Formation of copper clusters on the surface of a xenon buffer layer

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Abstract. We applied the molecular dynamics technique to the study of the formation of three-dimensional nanoclusters on a xenon surface. The main physical mechanisms were established of the processes of formation of their structure. Equilibrium configurations of copper clusters on the solid xenon layer were determined and the energies of their formation were calculated.

1. Introduction

Studying the formation processes of three-dimensional nanoclusters on different solid surfaces is of great importance for the development of new technologies. One of the most promising technologies used for the development of such nanocluster structures is the buffer-layer-assisted growth (BLAG) [1]. During the BLAG process atoms, (or molecules) are deposited from vapor phase onto a solid inert gas multilayer (as Xe) that prevents their immediate contact with the substrate. Experiments have shown that these species are mobile and form 3D nanostructures on the Xe layer. Thermal desorption of the rare gas then delivers them to the substrate.

The buffer-layer-assisted growth allows one to form nanostructures of single elements or compounds on any substrate, potentially with control over the size and spatial distribution of the nanostructures. These nanostructures can be incorporated to form composites by a sequential growth of nanostructures and thin film deposition.

The efficient use of the BLAG method requires information on the energy profile of the cluster creation and diffusion on the buffer layer of an inert gas. So far, data are lacking on the nucleation of such structures and the physical mechanisms of their growth. No studies have been carried out of the mobility of both adatoms and clusters of different sizes on the surface of a solid phase of inert gas, making it difficult to develop adequate theoretical models describing the aggregation of clusters. Computer simulation methods are widely used for studying the properties of complex systems. The method of molecular dynamics is considered to be an efficient tool that allows one to study different defects in crystals. The essence of this method consists in the computer solution of the equations of motion for each atom of the system with a specified Hamiltonian system interaction.

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The goal of the present study was to use the molecular dynamics method for the investigation of the physical processes of the formation of three-dimensional copper clusters on the surface of solid xenon.

2. Simulation details

The molecular dynamics method was used to study the mobility of copper clusters on the surface of solid xenon. The interaction of the metal atoms was described by the embedded atom model [2]. The interaction energy of the copper atoms was calculated as the sum of pair interactions and the energy of "embedding":

$$E = \sum_i F_i(\rho_i) + \frac{1}{2}\sum_{j \neq i} \phi_{ij}(R_{ij}), \tag{1}$$

where ϕ_{ij} is the pair interaction potential, and $F_i(\rho_i)$ is the energy necessary for embedding atom *i* in an electron gas at a point with electron density ρ_i . The electron density is found as

$$\rho_i = \sum_{j \neq i} \rho_j^0(R_{ji}), \tag{2}$$

where $\rho_j^0(R_{ij})$ is the electron density from an atom of type *j* at a distance R_{ij}. The functions describing the interatomic pair interaction, the atomic electron density, and the embedding function in the electron gas for copper atoms were obtained with the use of experimental data and quantum-mechanical calculations of the various crystallographic structures and the Cu dimer [3]. We could then use those results for calculating the characteristics of small copper clusters.

The Xe–Xe and Cu–Xe interactions are described by Lennard-Jones potentials with an auxiliary function that changes the potential in such a way that the potential value and its first derivative become equal to zero at a distance equal to the cutoff radius r_c [4]:

$$\phi(r) = 4\varepsilon\left[\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\} + \left(6r_c^{-12} - 3r_c^{-6}\right)\left(\frac{r}{r_c}\right)^2 - \left(7r_c^{-12} - 4r_c^{-6}\right)\right]. \tag{3}$$

The value of r_c was chosen equal to r_c = 0.995 nm for both potentials. The values of σ and ε for the Xe–Xe interaction were taken from [5]: ε = 0.01997 eV, σ = 0.398 nm.

The Lennard-Jones potential has been used previously by other authors for studying the interaction of metals with a rare gas surface [6]. In analogy with [6], the parameters of the potential describing the Cu–Xe interaction were chosen consistent with the experimentally observed value of the binding energy of the xenon atom to the (111) surface of copper (0.20 eV) and the value of the equilibrium distance of a xenon adatom from the copper surface (0.36 nm) [7]. The values obtained for the parameters of the potential are ε = 0.0212 eV and σ = 0.369 nm.

The computer simulation of the formation and diffusion of metallic clusters was carried out by the molecular dynamics method. The calculated cell is a parallelepiped with dimensions of 5.26, 4.55, and 5.37 nm along the X, Y, and Z axes, respectively. The X axis had the crystallographic direction $\left[10\bar{1}\right]$, the Y axis $\left[1\bar{2}1\right]$, and the Z axis $[111]$. Periodic boundary conditions were used along the X and Y directions. The diffusion of copper clusters occurred on a substrate represented by 13 atomic layers of closely-packed (111) Xe planes. The first three layers were fixed in positions of an ideal fcc lattice.

3. Results and discussion

The copper deposition on the buffer xenon layer at 50 K was calculated using the method of molecular dynamics. Figure 1 gives an example of the computational results for a structure formed on the Xe-surface during the deposition of 0.1 copper monolayer (a typical deposition value for BLAG).

Figure 1 shows two large metal clusters embedded into a solid xenon layer. These clusters result from the merging of copper adatoms and clusters of a smaller size. The large metal clusters are surrounded by xenon atoms forced out of the substrate. The implanted copper clusters are immobile nuclei of three-dimensional metal clusters. The figure also shows clusters of a smaller size formed via merging of individual surface-migrating copper adatoms. Their diffusion was studied earlier [8].

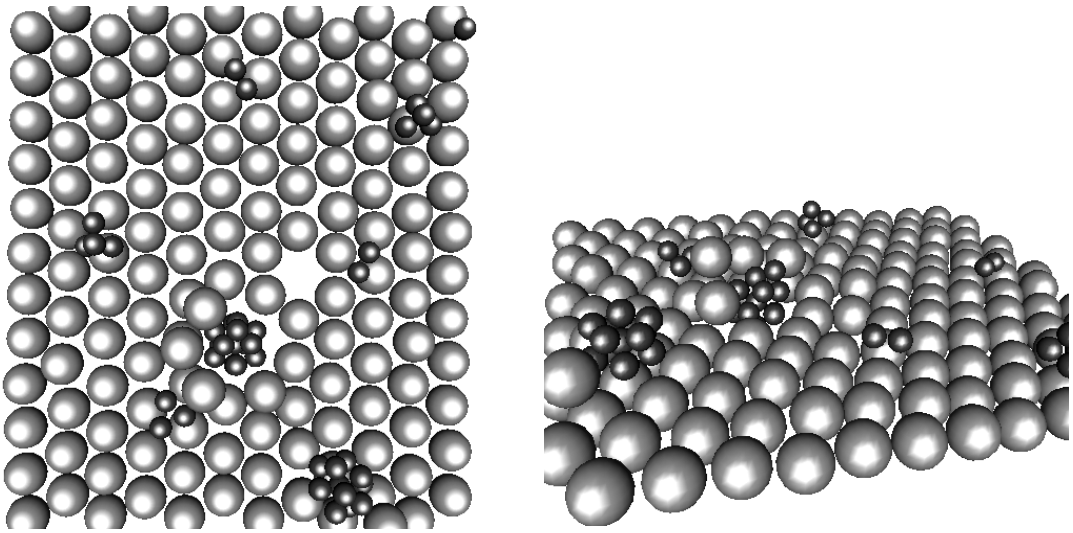


Figure 1. Different projections of the atom surface structure obtained through simulation of the deposition of 0.1 copper monolayer onto the xenon substrate (111), T = 50 K. The balls of a larger radius are xenon atoms, the copper atoms have a dark color.

The results allow us to represent the growth of three-dimensional nanoclusters in the following way. On reaching a critical size, the metal cluster is embedded into the xenon layer and forms a cluster with a surface vacancy. A displaced atom of inert gas is bound to the cluster and remains next to it. Figure 2 gives an example of a change in the Xe-surface structure observed during the investigation of

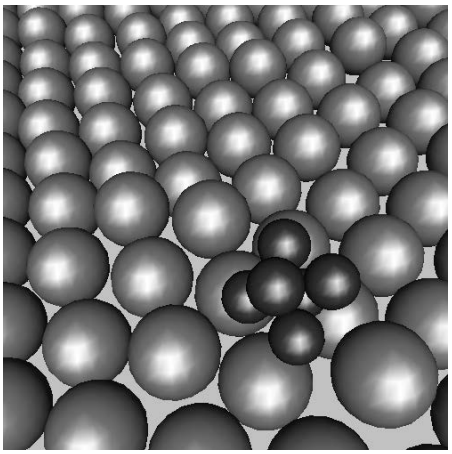
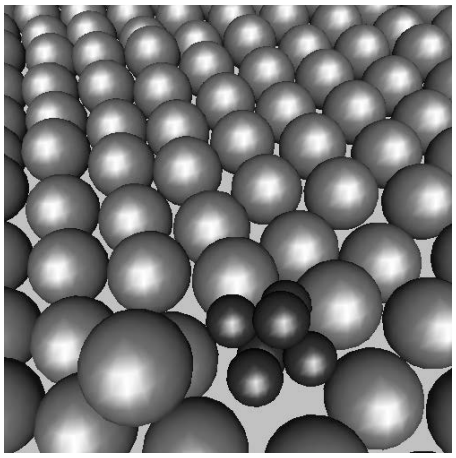
a)  (b) 

Figure 2. Atomic configuration of copper clusters (balls of a smaller size) before and after the displacement of xenon atom from the surface layer, T = 50 K. The bright balls of larger radius are xenon atoms; the copper atoms have a smaller radius and a dark color.

the migration of the cluster. The time interval for a change in the structure as shown in figures 2a and 2b is less than 0.1 ns. The figures show that after the displacement of xenon atoms the cluster embeds itself into the layer of inert gas. This cluster can grow by other approaching small-size metal clusters that can freely migrate on the buffer surface layer. Subsequently, the displaced inert gas atoms wrap up the cluster from the top forming a xenon "coat".

To determine the reasons for the initial embedment of metal clusters into the inert gas layer, we calculated the formation energy of the complex of copper clusters with the surface vacancy. The formation energy was calculated as the difference of energies between two systems. One system was represented by the $Cu^{(n)}$ cluster located on the atomically smooth surface of xenon. Figure 3 shows the atom configurations of $Cu^{(n)}$ clusters located on the atomically smooth surface of xenon that have a minimum formation energy. The other system was represented by the relaxed configuration of the $Cu^{(n)}$ cluster located in the surface vacancy and the xenon adatom. A vacancy was formed next to the cluster on the Xe-surface.

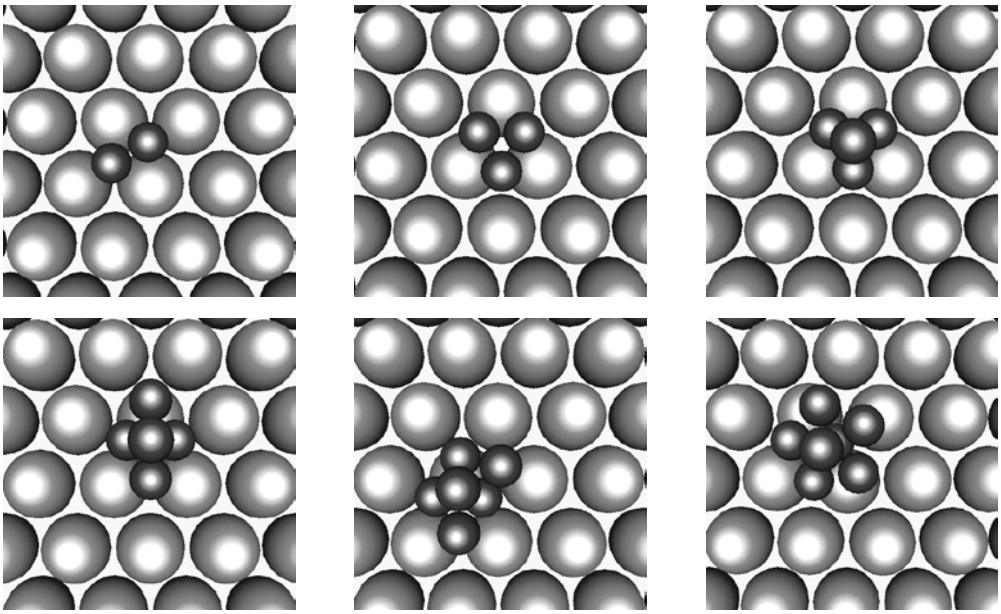


Figure 3. Atomic configuration of copper clusters on the xenon surface. The brighter balls of a larger radius are xenon atoms; the balls of dark color and a smaller size are copper atoms.

The xenon adatom was located at such a distance from $Cu^{(n)}$ that the elastic interaction between the defects could be neglected. The computations were performed in the following way: the initial defective configuration was kept at T = 50 K for a period of time sufficient for the system thermalization. Afterwards, the energy was diverted from the system by switching on the friction mode until T = 0 was reached.

The computational results are given in figure 4. The figure shows that it is energy-advantageous for the copper clusters to be implanted into the surface with the displacement of the xenon atom. However, the formation of the $Cu^{(6)} - V$ cluster is the most

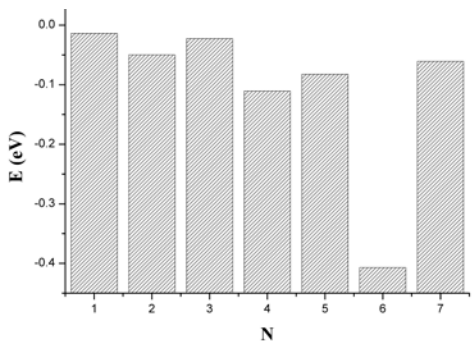


Figure 4. Formation energy of the complexes of copper cluster consisting of N copper atoms with a xenon surface vacancy on the {111} surface.

energy–efficient process. A decrease and an increase in the cluster size result in the decay of the probability of a cluster formation process. The energy gain is 0.4 eV. Presently, the mechanisms that produce such an essential change in energy are not clear. However, the interesting fact is that the volume of the $Cu^{(6)}$ cluster is approximately equal to that of the displaced xenon atom. The data presented show that a change in the bonding energy of vacancies and metal clusters can depend strongly on their sizes and influence significantly the kinetics of nucleation and growth of three-dimensional clusters on the buffer layer.

4. Conclusions

The paper describes an application of the method of molecular dynamics to the study of the formation of three-dimensional nanoclusters on a xenon surface. The main physical mechanisms of the formation processes of their structure were established.

Equilibrium configurations of copper clusters on the solid xenon layer were determined; the energies of their formation were calculated. The method of computer simulation was used for the computation of the formation energy of defects consisting of surface vacancies and copper nanoclusters.

It was established that copper clusters are embedded into the xenon substrate by displacing its atoms to the surface. This allows one to explain the available experimental data related to a change in the spectra of the X-ray photoemission with the deposition time [9]. The results obtained show that the change in the bond energy of surface vacancies and metal clusters of different sizes can significantly influence the kinetics of nucleation and growth of three-dimensional clusters on the buffer layer.

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