Structure of Ag Microclusters on the Surface of Silver Halide Crystals

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Abstract

Empirical two- and three-particle potentials were used to determine the structure of Ag microcrystals on the surface of silver halide crystals considered as a support. Two-dimensional periodicity of two-particle potential, describing interaction between the atoms in the microcluster and the support's atoms, was taken into account. Different possible orientations of microclusters with regard to support's surface and different initial configurations of microclusters were considered. It is analyzed in what way the initial structure of the microcluster is transformed as a result of the interaction with the support and how the tendency to create the planar microclusters, noted in [1,2], is affected by taking into account the two-dimensional periodicity.

Introduction

In [1,2] we used empirical two- and three-particle potentials to determine the structure of silver microclusters on the surface. The interaction of the atoms in the cluster was modelled by the empirical two- and three-body potential functions introduced in [3-10] for monoatomic solid bodies with cubic symmetry including both metals (alka-line metals, noble metals, aliminium, iron, calcium) and nonmetals (silicon, carbon). Parameters of these potentials were fitted to properties of the bulk solid (cohesive energy, lattice spacing, phonon frequencies, elastic constants and vacancy formation energy) and the potentials have been shown to give sensible structures for clusters [3-10]. The particular values of the potentials for Ag were obtained in [10]. In [1,2] the interaction of the atoms in the cluster with the surface was modelled by the Lennard-Jones potential and approximation used did not take into account the periodicity of the atoms in the surface.

In this paper we will use more subtle approximation for the potential describing the interaction between the atoms in the microcluster and the support's atoms, which takes into account the two-dimensional periodicity. We will consider in what way the structure of the clusters, obtained in [1,2], is transformed in this approximation.

The Potentials

The two- and three-body potentials of the interaction between silver atoms in the cluster are taken following paper [10]. We used these potentials in [1,2]. The pair potential is a Rydberg potential

$$U_{ij} = -D(1+a_2\rho_{ij})\exp(-a_2\rho_{ij}) + \exp[-50(\rho_{ij}+0.2)], \qquad (1)$$

where D is two-body dissociation energy, a_2 is the the pair potential parameter, (ρ_{ij} is the reduced interatomic distance

$$\rho_{ij} = (r_{ij} - r_e)/r_{e},, \qquad (2)$$

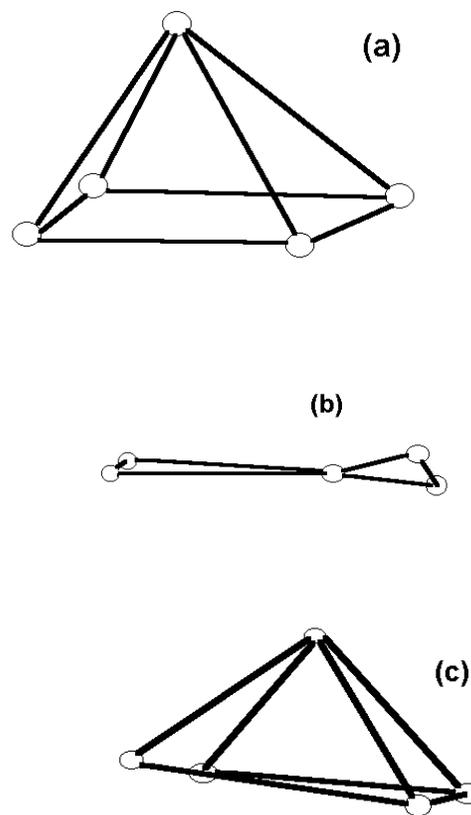r_e is the equilibrium distance of the two-body potential.

Figure 1. 5-atom case. Pyramid with a plane of the base parallel to the support.

The three-body potential has the form

$$W_{ijk} = DP(Q_1,Q_2,Q_3) \exp(-a_3Q_1), \qquad (3)$$

where a_3 is a three-body potential parameter and P(•) is a totally symmetric polynomial in the symmetry coordinates Q_i ($1 \leq i \leq 3$) for the permutation of the three indistinguishable particles:

$$\begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix} = \begin{pmatrix} (1/3)^{1/2} & (1/3)^{1/2} & (1/3)^{1/2} \\ 0 & (1/2)^{1/2} & -(1/2)^{1/2} \\ (2/3)^{1/2} & -(1/6)^{1/2} & -(1/6)^{1/2} \end{pmatrix} \begin{pmatrix} \rho_{ij} \\ \rho_{ik} \\ \rho_{jk} \end{pmatrix}. \quad (4)$$

The polynomial $P(\bullet)$ is quartic:

$$P(Q_1, Q_2, Q_3) = c_0 + c_1 Q_1 + c_2 Q_1^2 + c_3(Q_2^2 +$$

$$+ Q_3^2) + c_4 Q_1^3 + c_5 Q_1(Q_2^2 + Q_3^2) +$$

$$+ c_6(Q_1^3 - 3Q_3Q_2^2) + c_7 Q_1^4 + \quad (5)$$

$$+ c_8 Q_1^2(Q_2^2 + Q_3^2) + c_9(Q_2^2 + Q_3^2)^2 +$$

$$c_{10}Q_1(Q_3^3 - 3Q_3Q_2^2).$$

The coefficients in the polynomial were determined in [10] by the comparison with the elastic constants and chosen phonon frequencies for the face-centered cubic lattice and had the following values:

$a_2 = 6.0,$ $a_3 = 5.5,$ $D = 0.6208$ eV,

$r_e = 2.8792$ A,

$c_0 = 0.3872,$ $c_1 = 2.3220,$ $c_2 = 4.4846,$

$c_3 = -3,3658,$ $c_4 = -4.4065,$ $c_5 = -8.8459,$

$c_6 = 1.7918,$ $c_7 = -3.3523,$ $c_8 = 9.4557,$

$c_9 = 3.4883,$ $c_{10} = -10.2426.$

The equilibrium configurations of the silver clusters with the number of atoms from three to seven without support's influence are given in [10].

We will model an interaction of the atoms in the cluster with the support following [11,12]. Generally this interaction can be written as follows:

$$U(\mathbf{r}) = \sum_\alpha \sum_g \mathbf{u}_g(z_\alpha)\exp(\mathbf{ig}\tau), \quad (6)$$

where summing over α means summing over the planes parallel to the surface ($\alpha = 1$ corresponds to the surface), z is a distance from the atom to the corresponding layer, a vector τ determines the position of the support's atom on the plane, $\mathbf{g} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2$, $\mathbf{b_1}$ and $\mathbf{b}_2$ are the base vectors of the two-dimensional reciprocal lattice.

As in [1,2], we will neglect the effects of charge redistribution between the cluster and the solid bulk and will model the interaction between the cluster and the surface by the Lennard-Jones potential [12]:

$$u(\mathbf{r}) = 2\pi\varepsilon/\mathbf{a}\sum_\alpha \{\mathbf{q}(\sigma^{12}/z_\alpha^{10} - \sigma^6/z_\alpha^4) +$$

$$+ \sum_{g \neq 0}\sum_{k=1}^q \exp[\mathbf{ig}(\mathbf{m}_k + \tau)] \quad (7)$$

$$\left[\sigma^{1/2}/30(g/2z_\alpha)^5 K_5(gz_\alpha) - 2\sigma^6(g/2z_\alpha)^2 K_2(gz_\alpha)\right]\}$$

where q is a number of atoms per unit surface cell, a is the cell's area, $\mathbf{m}_k$ determines the atom's position in this cell, K_n is the modified Bessel function of the 2-nd kind, σ and ε are the Lennard-Jones potential parameters.

Further, instead of the approximation, when a summation over the pair-wise interactions is replaced by an integration, used in [1,2], we will use the following expression (we limit ourselves to the case $\alpha = 1$, i.e. only to the surface layer, that makes the most appreciable contribution to the interaction energy over the physically relevant range of z) [12]:

$$u(\mathbf{r}) = 2\pi\varepsilon A^6/\mathbf{a}*\{\mathbf{q}(2A^6/z*_\alpha^{10} - 1/z_\alpha^4 +$$

$$+ \sum_{g \neq 0}\sum_{k=1}^q \exp[\mathbf{ig}*(\mathbf{m}*_k + \tau*)] \quad (8)$$

$$\left[A^6/30(g*/2z*_\alpha)^5 K_5(g*z*_\alpha) - 2\sigma^6(g*/2z*_\alpha)^2 K_2(g*z*_\alpha)\right]\}$$

where

$$z^* = z/a_1, \ a^* = a/a_1^2, \ g^* = ga_1, \ \mathbf{m}^*_k = \mathbf{m}_k^*/a_1, \ \tau^* = \tau/a_1$$

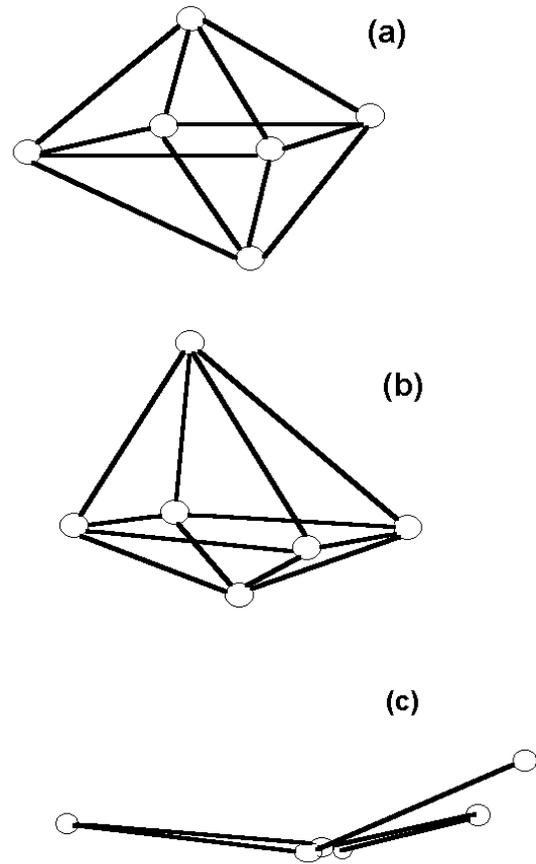are dimensionless parameters, a_1 is elementary cell spacing and $A = \sigma/a$.

Figure 2. 6-atom case. Octahedron with 4-th order axis along a perpendicular to the support's surface.

To make the quantitative estimates we will consider the (100) face of AgBr fcc lattice. For this case we have

$$u*(r) = u(r)/\varepsilon = E_0(z*) + \sum_{n>0} E_n(z*) f_n(s_1, s_2), \qquad (9)$$

where E_0 is approximated by [12]:

$$E_0(z*) = 2\pi A^6 [2A^6/5z*^{10} - 1/z*^4 - \sqrt{2}/3(z* + 0.61/\sqrt{2})^3], \quad (10)$$

the approximation for E_n is [12]:

$$E_n = 1/2\, b\, \exp[-c(z* - z_s*)], \, n>0, \qquad (11)$$

b, c and z_s^* being constants, depending on the value of A. We took n ranging from 1 to 4, corresponding expressions for $f_n(\bullet)$ being:

$$f_1(s_1, s_2) = 2(\cos 2\pi s_1 + \cos 2\pi s_2),$$

$$f_2(s_1, s_2) = 2[\cos 2\pi(s_1 + s_2) + \cos 2\pi(s_1 - s_2)], \qquad (12)$$

$$f_3(s_1, s_2) = 2(\cos 4\pi s_1 + \cos 4\pi s_2),$$

$$f_4(s_1, s_2) = 2[\cos 2\pi(2s_1 + s_2) + \cos 2\pi(s_1 + 2s_2) +$$

$$+ \cos 2\pi(2s_1 - s_2) + \cos 2\pi(s_1 - 2s_2),$$

where $s_1 = x/a_1$, $s_2 = y/a_1$.

The considered aproximations give a possibility to estimate qualitatively an influence of the two-dimensional periodicity of the cluster-support interaction potential on the cluster's structure.

The equilibrium configurations of the clusters were determined by the minimizing the total interaction energy as a function of atom's position in the cluster by the Fletcher-Powell method. The parameter A was chosen in the interval o.8 - 1.5 and was fixed.

Results and Discussion

Let us consider now in what way the approximation, taking into account the two-dimensional periodicity of the surface, influences the results, obtained in [1,2] in rougher approximation. We will discuss the most essential changes, omitting identical results.

Ag_5

The most interesting results are obtained for the case the pyramid with a base whose plane is parallel to the support's surface (fig.1a, 1b, 1c) (here and everywhere below case a) corresponds to the cluster configuration without the interaction with the support and cases b) and c) correspond to the different values of s_1 and s_2 with the shift $\Delta s_1 = \Delta s_2 = a_1/2$). We see that both planar and three-dimensional structures are possible, the minimum of the energy corresponding to the planar structure with a slightly deformed plane parallel to the support surface.

Ag_6

An octahedron with an axis of 4-th order along a perpendicular to the support's surface (fig. 2a) deforms along this axis as shown on fig. 2b. This is very close to the result of [1,2]. But after the shift the structure is very close

to planar and is more stable energetically. We have a different situation for a pentagonal pyramid (fig. 3a), As a result of the interaction with the support all 6 silver atoms occur practically in one plane, parallel to the surface, for both initial positions (fig. 3b, 3c) with approximately the same energy.
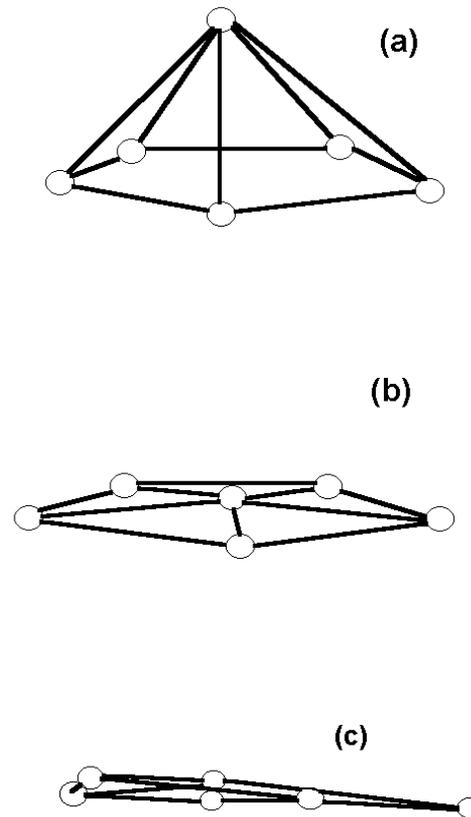

Figure 3. 6-atom case. Pentagonal bipyramid with a plane of the base parallel to the support's surface.

Ag_8 - Ag_13

In these cases the results are very close to that of [1,2] and practically do not depend on the shift. The most stable structure is icosahedron. Its deformation and a deformation of the other clusters are in general quite similar, a distance between the atoms of the upper layer and the atoms of the middle layer being larger than a distance between lower and middle layers. When we have an atom in the center of the polyhedron a deformation is clearly less.

Conclusions

We can see that the new approximation, taking into account the two-dimensional periodicity of the cluster - support interaction, does not essentially change the previous results [1,2], though quite clearly influences them. The influence is especially strong for small clusters (with the number of atoms up to 6), but the main features of the previous approximation are valid. The clusters with small number of atoms tend to form a planar structure, but this structure

corresponds to a certain position of the cluster according to the support's surface. Starting from 8 atoms the deformed clusters remain three-dimensional and their structure and energy do not substantially depend on the position. The bigger is the number of atoms, the more stable is the initial structure of the cluster, and the interaction with the support only partially deforms it. The atom situated in the center of the polyhedron stabilizes the structure.

Acknowledgment

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