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Adsorption interaction of silver nanoparticles with a silicon substrate

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Received August 26, 2024
Revised December 28, 2024
Accepted January 4, 2025

Spherical silver nanoparticles deposited on an atomically smooth silicon surface (physical adsorption) are considered. Formulas for the interaction potential of nanoparticles with each other and with a thick substrate are derived using the Sutherland interatomic potential and the continuum approximation. The formulas allow us to calculate the most important physical parameters of the nanoparticle coating. These parameters primarily include the „particle—particle" coupling energies and the „particle—substrate" as well as the specific work of adhesion. Within the framework of the theoretical approach used, the problem of homogeneous nucleation of a nanoparticle has been solved and the radius of the critical nucleus has been calculated. The numerical calculations are in satisfactory agreement with the available experimental data.

Keywords: silver nanoparticles, silicon substrate, hybrid nanomaterials, interaction potential, specific adhesion, adsorption.

DOI: 10.61011/PSS.2025.01.60597.224

1. Introduction

Superstructures of silver nanoparticles on the silicon surface are of great interest for optoelectronics, surface-enhanced Raman spectroscopy, and various biomedical technologies. Moreover, silicon can be used in various practical applications not only as a massive or porous material [1–7], but also in the form of nanopillars or nanowires [5,8]. The resulting ultra-small silver clusters on the surface of monocrystalline silicon have a fixed orientation and an ordered structure relative to the substrate [9], which indicates the manifestation of interatomic interaction forces.

Silver nanoparticles have been theoretically studied, for example, in Refs. [10–13]. It was shown in Ref. [10] that the melting point, and with it, of course, the thermal strength of nanoparticles, depend on their shape, with the lowest melting point corresponding to the spherical shape. The energy of interaction between two nanoparticles in Ref. [10] was calculated by summing individual atoms, i. e. no explicit formulas were obtained. The interaction of silver nanoparticles with a silicon dioxide substrate was modeled in Ref. [11] using the Monte Carlo method, and the important role of Van der Waals forces was noted. The adsorption and adhesion energies were calculated numerically. The Lennard—Jones potential was used, whose parameters were estimated using the electron density functional method.

Thermal effects observed when the particle sizes decrease are of independent interest. For instance, a rapid heating due to the exposure of silver nanoparticles to the pulsed laser leads to the appearance of cavities in them, which was revealed using molecular dynamic modeling in Ref. [12]. The inner cavity is formed at high temperature and in case of slow cooling of nanoparticles. The molecular dynamics method also makes it possible to trace the sintering process of silver nanoparticles at high temperatures [13]. In this case, the following interesting features of the process are found: the addition of small particles to large particles helps to reduce the porosity of the structure; small particles sinter faster than large ones because of the increased rate of surface diffusion of atoms when heated; the use of nanoparticles can significantly reduce the sintering time and temperature compared with massive phases.

In general, an analysis of the numerous papers shows that the properties of silver nanoparticles on the silicon surface were theoretically studied only by computer experiments using the method of molecular dynamic modeling. No analytical methods were used. This article addresses this gap. The paper suggests using a continuum approximation to describe silver nanoparticles on a silicon substrate. The potential energy of the interaction is calculated by integrating the paired interatomic potential over the volumes and surfaces of the bodies [14]. The application of the approximation is justified by the fact that metal nanoparticles of size 1—100 nm can be considered solid macroscopic phases from the point of view of thermodynamics [15]. It is assumed that there is no chemical bonding and mutual dissolution of materials. This actually means that sufficiently low temperatures are considered, which, in any case, are lower than the Debye temperature. It is also believed that interatomic interaction does not create deformations of nanoparticles and the substrate. The potential of interatomic

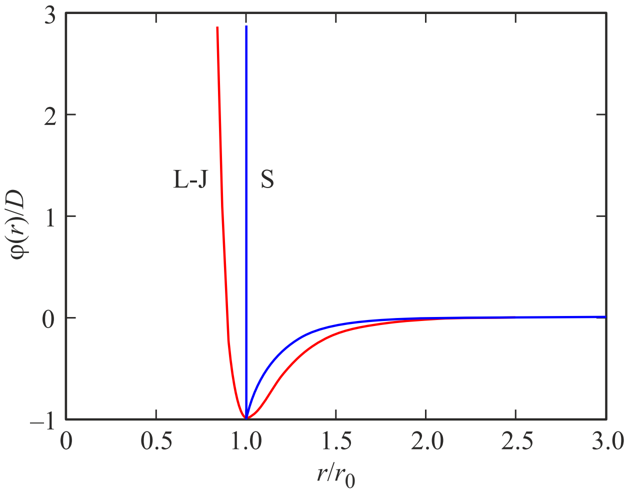

Figure 1. Paired interaction potentials: (L–J) — Lennard–Jones; (S) — Sutherland.

interaction is selected in the Sutherland form ([16], p. 206) (Figure 1):

$$\varphi(r)=\begin{cases}\infty, & r<r_0,\\ -D\left(\frac{r_0}{r}\right)^6, & r\geq r_0,\end{cases}\qquad (1)$$

where r is the distance between the atoms, D and r_0 is the depth of the potential well and the equilibrium distance. This choice is dictated by the fact that the proposed theoretical model neglects the „softness“ of repulsion forces in favor of the possibility of obtaining simple expressions for the interaction energies between nanoparticles and the substrate. Another advantage is that the Van der Waals dispersion forces are correctly taken into account in (1). For this reason, the Sutherland potential is especially often used for building statistical models of thermodynamic properties of substances.

2. Theoretical model

The adhesion of liquids, films and solids is distinguished based on their specific features on the surfaces of solids [17]. We consider silver nanoparticles with an average radius R, which interact with each other and with the surface of a thick silicon substrate. The concentrations of atoms of interacting bodies are considered constant: $n_1=n(\mathrm{Ag})=58.5\,\mathrm{nm}^{-3}$ and $n_2=n(\mathrm{Si})=50.0\,\mathrm{nm}^{-3}$ ([18], c. 55).

First, let us calculate the interaction potential of an outside atom with a solid spherical nanoparticle. To do this, we integrate (1) over the nanoparticle volume

$$u=n_1\int\varphi(r)dV,\qquad (2)$$

where r is the distance between an atom and a certain point in the volume of the nanoparticle. The expression (2) has the following form in the spherical coordinate system

$$u(z)=2\pi n_1\int\limits_{-1}^{1}\int\limits_{0}^{R}\varphi\left(\sqrt{z^2+\rho^2-2\rho zx}\right)\rho^2d\rho dx,\qquad (3)$$

where z is the distance from the atom to the center of the nanoparticle. Substituting (1) in (3) and performing integration, we find

$$u(z)=-\frac{4\pi R^3Dn_1r_0^6}{3\left(z^2-R^2\right)^3}.\qquad (4)$$

The equilibrium distance between an atom and a nanoparticle is obviously equal to $z_0=R+r_0$. Given this distance in the formula (4) and decomposing this formula into a series of powers r_0, under the natural condition $R\gg r_0$ we find the binding energy of an atom with a nanoparticle

$$u_0=u(z_0)\approx-\frac{1}{6}\pi Dn_1r_0^3,\qquad (5)$$

moreover, it turns out that this energy in the first approximation does not depend on R.

Let us now calculate the interaction potentials of a nanoparticle with a thick substrate and with a nanoparticle of the same radius. Let us integrate (4) over the infinite half-space and volume of the sphere

$$U_A(z)=2\pi n_2\int\limits_{z}^{\infty}u(\rho)(\rho^2-\rho z)d\rho,\qquad (6)$$

$$U_B(z)=2\pi n_2\int\limits_{-1}^{1}\int\limits_{0}^{R}u\left(\sqrt{z^2+\rho^2-2\rho zx}\right)\rho^2d\rho dx,\qquad (7)$$

where z already means the distance from the center of the nanoparticle to the surface of the substrate in the formula (6) and the distance between the centers of the nanoparticles in the formula (7). We obtain the desired potentials substituting (4) in (6), (7) and by performing integration

$$U_A(z)=-\frac{\pi^2Dn_1n_2r_0^6}{6}\left[\frac{2Rz}{z^2-R^2}+\ln\left(\frac{z-R}{z+R}\right)\right],\qquad (8)$$

$$U_B(z)=-\frac{\pi^2Dn_1n_2r_0^6}{6}\times\left[\left(\frac{z^2-2R^2}{z^2-4R^2}\right)\left(\frac{2R}{z}\right)^2+\ln\left(1-\left(\frac{2R}{z}\right)^2\right)\right].\qquad (9)$$

Formulas (8) and (9) have the same multipliers with the dimension of energy, and the dimensionless functions in square brackets determine the dependence of potentials on distance (see Figure 2). The equilibrium distances are $z_0=R+r_0$ and $z_0=2R+r_0$ for (8) and (9), respectively. Taking this into account, at $R\gg r_0$, from formulas (8)

Parameters of interacting atoms

Element	r_W, nm	α, a.u.	N
Si	0.210	37.3	4
Ag	0.172	55	1

and (9) by their expansion in series by powers of r_0, we find expressions for the binding energies of a nanoparticle with a thick substrate and with an equal-sized nanoparticle

$$U_{A0} = U_A(z_0) \approx -\frac{1}{6}\pi^2 n_1 n_2 D R r_0^5 = \pi n_2 R r_0^2 u_0, \tag{10}$$

$$U_{B0} = U_B(z_0) \approx \frac{U_{A0}}{2}. \tag{11}$$

Therefore, with the same values of all physical parameters, the binding energy of a nanoparticle with a thick substrate is twice as high as the binding energy of two nanoparticles. This conclusion is consistent with the results of Hamaker and Deryagin ([19], pp. 50–53), however, formulas (8)–(11) differ fundamentally in that they take into account the equilibrium distance between bodies r_0. The normal and lateral energy strengths of nanoparticle coatings on the solid surface are determined by multiplying (10) and (11) by the required number of bonds. It should be noted that such coatings are experimentally formed in the form of quasi-one-dimensional and quasi-two-dimensional densely packed structures [20].

Next, let us find the maximum specific adhesion of a monolayer coating of silver nanoparticles on the silicon surface. To do this, let us consider a hexagonal dense packing of nanoparticles. The minimum distance between nanoparticles with a radius R, as indicated above, is $z_0 = 2R + r_0$. The area of an elementary hexagon made up of nanoparticles is $S = 3\sqrt{3}(2R + r_0)^2/2$. The number of nanoparticles per hexagon is $N = 3$. Therefore, for the specific adhesion performance at $R \gg r_0$, we have

$$W = -\frac{NU_A(z_0)}{S} = -\frac{2U_A(z_0)}{\sqrt{3}(2R + r_0)^2} \approx \frac{\sqrt{3}\pi^2 n_1 n_2 D r_0^5}{36R}. \tag{12}$$

It should be noted that the formula (12) characterizes the dimensional effect: $W \propto 1/R$. Together with (12), let us present the well-known Girifalco–Good formula for the specific adhesion of a thick solid film ([21], p. 453):

$$W = 2\sqrt{\sigma_1 \sigma_2}, \tag{13}$$

where $\sigma_1 = 1.14\,\mathrm{J/m^2}$ is the surface tension of solid silver [22], $\sigma_2 = 1.23\,\mathrm{J/m^2}$ is the surface energy Si (111) [23].

Silver and silicon atoms do not form a chemical compound without oxygen, so Van der Waals forces mainly act between them. In order to consistently set the numerical values of D and r_0 in (12), we use the Slater-Kirkwood formula for the dispersion interaction constant [19], p. 36:

$$C_6 = D r_0^6 = \frac{3}{2}\hbar\sqrt{\frac{e^2}{m}}\,\frac{\alpha_a \alpha_b}{\sqrt{\alpha_a/N_a} + \sqrt{\alpha_b/N_b}}, \tag{14}$$

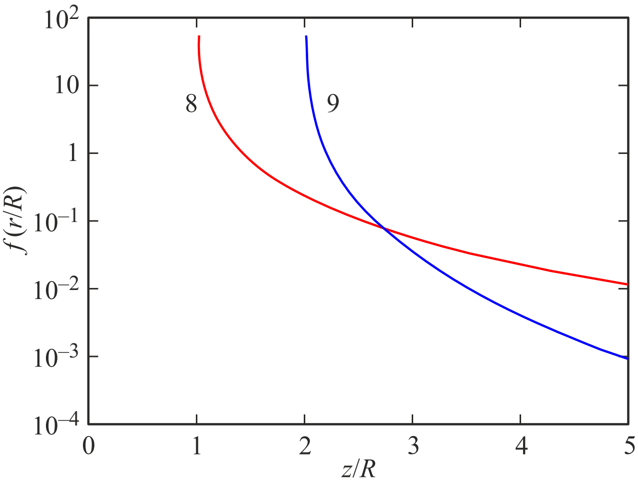

Figure 2. Graphs of functions that determine the dependence of the potentials „nanoparticle–substrate“ (8) and „nanoparticle–nanoparticle“ (9) on distance. A semi-logarithmic scale is used.

where $\alpha_{a,b}$ and $N_{a,b}$ are static polarizabilities and valence of atoms, $\hbar$ is the Planck's constant, e and m is the charge and mass of the electron. The sum of the Van der Waals radii r_W of interacting atoms is taken as r_0. The calculation data for (14) are taken from [24,25] and shown in the table. The found values of the parameters of the paired interatomic interaction Ag–Si: $D = 0.057\,\mathrm{eV}$ and $r_0 = 0.382\,\mathrm{nm}$. The following values of specific adhesion are obtained from (12) at $R = 1\,\mathrm{nm}$ and (13): $0.034\,\mathrm{J/m^2}$ and $2.37\,\mathrm{J/m^2}$. Thus, we come to the key conclusion that the specific adhesion of a solid silver film on a silicon substrate is more than an order of magnitude higher than the specific adhesion of a coating of silver nanoparticles of minimal size on a similar substrate. This is explained by the presence of a free volume at the interface „coating–substrate“, i. e., in essence, by the fact that physical contact is created not over the entire area of the boundary, but only at its individual points.

The present theoretical model makes it possible to quantify the homogeneous nucleation of silver nanoparticles. The change of Gibbs energy under isobaric-isothermal conditions is attributable to the surface and volume components

$$\Delta G = 4\pi R^2 \sigma_1 + 4\pi n_1 \int_{R+r_0}^{\infty} u(\rho)\rho^2 d\rho, \tag{15}$$

where $u(\rho)$ is the energy of interaction of an atom with a nanoparticle. Substituting (4) in (15) and performing integration, we obtain

$$\Delta G = 4\pi R^2 \sigma_1 - \frac{1}{3}(4\pi n_1)^2 (R r_0)^3 D. \tag{16}$$

The radius of the critical nucleus, as usual, is determined from the condition

$$\left(\frac{d\Delta G}{dR}\right)_{R=R_c} = 0. \tag{17}$$

From (16), (17), taking into account the ratio $n_1 = 1/r_0^3$, we find

$$R_c = \frac{3\pi\sigma_1 r_0^3}{2D}. \tag{18}$$

The parameters of the pair interatomic interaction Ag−Ag are calculated from the melting point T_m and the atomic radius r_A for silver so that to correctly take into account the properties of the critical nucleus:

$$D = \frac{k_B T_m}{e} = 0.1\,\text{eV}, \quad r_0 = 2r_A = 0.32\,\text{nm}.$$

The radius of the critical nucleus is estimated as $R_c \sim 1$ nm, which practically coincides with the smallest size values of silver nanoparticles obtained experimentally by various methods [26–29].

3. Conclusion

Silver nanoparticles are promising for electronics, pharmaceuticals, and catalysis [30]. For instance, conductive polymer composites and inks based on silver nanoparticles are being actively introduced into modern flexible electronics technologies. Silver nanoparticles deposited on the silicon surface have unique optical properties, since at certain wavelengths there is strong absorption or scattering of incident light due to plasmon resonance. Such structures can be used as optical sensors and detectors. Layers of silver nanoparticles on the surfaces of functional silicon structures act as peculiar optical antennas, therefore they can find effective application in solar energy.

New formulas (10) and (11) for the equilibrium binding energy of nanoparticles to the substrate and to each other are derived in this paper within the framework of the approach provided in Ref. [14]. The specific work of adhesion of a densely packed coating of nanoparticles on the surface of a solid is calculated (formula (12)). It is shown that the specific adhesion of a coating of silver nanoparticles on a silicon substrate is more than an order of magnitude less than the specific adhesion of a solid silver film on the same substrate. The formula (18) for the radius of the critical nucleus is derived. Numerical calculations for (18) show that the extreme value of the radius of a silver nanoparticle is ~ 1 nm; nanoparticles with smaller sizes are apparently thermodynamically unstable.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by A.Akhtyamov