

## Modelling the Initial Stages of Condensation of As-S Atomic Clusters

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With the use of first-principle quantum-mechanical method DFT the initial phases of condensation processes of 4- and 5-atomic  $As_nS_m$  clusters on the carbon substrate have been studied. It has been determined that due to the break of one or two chemical bonds most clusters during adsorption on the surface of the carbon substrate are transformed from their initial structural shapes into the chain whose ends are covalently bonded with the substrate. The calculated adsorption energies of such clusters on the carbon substrate are equal to 1.7-1.9 eV/atom. Pentagon-shaped  $S_5$ ,  $As_2S_3$  and  $As_4S$  clusters are also highly likely to be adsorbed on the carbon substrate without the change of their spatial shape under the influence of van der Waals forces. For  $As_4$  clusters-molecules such adsorption mechanism is the main one. The energy of such adsorption of clusters is 0.4-0.5 eV/atom. It has been determined that the energy and mechanism of adsorption of  $As_nS_m$  clusters are significantly affected by the dynamics of changes in internal tensions of the atomic system before and after adsorption. Such effect may be more significant in case of adsorption not on the model, but on real, more "rigid" carbon substrates.

**Keywords:** Adsorption, Chalcogenide clusters, First-principle modelling.

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### 1. INTRODUCTION

The use of amorphous materials is becoming more and more widespread nowadays. At the same time the disorder in atomic positions leads to the emergent phenomena unknown in crystals. The experiments also often show an incomprehensible behaviour of amorphous materials characterised by changes in their chemical composition. This suggests that the properties of a large collection of atoms with the disorder reveal the features that are unique, important and useful. Thus, amorphous materials present both a challenge and also an opportunity for the theoretician dealing with the condensed matter.

There exists confusion and disorder of interesting physical processes unique for these systems and important technological applications that could benefit from optimization of materials and their basic understanding. The first step in such researches is modelling the processes of structure formation of amorphous materials under conditions close to the actual technological process of their preparation. Especially, this holds true when dealing with the amorphous films which condensate on substrates.

At the same time, the analysis of the existing state of research studying condensation processes of amorphous films shows that there remains a number of unresolved problems. Both macrothermodynamic and microkinetic theoretical methods studying the kinetics of creation and growth of amorphous films on the surface of substrates pose a range of limitations. This is especially true with regards to deposition processes of the materials with complex chemical composition in

the vapour flows of which various atomic complexes and clusters are formed. Most approximations employed in the theoretical models of such processes are not fully implemented under real conditions or reproduced only within a narrow range of changes in technological parameters of condensation. Yet the forced limitation of the number of differential equations in micro-kinetic approaches makes it impossible to accurately calculate the main parameters of the vacuum deposition of thin layers. All this leads to a very small amount of theoretical and experimental studies of condensation processes of amorphous films, especially for substances with complex chemical composition. Therefore, in this paper, first-principle quantum mechanical methods are used to study the first stages of vacuum condensation on the carbon substrate of disordered embryos of As-S amorphous films, that have many potential applications.

Non-empirical first-principle quantum-mechanical calculations are based on the numerical methods of solving the Schrödinger equation by various methods which consider the entire polyatomic system as a whole. Therefore, non-empirical calculations reflect the behaviour of vapour phase particles during their adsorption on the substrate most really and allow to get their parameters with the required accuracy. But for polyatomic and polyelectronic systems studied by us the practical use of non-empirical methods is limited by a large duration of calculations even when using modern computers. For this reason, in our study we have limited both the size of the substrate cluster and vapour particles condensed on it.

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## 2. CALCULATION METHOD

The correctness of the chosen method and calculation software is a key prerequisite for successful first-principle quantum-mechanical research. Modelling the initial stages of the condensation process for different materials is often performed on the GAMESS software package [1]. Therefore, for modelling the behaviour of vapour phase particles of As-S system on carbon substrates the method of molecular orbitals of this quantum-chemical software has been used. The theoretical bases of this method are broadly enlightened in numerous monographs and manuals [2].

Since we assumed the existence in the analyzed systems of both the fully occupied electronic orbitals and electron orbitals with one electron, that is why the initial optimization calculations were performed by an unlimited Hartree-Fock (UHF) method. The geometrical parameters of the structure of studied systems are considered to be determined by this method reasonably accurately [3]. In order to take into account the contribution into the energy of formation of the system of electronic correlations and interaction of excited electrons with unexcited ones, the final calculations of energy capacity of the system were conducted by using the density functional theory (DFT). Our studies have shown that this method, provided the conditions and parameters of the potential are chosen correctly, ensures quite an accurate definition of the geometric structure and energetic properties of complex atomic systems [4]. Together with the B3LYP potential it provides good calculation results of contribution and energy of van der Waals interaction [5, 6], which is an important consideration when studying condensation processes.

During all stages of calculations valence-split bases 6-31 GF and 6-31 GF\* were used with inserting wave functions of *d*- and *f*-orbitals for "heavy" sulphur and arsenic atoms. Today these bases are widely used for first-principle calculations of various atomic systems [6, 7]. The disadvantage of these bases is a significant increase in the time of calculations. Therefore, for initial estimates of the approximate geometry of modelled systems we often used a standard minimum basis 3 – 21 GF.

In order to accelerate quantum-mechanical calculations, the polarizing *p*-orbitals were not included in the bases of wave functions of hydrogen atoms. At the same time, *d*-orbitals were included in the basis set for carbon atoms. According to the results of the study [8], such basis set with the BLYP potential in DFT method gave very good results of modelling condensation processes of different clusters on the boron nitride substrate. Since the atoms of carbon, boron and nitrogen are quite close to each other in the periodic table, we believe that the parameters of quantum-mechanical calculations will also provide a good description of condensation on carbon substrates.

For atomic clusters with closed rings during the optimization process of the geometry, the change of one geometric parameter causes a change of many other parameters, too, that is often accompanied by slow convergence. Since our carbon substrate was modelled

with the help of the cluster with C<sub>6</sub> rings, then for overcoming this deficiency, we set internal coordinates of system atoms in the calculations by the GAMESS program. In particular, for a six-membered ring the set of internal coordinates contained the lengths of all six chemical bonds, all valence angles between bonds as well as three torsion angles, which take into account the bends of C<sub>6</sub> cycle. The use of advanced internal coordinates provided the best combination of convergence speed of the calculation process and quality of optimization of the system geometry.

During calculations free valences of atoms of the cluster which was imitating the substrate, were saturated with fictitious hydrogen atoms. Such a methodological approach is often used by researchers in the calculations of clusters-radicals [9]. It helps to get rid of undesirable "edge" effects on the received modelling results.

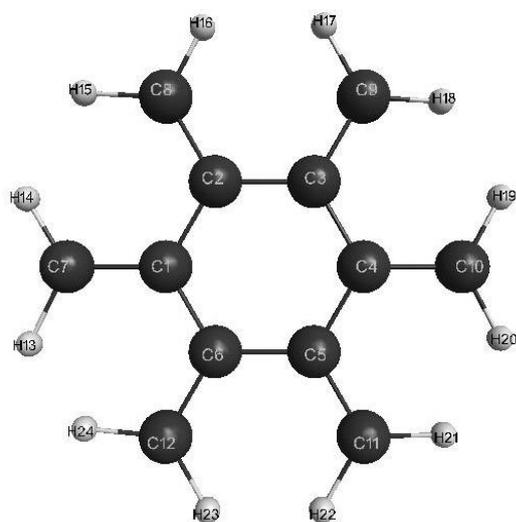
The GAMESS software calculates the total energy  $E_t$  of the model system which is a quantitative characteristic not convenient for the analysis. Therefore, based on the modelling results we determined the adsorption energy  $E_a$  of As<sub>n</sub>S<sub>m</sub> clusters during their condensation on the carbon substrate. It was defined as  $E_a = E_t - E_{ba} - E_v$ , where  $E_{ba}$  is the energy of the cluster- substrate before adsorption of certain As<sub>n</sub>S<sub>m</sub> cluster on it and  $E_v$  is the energy of the appropriate As<sub>n</sub>S<sub>m</sub> cluster in the vapour phase. At the same time the energy of zero fluctuations for the studied system was not taken into account because it is expected not to exceed just few tenths of an electron volt, the value that is within the absolute error of quantum mechanical methods employed [10].

The material for the substrate to model the condensation of As<sub>n</sub>S<sub>m</sub> clusters was chosen to be a thin film of carbon. This choice is conditioned by the fact that most of direct studies of the microstructure by electron microscopy and electronography methods are performed for islet amorphous chalcogenide films deposited on thin supportive carbon layers.

## 3. RESULTS AND DISCUSSION

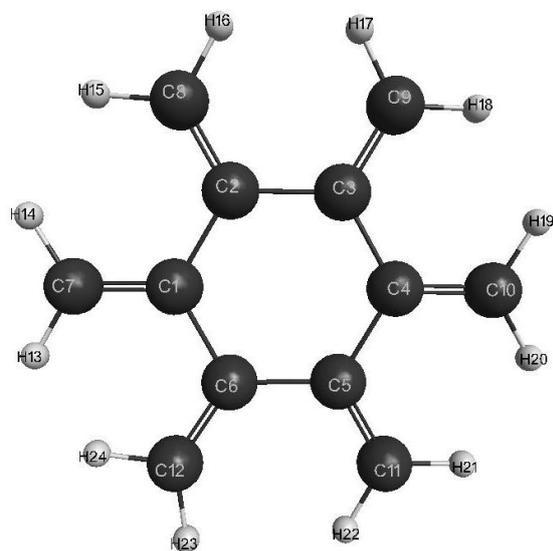
Amorphous carbon films have a layered structure, close to the crystal structure of graphite. This is indicated by the proximity between the parameters of the first two coordination spheres of these two materials. However, in the amorphous films separate layers bend significantly, causing severe deviation from parallelism of their position towards each other. But as a first approximation, we isolated a local area of the carbon substrate on which the condensation of a particular As<sub>n</sub>S<sub>m</sub> cluster in the form of a flat monolayer of 12 carbon atoms is carried out (Fig. 1). At this, dangling bonds of end carbon atoms were saturated with 12 boundary hydrogen atoms. As a result, the system that modelled the substrate contained 24 atoms. For the initial cluster - substrate the average interatomic distance of covalent C-C chemical bond was taken to be equal to 0.142 nm, and of C-H bond equal to 0.11 nm. The calculated energy of formation of such a cluster was equal to 133.5 eV, corresponding to the average energy of one chemical bond, i.e. 5.5 eV. Since the average dissociation energy of C-C and C-H

chemical bonds in carbon layers is close to 5 eV [11], the calculated value of the energy of the initial  $C_{12}H_{12}$  cluster is consistent with the experimental data quite well.



**Fig. 1** – The initial model of the local area of  $C_{12}H_{12}$  carbon film for condensation of  $As_nS_m$  clusters

The optimization of the initial  $C_{12}H_{12}$  cluster showed the restructuring of its boundary area (Fig. 2) with further decrease in the energy of formation by 3.5 eV. The main change in this structure is the formation of double  $C=C$  chemical bonds by the atoms of the central 6-atomic ring with their nearest neighbours in place of the initial single bonds.



**Fig. 2** – The structure of the carbon film cluster after optimization

The above changes in the structure of edge areas of  $C_{12}H_{12}$  initial cluster occurred while optimizing the geometry of the system during condensation of vapour particles on such  $As_nS_m$  clusters. And the nature of these changes significantly depended on the type and peculiarities of the condensed particle structure. Such uncontrollable effects did not allow us to determine the adsorption energy of various vapour particles of  $As_nS_m$

cluster on the carbon substrates in a "pure" form, because different restructuring effects of the substrate itself contributed to its calculated value during the computer optimization of the system geometry.

Our studies have shown that such "edge" effects can be eliminated by increasing the size of the local area of the substrate, adding to it an additional edge chain of 12 carbon atoms. Thus, to study condensation processes in the optimization mode one should take a flat cluster of the carbon substrate not less than  $C_{24}H_{12}$ .

However, we were not able to increase the size of the cluster to such proportions because the calculation time for our computers during optimization of  $C_{24}H_{12}$  structure was about 50 hours. With adding  $As_nS_m$  particles to the system the duration of optimization would increase significantly.

Therefore, we used another way to get rid of "edge" effects. For this, modelling the condensation process was conducted at the initial  $C_{12}H_{12}$  cluster whose geometry describes the atomic structure of real amorphous carbon films more adequately and does not change during simulation. Moreover, this approach is consistent with the energy parameters of both clusters. Thus, the formation of one double  $C=C$  bond in the initial cluster in place of a single one results in the reduction in the energy of the system by 0.6 eV. The experimental value of the energy difference of such bonds exceeds 2 eV [11]. Thus, the optimized geometry of  $C_{12}H_{12}$  cluster as to the energy of the system is not as accurate with relation to the experiment, as compared with its initial structure.

Taking into account these facts, all studies of condensation processes were conducted with the use of the GAMESS software in the mode of calculating the dependence of the energy of the system versus its particular geometrical parameter (mode «surface»).

Such main parameters were: the distance from the condensed  $As_nS_m$  cluster to the substrate; the inclination angle between the cluster plane and the substrate; lengths of various chemical bonds of  $As_nS_m$  cluster and the angles between them. While being studied  $As_nS_m$  clusters were "condensed" in the centre of the selected initial  $C_{12}H_{12}$  monolayer (Fig. 1). Its diameter excluding fictitious hydrogen atoms is 0.56 nm. In the calculations only those 4- and 5-atomic  $As_nS_m$  clusters were condensed on this monolayer, for which the size of the surfaces contacting with the substrate didn't exceed 0.5 nm. At this, the fictitious saturating hydrogen atoms of the substrate didn't form chemical bonds with the atoms of  $As_nS_m$  deposited cluster and had a little impact on energy and geometric parameters of its adsorption. Since we did not conduct the full optimization of the atomic systems from the substrate and the condensed cluster, therefore the adsorption energies of  $As_nS_m$  particles on the carbon substrate were defined by us with a significant relative error, which according to our estimation could reach up to 10-20 %.

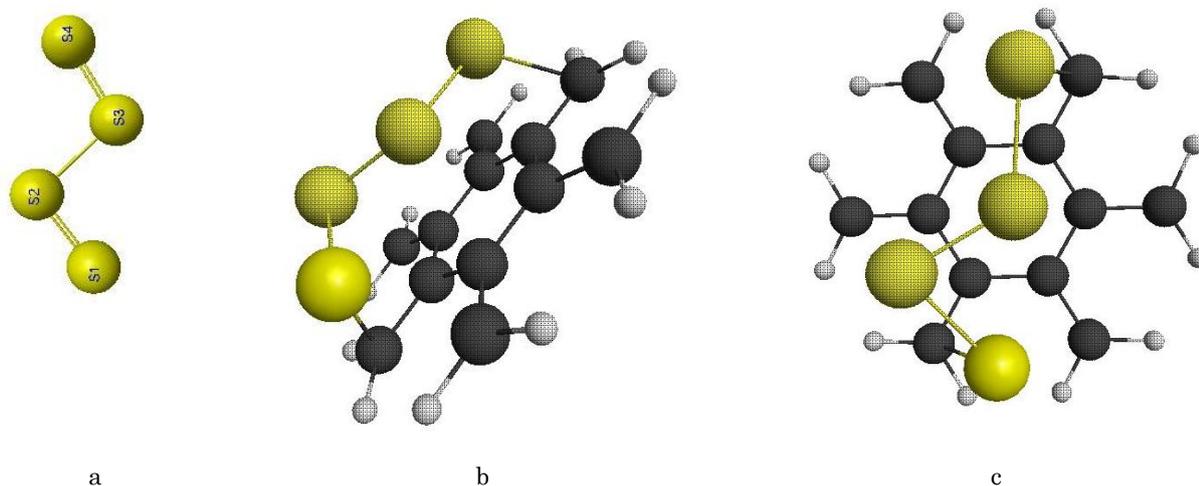
We investigated condensation processes of 12 different most stable 4- and 5-atomic  $As_nS_m$  clusters in the vapour phase with varying spatial structure.

They all can be divided into five groups depending on the type of the geometry of reciprocal positioning of atoms: chains, tetragons and pentagons, branched structures of a "star" shape, spatial "roof"-like shapes,

enclosed polyhedrals.

Let's illustrate the peculiarities of condensation of chain clusters using  $S_4$  atomic particle as an example (Fig. 3a). When being in the vapour phase such a particle has a zigzag – like chain consisting of three links: the central element in the form of a single S-S chemical bond and two ending links with double S = S bond. During condensation, the general zigzag-like

shape of the cluster does not change (Fig. 3b). But the modelled system reached its energy minimum when the chain became practically parallel to the substrate surface. At this, sulphur atoms tend to occupy the spatial location close to the centres of six-membered cells consisting of carbon atoms of the substrate (Fig. 3c).



**Fig. 3** – Geometry of adsorption of  $S_4$  chain cluster on the carbon layer surface

The covalent bonding of  $S_4$  chain with the carbon substrate occurs by transforming its end double S = S bonds into single S-S bonds and forming two single covalent C-S bonds with substrate atoms. The minimal energies of such a system are consistent with the following values of its geometrical parameters: lengths of S-S bonds are within 0.20-0.22 nm, lengths of C-S bonds are within 0.15-0.18 nm, the distance of sulphur atoms to the surface not connected with it is from 0.3 to 0.35 nm, angles between chemical bonds are from 98 ° to 113 °. Such values are 10-20 % more than typical balanced geometric parameters of molecules and condensed states of substances with the participation of sulphur and carbon atoms.

We would like to point out, that during the adsorption process the atomic structure of the carbon substrate also changed to some extent. The main changes occurred in the vicinity of those carbon atoms, which are covalently bonded with the chain. Firstly, such atoms change the type of hybridization from  $sp^2$  to  $sp^3$ . Secondly, the parameters of their first coordination sphere are changed: the interatomic C-C distance slightly increases to 0.15 nm, the angles between bonds become smaller from 120 ° to ~100 °, which is typical for the diamond crystal grid. Thirdly, such atoms "rise" above the substrate approximately by 0.05 nm. Lastly, the H neighbors of these atoms occupy spatial locations more characteristic for the symmetry of  $sp^3$ -hybridization of carbon atoms.

The energy of formation of  $S_4$  cluster equals 9.2 eV. During its adsorption on the carbon surface, the energy of the system decreased to 16.3 eV, which is equal to the total adsorption energy of cluster  $E_a = 7.1$  eV or around 1.8 eV if calculated per one atom. Let's take into account the average values of energy for bonds E

(S-S) = 2.4 eV, E (S = S) = 3.4 eV, E (C-S) = 3.1 eV, E (C-C) $_{sp^2}$  = 4.6 eV and E (C-C) $_{sp^3}$  = 7.3 eV. Thus, when the system is fully free, the reduction of its energy due to the changes in the structure of both the chain and cluster-substrate would approximately be equal to the value of  $\Delta E = [2 \cdot E(S-S) + 2 \cdot E(C-S) + 2 \cdot E(C-C)_{sp^3}] - [2 \cdot E(S=S) + 2 \cdot E(C-C)_{sp^2}] = 9.6$  eV. In this equation, the energy of intermolecular interaction between the cluster and substrate after adsorption is not taken into account. Thus, calculated by this way the value of  $\Delta E$  highly exceeds the value of energy  $E_a$  calculated by the quantum chemistry methods. Such a large deflection cannot be explained only by the presence of weak intermolecular forces in the system. A more significant reason for such considerable differences between the parameters  $\Delta E$  and  $E_a$  is the presence of certain mechanical tensions in adsorbed  $S_4$  chain. Such assumption is supported by deflections in the lengths of chemical bonds and the angle between the bonds of the adsorbed cluster compared to their equilibrium values, which were mentioned earlier.

Many stable  $As_nS_m$  clusters have a zigzag-like shape of spatial polygons. We will examine the peculiarities of their adsorption on the carbon substrate taking  $As_2S_3$  pentagon as an example (Fig. 4a). It consists of one double As = As bond and four single bonds (two of each As-S and S-S bonds).

When such cluster approached the carbon surface and was adsorbed on this surface without transformation of covalent bonds, the energy of the system decreased insignificantly by 1 eV. Therefore, while modelling two more variants of more substantial reduction in the energy of adsorption of  $As_2S_3$  cluster were also considered.

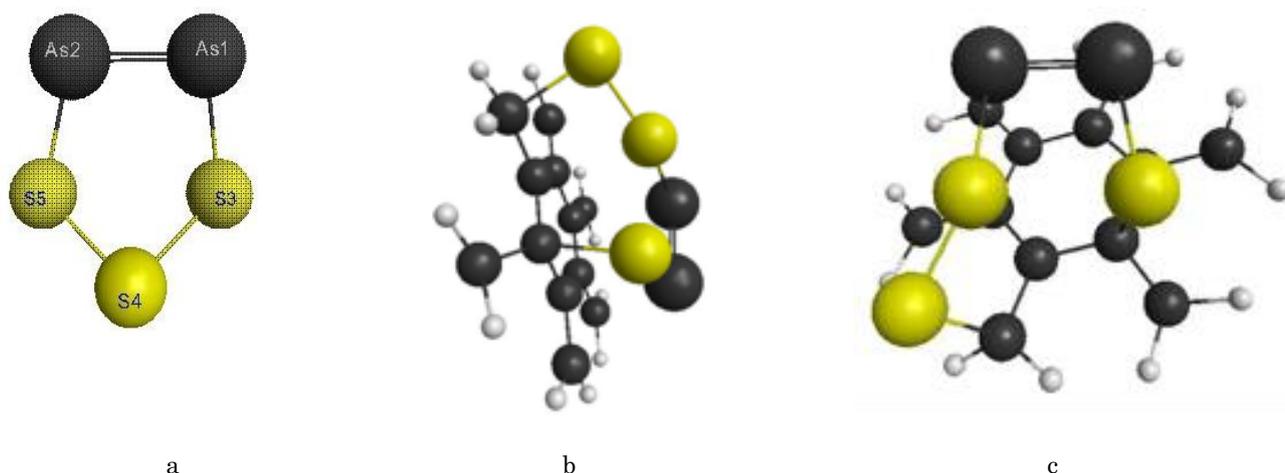


Fig. 4 – Geometry of adsorption of  $\text{As}_2\text{S}_3$  pentagonal cluster on the carbon layer surface

The first variant was the transformation of the double  $\text{As}=\text{As}$  bond into a single one with  $\text{sp}^2$  hybridization of As atoms, followed by the formation of two additional single covalent C-As bonds of the cluster with the substrate. The pentagonal shape of the cluster itself remained unchanged. To some extent, only its interatomic distances changed and especially the angles between the bonds in accordance with a new state of arsenic atoms. With the optimum geometry of both the  $\text{As}_2\text{S}_3$  cluster itself and its placement on the substrate the energy of the system reduced by 8.4 eV (1.7 eV per atom). The following average values of geometric parameters of the system correspond to such state, namely: lengths of S-S bonds are 0.21 nm, lengths of As-S bonds are 0.23 nm, lengths of As-As bonds are 0.25 nm, lengths of As-C bonds are 0.19 nm, angles relative to all atoms  $\sim 100^\circ$ .

In the second variant, the transformation of the adsorbed cluster occurred due to the break of one of single S-S chemical bonds and the formation of two sulphur atoms created by free-valences of two single C-S covalent bonds with the substrate (Fig. 4). As a result, a pentagonal cluster turned into a zigzag-shaped chain which was bonded with the substrate by both covalent and molecular bonds. We would like to point out, that along with the described transformations the atomic structure of  $\text{As}_2\text{S}_3$  cluster in the vicinity of the double  $\text{As}=\text{As}$  bond practically did not change (Fig. 4c). This is due to the fact, that for three-coordinated arsenic atom without its hybridization, its three valence orbitals are located at the angles close to  $90^\circ$ . Besides, such type of bonding geometry is energetically favourable for all stable  $\text{As}_n\text{S}_m$  cluster structures revealed by us which are characterized by the double  $\text{As}=\text{As}$  bond. At the same time the valence angles at sulphur atoms assumed the values typical for the equilibrium magnitude, i.e.  $100^\circ$ .

In such a variant of adsorption the energy of the system reduced by 8.7 eV. Such average values of geometric parameters of the system, as lengths of S-S bonds being 0.205 nm, lengths of As-S bonds being 0.23 nm, lengths of  $\text{As}=\text{As}$  bonds being 0.22 nm, lengths of S-C bonds being 0.16 nm, angles at arsenic atoms  $\sim 90^\circ$  and all other angles  $\sim 100^\circ$ , correspond to

the given state.

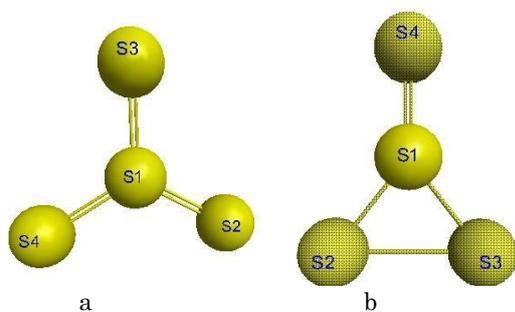
We would like to highlight that in both described variants the adsorbed cluster was placed almost in parallel to the substrate surface at the average distance of 0.4 nm from it. Thus, in the reciprocal placement of atoms of the adsorbed  $\text{As}_2\text{S}_3$  cluster and the substrate, one doesn't observe separate spatial correlations as it was observed in case of  $\text{S}_4$  chain adsorption (Fig. 4 c). The mentioned above geometric parameters of both variants of adsorption are typical for molecules and condensed states of various substances. In addition, with adsorption the substrate structure was also changed in the vicinity of those carbon atoms which were covalently bonded with  $\text{As}_2\text{S}_3$  cluster in both variants. Such changes were analogous to those observed in the case of  $\text{S}_4$  cluster adsorption.

According to our calculations, the energy of formation of free  $\text{As}_2\text{S}_3$  cluster is equal to 11.7 eV. Going forward, we will take into account both the mentioned above average values of energy of different bonds and the average values  $E(\text{As}=\text{As}) = 2.3$  eV,  $E(\text{As-As}) = 1.7$  eV,  $E(\text{As-S}) = 2.1$  eV and  $E(\text{C-As}) = 2.8$  eV. Then, the reduction in the energy of the system during  $\text{As}_2\text{S}_3$  cluster adsorption for the first variant should be approximately equal  $\Delta E = [2 \cdot E(\text{C-As}) + E(\text{As-As}) + 2E(\text{C-C}_{\text{sp}^3})] - [E(\text{As}=\text{As}) + 2E(\text{C-C}_{\text{sp}^2})] = 10.4$  eV. The value of  $\Delta E$  defined in this way exceeds the energy  $E_a = 8.4$  eV by 2 eV calculated by the quantum mechanical methods. Such difference between the estimated value of  $E_a$  and determined by calculations, to a large extent, is caused by the fact that after adsorption a pentagonal shape of  $\text{As}_2\text{S}_3$  cluster didn't change. Consequently, the change of its main structural and energy parameters during adsorption is insignificant and the main contributors to the energy of adsorption were the changes in the type of hybridization of two atoms of the substrate and the emergence of two new covalent As-C bonds in the system. At the same time, serious tensions both in the cluster itself and in local areas of its bonding with the substrate remain in the final structure.

According to the second variant, analogous calculations of the reduction in the energy of the system during adsorption of  $\text{As}_2\text{S}_3$  cluster would

approximately make up the value  $\Delta E = [2 \cdot E(\text{CS}) + 2 E(\text{C-C}_{\text{sp}^3})] - [E(\text{S-S}) + 2 \cdot E(\text{C-C}_{\text{sp}^2})] = 9.2 \text{ eV}$ . This  $\Delta E$  value is very close to the value of energy  $E_a = 8.7 \text{ eV}$ , calculated by the method DFT. At this the reduction (loss) in the energy of the system occurs both due to the formation of two new C-S chemical bonds, and due to the transformation of the closed pentagonal  $\text{As}_2\text{S}_3$  cluster into a more energy favourable open zigzag-shaped chain. The proximity of the estimated energy of chemical bonds with that of calculated with the quantum mechanical methods shows that the structure of 5-atomic  $\text{As}_2\text{S}_3$  chain adsorbed on the carbon substrate is close to its equilibrium state. This assumption is also supported by the values of lengths of chemical bonds and the angle between the bonds of the adsorbed cluster which practically coincide with the equilibrium values.

Some of relatively stable  $\text{As}_n\text{S}_m$  clusters have "star" or "antenna" shapes, as illustrated in the case of  $\text{S}_4$  atomic structures (Fig. 5). Their central element is three-coordinated sulphur atom. During adsorption of such clusters on the carbon substrate, in order to significantly reduce the energy of the system it is necessary to break apart or transform one of their chemical bonds. The calculations showed that in such case the three-coordinated state of the central sulphur atom becomes impossible. As a result, during adsorption, for clusters with "star" and "antenna" shapes the transformation into the chain or dissociation into two  $\text{S}_2$  molecules becomes energetically preferable. In the first case, covalent bonding of clusters with the substrate is realized as described in Fig. 3, and in the second case, two  $\text{S}_2$  molecules are adsorbed on the substrate by means of van der Waals forces.



**Fig. 5** – The structure of  $\text{S}_4$  clusters with "star" (a) and "antenna" (b) shapes

The calculation of energy balance of such processes will be conducted for more stable  $\text{S}_4$  cluster of a "star" shape with the energy of formation of 8.5 eV (for an "antenna" shape the energy of formation is equal to 6.0 eV). With its transformation into the chain during adsorption the energy of the system can fall to 15.3 eV (in accordance with the mentioned above calculations). Then the energy gained at the expense of such processes is 6.8 eV. During the cluster conversion into two  $\text{S}_2$  molecules (the energy of formation of each is equal to 4.4 eV) the energy of the system decreases by 0.3 eV with its additional decreasing due to physical adsorption on the substrate surface by additional 1 eV.

Thus, the adsorption of four- and five-atomic

clusters of "star" and "antenna" shapes most likely occurs through their transformation into the chain shape.

Let us examine the peculiarities of adsorption for clusters of the "roof" type taking the atomic  $\text{As}_3\text{S}$  particle as an example (Fig 6 a.) with the energy of formation equal to 8.2 eV. Several variations for its bonding with the carbon substrate were also considered.

1. When only the intermolecular forces participated in the process, the energy of the system decreased by an insignificant value of  $\sim 1 \text{ eV}$ .

2. While taking into account the break of the most intense  $\text{As}_1\text{-As}_2$  chemical bond the tendency towards transformation of the initial cluster into a quadrangle shape with the energy reduction ranging from 8.2 eV to 8.9 eV was observed. In this cluster a double  $\text{As}=\text{As}$  chemical bond was formed, analogous to  $\text{As}_2\text{S}_3$  pentagon. In this case, general processes of next  $\text{As}_3\text{S}$  cluster adsorption were very similar to  $\text{As}_2\text{S}_3$  particle.

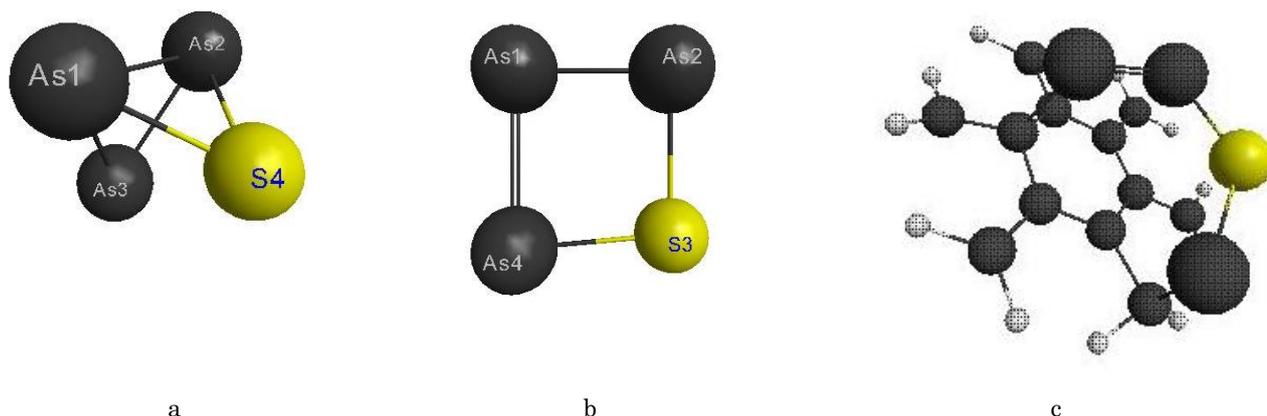
That is, the biggest energy reduction in the energy of the system by  $\sim 7 \text{ eV}$  was achieved during further transformation of  $\text{As}_3\text{S}$  cluster into a zigzag-shaped chain with covalent bonding between its end arsenic atoms and the substrate (Fig. 6 c).

3. The direct formation out of the "roof" of the chain and its adsorption. However, such process requires a simultaneous break of three chemical bonds. This is possible only with overcoming of a very high energy barrier and, therefore, in our opinion, is very unlikely during the time when the cluster is on the surface of the substrate at the excited activated state.

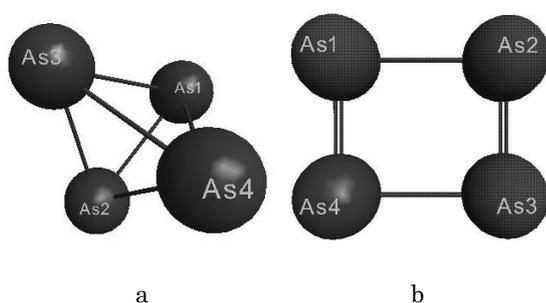
The most stable isomorphous form for the cluster in the shape of  $\text{As}_4$  molecule is tetrahedron (Fig. 7 a), in which each arsenic atom is covalently bonded with three of its neighbours. The energy of formation of this cluster is 9.9 eV. During the investigation of its adsorption several variations of bonding with the carbon substrate were also considered, similar to the three variants discussed earlier for the  $\text{As}_3\text{S}$  cluster. As a result, several differences were discovered in the behaviour of tetrahedral clusters compared to "roof"-shaped clusters.

In particular, the transformation of the initial  $\text{As}_4$  tetrahedron into an intermediate tetragonal form (Fig. 7 b) is energetically very unfavourable, since the energy needed for a quadrangle shape formation equals 7.8 eV, that is 2.1 eV higher than the energy needed for the tetrahedral cluster formation. In addition, this process requires the simultaneous breaks of two covalent As-As chemical bonds. Therefore, we consider that the adsorption of  $\text{As}_4$  molecules on the carbon substrate through an intermediate quadrangle shape is a very unlikely process.

The tetrahedron transformation into the chain shape with subsequent formation of two As-C bonds on the substrate requires the break of three chemical As-As bonds. The total expenses of energy on such transformation are 5.4 eV, which nearly offsets the energy gains from the covalent bonding of the chain with the substrate (5.6 eV). However, at the same time two double  $\text{As}=\text{As}$  bonds instead of single ones are



**Fig. 6** – The structure of  $As_3S$  clusters in the "roof" (a), tetragon shapes (b), and the geometry of its adsorption on the carbon substrate (c)



**Fig. 7** –  $As_4$  cluster structure with tetrahedron (a) and rectangle (b) shapes

additionally formed in the chain. Quantum-mechanical calculations of such processes show that during transformation of tetrahedral-shaped  $As_4$  cluster into a chain with the most optimal position on the substrate, the energy equals to  $E_a = 3.7$  eV. The reduction in the energy of the system by such value occurs mainly due to the transition of two carbon atoms of the substrate into a new  $sp^2$ -hybrid state. Such  $E_a$  value is quite close to the energy of adsorption of  $As_4$  molecule on the carbon surface due to the intermolecular forces only. Thus, the cluster-tetrahedron is placed in such a way that one of its faces is practically parallel to the substrate surface. The data obtained by us show that two variants of adsorption of the molecule  $As_4$  on the carbon substrate may be probable: its placement exactly on the surface due to Van der Waals forces or the transformation of its tetrahedron shape into a chain shape.

The table below lists the calculated energy values of adsorption of various  $As_nS_m$  clusters on the carbon substrate. Their analysis shows that the most probable mechanism for the initial stages of condensation of polyatomic parts of vapour phase of As-S materials is their transformation into the chain shape with covalent bonding of the end atoms of the newly formed chain with the substrate. At the same time, in most cases the values ( $\Delta E$ ) of the reduction in the energy levels of the system calculated on the basis of the energy balance of chemical bonds exceed the  $E_a$  values which are calculated by quantum mechanical method DFT. Such difference can be explained by the fact that simple

calculations of changes in the energies of the system only due to the break of some bonds and the formation of other chemical bonds do not take into account the important energy component. It is conditioned by the presence of significant mechanical tensions both in the initial  $As_nS_m$  cluster and in the substrate-cluster system after condensation of the latter. At the first principle calculations with the use of DFT method the presence of such tensions is taken into account directly in the value of clusters adsorption. Therefore, in our opinion,  $E_a$  values are more accurate parameters to describe the processes of  $As_nS_m$  cluster condensation on the carbon substrate.

During modelling the adsorption, of  $As_nS_m$  clusters the changes in geometric parameters of the entire system were observed on the surface of the limited area of the carbon substrate in the form of one-atomic layer, that is the changes of the cluster itself and of the substrate. In particular, the main structural changes in the substrate took place at its ends (Fig. 3, Fig. 4). Such changes were possible because of the existence of various levels of freedom for the relocation of atoms in the monolayer, especially near its free ends. The high mobility of atoms of the substrate allowed to reduce the energy of the studied systems that was reflected by the values of  $E_a$ . In the real massive substrates the dimensional mobility of the atoms will be much lower. It will significantly limit the possibilities of structural relaxation of different clusters at their adsorption on the massive carbon substrate. That is why, in real processes of  $As_nS_m$  clusters condensation the values of  $E_a$  should be lower than those listed in the table.

According to our assessments such reduction may make up 1 – 2 Ev, and the real energies of adsorption of most 4 –and 5 –atomic clusters of vapours of As-S materials will be equal to 6 – 7 Ev or  $\sim 1.5$  eV per atom.

If to take the reduction in the value of  $E_a$  mentioned above for real processes of condensation into consideration, then in case of tetrahedral  $As_4$  clusters the energy of their adsorption with the transformation into the chain will be equal to  $\sim 2$  Ev. It is very close to the calculated value  $E_a = 1.3$  Ev during adsorption of  $As_4$  tetrahedrons without their structural transformations. However, in this case we should take into account that for transformation of the tetrahedron into an isomorphic chain shape it is necessary to overcome a

**Table 1** –The energies of adsorption of various  $As_nS_m$  clusters during condensation on the carbon substrate, calculated by the DFT method ( $E_a$ ) and by the energies of chemical bonds ( $\Delta E$ )

Cluster	Structure in vapor phase	Structure after absorption	$E_a$ , eV	$\Delta E$ , eV
$S_4$	Chain	Chain	7.1	9.6
$S_4$	Star	Chain	7.8	6.8
$As_2S_3$	Pentagon	Pentagon	8.4	10.4
$As_2S_3$	Pentagon	Chain	8.7	9.2
$As_3S$	Roof	Chain	7.1	7.7
$As_4$	Tetrahedron	Chain	3.7	2.2
$As_4$	Tetrahedron	Tetrahedron	1.3	–

very high energy barrier, which exceeds 5 Ev. Under such conditions, realistically more likely is the adsorption of  $As_4$  clusters on the carbon substrate in a tetrahedral form due to the influence of weak intermolecular forces. Such conclusion is also supported by the condensation of amorphous arsenic films, whose basis of the atomic structure are  $As_4$  molecules.

#### 4. CONCLUSION

For modelling with the use of first-principle quantum mechanical methods of condensation processes of four- and five-atomic  $As_nS_m$  clusters, it is sufficient to take a flat monolayer of the graphite structure with 12 carbon atoms the free valences of which are saturated with hydrogen as the smallest fragment of the carbon substrate. Theoretically, there have been investigated the condensation processes of 12 different clusters which are more stable in vapour phase and have different dimensional structure: chain, polygon, branched structure of a “star” shape, spatial shape of a “roof” type and closed polyhedron. For all such shapes of isomorphic forms of clusters the energies of their adsorption on the carbon substrate have been determined. For this, there has been used the value of full energy of the atomic system, consisting of a monolayer, substrate and the appropriate  $As_nS_m$  cluster optimally placed above its centre.

The analysis of modelling results shows that the adsorption on the carbon substrate of most  $As_nS_m$  clusters occurs due to the break of one or two of their chemical bonds followed by their transformation into the chain shape, which is covalently bonded with the substrate by its end atoms. Thus, the saturating hydrogen atoms of the substrate didn't form strong chemical bonds with atoms of clusters and had a little effect on energy and geometric parameters of their adsorption. Separate clusters with pentagon and polygon shapes are highly probable to be also adsorbed on the carbon substrate without changes in their spatial shape due to Van der Waals forces (for  $As_4$  molecules this is the main adsorption mechanism). In all

cases the area of  $As_nS_m$  clusters during adsorption is positioned in parallel to the substrate surface.

The system achieves a deeper energy minimum if during adsorption not only the structure transformation of  $As_nS_mO$  clusters occurs, but also the atomic structure of the carbon substrate changes, to a certain extent, especially on the edges and in the vicinity of those carbon atoms which are covalently bonded with the cluster. The most important of them are the change in their hybridization type from  $sp^2$  to  $sp^3$  by such atoms and their elevation above the surface of the graphite monolayer. Also, such changes have been substantially more significant if the covalent bonding of the cluster had occurred with the participation of more independent edge atoms of carbon.

The lengths of chemical bonds and the angles between them in the atomic structure of the substrate with the adsorbed cluster to certain extent differ from equilibrium ones. This points to the presence of significant mechanical tensions in such systems. Moreover, for some clusters their own internal tensions are reduced after adsorption, but for others – they increase. But in the carbon substrate-monolayer the internal tensions always increase after adsorption of the clusters. Upon condensation of the clusters on real carbon substrates the increase of internal tensions in the system will be even more significant, as the possibility of their partial relaxation due to “flexibility” of the structure, which is characteristic for the model-substrate in the form of a small monolayer area, will disappear.

In most cases the value of adsorption energy of  $As_nS_m$  clusters on the carbon substrate can be approximately calculated based on the difference in energy levels of chemical bonds of the system before and after adsorption. However, such values are approximately  $\sim 20\%$  higher than the values calculated with the use of the quantum-mechanical method DFT. Such differences are namely due to the forces of the mechanical tensions inside the system.

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