E_s consists of two main components.

2. The first component is typical for clusters which are composed of atoms with unsaturated valences. In this case, we believe that while finding such a cluster on the evaporation surface these valences will be saturated at the expense of covalent chemical bonds of the cluster with the evaporated material. At this, binding the cluster with the surface may be realized by any of three possible chemical As-As, As-S or S-S bonds in As-S system. The calculations and experimental data [3] indicate that the energies of these three bonds are close enough. Therefore, for approximate calculations one can attribute the average value of $E_b = 2.1$ eV to such bonds on the evaporation surface. Then, the component of the activation energy of evaporation of As_nS_m cluster at the expense of breaking certain chemical bonds

$$E_{s1} = E_b \cdot V,$$

where V is the value of free valences of the chosen cluster (the value V was taken by us directly from first principle calculations of clusters and that's why it can have a non-integral value).

3. The second component of the energy E_s is caused by intermolecular interaction forces and is common to all clusters that are formed on the surface. It can be approximately calculated by using the average energy of Van der Waals interactions per one atom between the cluster and evaporation surface E_W . The quantitative value of this energy for As-S materials can be estimated by the magnitude of 0.1 - 0.3 eV. For calculations we will take the average value $E_W = 0.2$ eV. Also note that only cluster atoms have Van der Waals interaction which are not bound to the surface by covalent bonds. If the number of such atoms in As_nS_m cluster is equal to W , then that second part of the activation energy of evaporation for it will be

$$E_{s2} = E_W \cdot W.$$

Taking into account the introduced approximations for the value E_s we can write such a final relationship:

$$E_s = E_{s1} + E_{s2} = E_b \cdot V + E_W \cdot W.$$

Applying introduced above physical approximations and mathematical formulas obtained, we calculated the energy parameters of evaporation of the most stable isomorphous forms of different As_nS_m clusters. The results of these calculations are shown in Table 1.

Using the data in Table 1, according to the proposed above relations the probabilities of the formation on the surface of different As_nS_m clusters, probabilities of their evaporation and probabilities of their occurrence in the vapor flow at evaporation temperature of 600 K were also calculated. The results of calculation are shown in Table 2. In addition, in the same table the functions of probabilities $P(x)$ are put down which define the dependence of probabilities of existence in the vapor flow of different As_nS_m clusters on the chemical composition of evaporated As_xS_{1-x} material.

4. Discussion

The calculation results show that at accepted approximations the probabilities of dissociation of already formed As_nS_m clusters on the evaporation surface are close to zero. This means that after their self-organization the majority of such clusters can exist for a long time in the surface area of the evaporated material, having

probabilities P_c , which approximately lie within the range of 0.7 - 0.9 arbitrary units (Table 2). Such their behavior is quite natural because of the high energies of formation of clusters discussed in the Table 1 and 2. Therefore, their fluctuation formation leads to a significant reduction of the energy of the system and creates significant potential barriers for further dissociation.

Table 1. Energy parameters of formation on the surface and evaporation of different small As_nS_m clusters

Cluster	Isomorphic form	E_1 , eV/at.	V	E_{s1} , eV	W	E_{s2} , eV	E_s , eV
1.	2.	3.	4.	5.	6.	7.	8.
S	atom	0	2	4.2	0	0	4.2
As	atom	0	3	6.3	0	0	6.3
S_2	S=S	2.2	0	0	2	0.4	0.4
As_2	$As\equiv As$	2.0	0	0	2	0.4	0.4
AsS	-As=S	2.0	0.7	1.5	1	0.2	1.7
S_3-1	S=S=S	2.3	0	0	3	0.2	0.6
S_3-2	triangle	2.2	0	0	3	0.6	0.6
AsS_2-1	-S-As-S-	1.7	2	4.2	1	0.2	4.4
AsS_2-2	S=As=S	2.2	0.6	1.2	1	0.2	1.4
AsS_2-3	ring with As radical	2.2	0.7	1.5	2	0.4	1.9
As_2S-1	-S-As=As-	1.8	1.4	2.9	1	0.2	3.1
As_2S-2	triangle	2.1	0	0	3	0.6	0.6
As_3-1	=As-As=As-	2.2	2.1	4.4	1	0.2	4.6
As_3-2	triangle	2.0	0.7	1.5	2	0.4	1.9
S_4-1	S=S-S=S	2.3	0.8	1.7	2	0.4	2.0
S_4-2	square	2.1	0	0	4	0.8	0.8
S_4-3	star	2.1	0	0	4	0.8	0.8
S_4-4	ring	2.2	0	0	4	0.8	0.8
AsS_3-1	S=S-As=S	2.4	0.4	0.8	3	0.6	1.0
AsS_3-2	ring	2.3	0.4	0.8	3	0.6	1.0
AsS_3-3	star	2.1	0	0	4	0.8	0.8
As_2S_2-1	square	2.2	0	0	4	0.8	0.8
As_2S_2-2	As=S-S=As	1.8	0	0	4	0.8	0.8
As_3S-1	ring	2.2	0.5	1.1	3	0.6	1.7
As_3S-2	roof	2.1	0.5	1.1	3	0.6	1.7
As_4-1	square	2.0	0	0	4	0.8	0.8
As_4-2	tetrahedron	2.5	0	0	3	0.6	0.6

From the analysis of the obtained data one more relationship follows. The probability of existence of a specific As_nS_m cluster in the vapour flow is presumably determined by the probability of its evaporation. According to Table 2, this value is significant for those atomic formations whose total activation energy of evaporation is $E_s < 2.0$ eV. In its turn, this condition in most cases is only satisfied by those isomorphic forms of As_nS_m clusters, in which the total value of free valences of atoms does not exceed one.

All As_nS_m clusters with the formation energy per one atom E_1 from 1.5 eV/at. to 2.5 eV/at. at the evaporation temperature of 600 K have significant probabilities of formation $P > 0.5$. Thus for vast majority of clusters with the value E_1 lower than 1.8 eV/at. the atomic structure with total free valency of atoms larger than one is typical. As a result, the probability of

evaporation of such clusters dramatically reduces and therefore their existence in the vapour flow will be scarcely probable. So, the vapour phase of As-S materials will contain mainly only those As_nS_m clusters, whose formation energy in terms of one atom is larger than 1.8 eV/at.

5. Conclusions

A physical mechanism of vacuum thermal evaporation processes running in As-S materials has been proposed. It is constantly formed on the surface of the evaporated material, broad as to the chemical composition, and spatial isomorphic forms of the spectrum of local atomic As_nS_m formations, which contain up to ten atoms. The relative amount of different

atomic formations is determined by the chemical composition of the evaporated material and its temperature. Formed on the surface separate formations have a long lifetime. While obtaining sufficient activation energy at the expense of thermal fluctuations

they are easily evaporated, forming the vapour flow. Further flying away in vacuum different as to the chemical composition the atomic particles organize themselves in such structures of As_nS_m clusters, for which the lowest formation energies are typical.

Table 2. Probabilities of formation P_c , evaporation P_e and occurrence P in the vapour flow of different small As_nS_m clusters of As_xS_{1-x} materials at the evaporation temperature of 600 K and their functions $P(x)$

Cluster	P_c , arbitrary unit	P_e , arbitrary unit	P , arbitrary unit	$P(x)$, arbitrary unit
S		0	0	-
As		0	0	-
S_2	0.86	0.46	0.40	$0.4 \cdot (1-x)^2$
As_2	0.79	0.46	0.37	$0.37 \cdot x^2$
AsS	0.79	0.04	0.03	$0.03 \cdot x(1-x)$
S_3-1	0.88	0.31	0.28	$0.55 \cdot (1-x)^3$
S_3-2	0.86	0.31	0.27	
AsS_2-1	0.63	0	0	$0.08 \cdot x(1-x)^2$
AsS_2-2	0.86	0.07	0.06	
AsS_2-3	0.86	0.03	0.02	
As_2S-1	0.69	0	0	$0.26 \cdot x^2(1-x)$
As_2S-2	0.83	0.31	0.26	
As_3-1	0.86	0	0	$0.02 \cdot x^3$
As_3-2	0.79	0.03	0.02	
S_4-1	0.88	0.02	0.02	$5.056 \cdot (1-x)^4$
S_4-2	0.83	0.21	0.18	
S_4-3	0.83	0.21	0.18	
S_4-4	0.86	0.21	0.18	
AsS_3-1	0.90	0.14	0.13	$0.44 \cdot x(1-x)^3$
AsS_3-2	0.88	0.14	0.13	
AsS_3-3	0.83	0.21	0.18	
As_2S_2-1	0.86	0.21	0.18	$0.33 \cdot x^2(1-x)^2$
As_2S_2-2	0.69	0.21	0.15	
As_3S-1	0.86	0.04	0.03	$0.06 \cdot x^3(1-x)$
As_3S-2	0.83	0.04	0.03	
As_4-1	0.79	0.21	0.17	$0.46 \cdot x^4$
As_4-2	0.92	0.31	0.29	

By using the structural and energy parameters of different As_nS_m clusters calculated by first principle methods of quantum mechanics, the probabilities of their formation on the evaporation surface and the probabilities of their transition into the vapor phase have been determined. It is shown that the probability of occurrence of a particular As_nS_m cluster in the vapour phase is presumably determined by the probability of its evaporation. In its turn, this value is significant only for those structural forms of As_nS_m clusters, in which the total value of free valences of atoms does not exceed one. It has also been found that this condition is satisfied by those atomic complexes whose formation energy calculated per one atom does not exceed 1.8 eV/at.

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