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Mechanisms of sputtering of nanoparticles embedded into solid matrix by energetic ion bombardment

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ABSTRACT

The mechanisms of sputtering of nanoparticles embedded in the solid matrix under ion bombardment are presented. The mechanism of sputtering by multicharged ions is based on the increase of the potential energy associated with the Coulomb interaction of charges. It is shown that the increase of the lifetimes of holes formed under ionization of the material in the track of the nanoparticles enlarges the sputtering yield due to the confinement of charges. The modification of the thermal spike mechanism has been studied, when the modifying factor is the interface between the nanoparticle and the matrix, which is characterized in the phonon and electron subsystems by the corresponding coefficients of the wave reflection. The process of heat injection into the lattice and following averaging of the probability of atoms' evaporation is described in framework of the two-temperature phenomenology. The expressions for the sputtering yield Y are obtained, which are dependent in all cases on the size of the nanoparticles.

The sputtering under ion bombardment, as a particular case of radiation effects, is subject to general laws of the radiation physics of solids [1]. This also holds for the new features, which appear in the radiation physics of nanoobjects [2]. There are two main features which must be considered at first: 1) the confinement of elementary excitations (electrons, holes, excitons, phonons, plasmons) and 2) the presence of an interface between the nanoparticle and the surrounding matrix (NM). It appears that these two features may change dramatically such effects as defect formation and amorphization [3]. In this paper we will consider the modification of the sputtering in the framework of ionization mechanism and the mechanism of thermal spikes, taking into account the above two properties of the nanoobjects.

1. Sputtering in the framework of the ionization mechanism

We consider a nanoparticle embedded within the surface layer of a matrix. Let an energetic multiple-charged ion fly into it. According to the existing concepts of radiation physics [4], in this case a great amount of dynamic holes positively charged and localized at the different levels of atoms are formed in the track, so that the density of charge Z accumulated along the ion path in each local area at a time t is:

$$N = \alpha(Z)\frac{1}{J}\left(-\frac{dE}{dx}\right)_e It, \tag{1}$$

where J is the average ionization potential of atoms of the nanoparticle, $\alpha(Z)$ is the probability of the Auger cascade in each atom, which can transfer the charge Z to the valence zone $(-dE/dx)_e$, is the electronic losses, I is the current density of the fast ions. These additional charges bring in to the system additional Coulomb energy $\Delta E = \gamma(Ne)^2/\sqrt[3]{V}$ [5], which leads to additional pressure $\Delta P = dE/dV = \tilde{\gamma}(Ne)^2/V^{4/3}$; here N is the number of charged ions in the track, V is the volume of the track, $\sqrt[3]{V^2}$ is the cross-section of the track, whose form is defined by the numerical factors γ and $\tilde{\gamma}$. Then, the average speed $\bar{v}$ of the movement of the charged ions to the surface will also increase by:

$$\Delta\bar{v} = \sqrt{\frac{3}{Mn}\Delta P} = \sqrt{\frac{3\tilde{\gamma}}{Mn}}\,\frac{Ne}{V^{2/3}}, \tag{2}$$

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where M is the mass of the atom, n is the density of ions. It gives the flux of atoms from the nanoparticle:

$$j = n\Delta\bar{v} = \sqrt{\frac{3\tilde{\gamma}n}{M}}\,\frac{N(t)}{V^{2/3}}, \tag{3}$$

Thus, j depends on the time t, when the atoms are in the ionized state. Neutralization process ("healing" of the ions) has the stochastic nature, so that $\langle j\rangle = \int_{\tau_+}^{\infty} j(t)\frac{1}{\tau_e}\exp\left(-\frac{t}{\tau_e}\right)dt$ [6]. Here $1/\tau_e$ is the probability of the positive charge to be "flooded" by electrons, τ_+ is the minimal time necessary for the ion acceleration. Further,

$$\langle j\rangle = \sqrt{\frac{n}{M}V^{-\frac{2}{3}}}\alpha(Z)\frac{1}{J}\left(-\frac{dE}{dx}\right)_e I\tau_e\exp\left(-\frac{\tau_+}{\tau_e}\right) \tag{4}$$

Obviously, if $I = 1/(\mathrm{cm}^2\ \mathrm{s})$ in (4), then $\langle j\rangle$ is the sputtering yield. The value $\langle j\rangle$ is dependent very strongly on τ_e, which is determined by the type of irradiated material. In particular, metals have $\tau_e = 10^{-16}$ s, which makes the ionization mechanism of sputtering impossible; in the dielectrics and semiconductors the τ_e values are much greater and effect is more pronounced there (see experiment in Ref. [3]).

What new happens when we deal with nanoobjects? The most important effect is the confinement, as it modifies significantly the electronic spectra of nanoparticles, which become quasi-discrete (Fig. 1). The situation here is the following: if the electronic level of the positive charge is inside the energy zone ($Z_1 < E_i < Z_2$), then sputtering is the same as in the bulk samples. If the level is either below Z_1 or above Z_2, the neutralization dramatically slows down and calculated as in the work by Schechter [7], who studied the Auger neutralization of multiple-charged ions near the surface at the strong mismatch of the levels of ion and zone. Thus, the decrease of the nanoparticle size due to the confinement narrows the Z_1–Z_2 zone, where $\tau_e = 10^{-16}$ s. It makes more probable the neutralization in the quasi-discrete region, i.e. outside the Z_1–Z_2 zone. This leads to $\tau_e \gg 10^{-16}$ s [7], therefore, the sputtering increases for small $\exp(-\tau_+/\tau_e)$

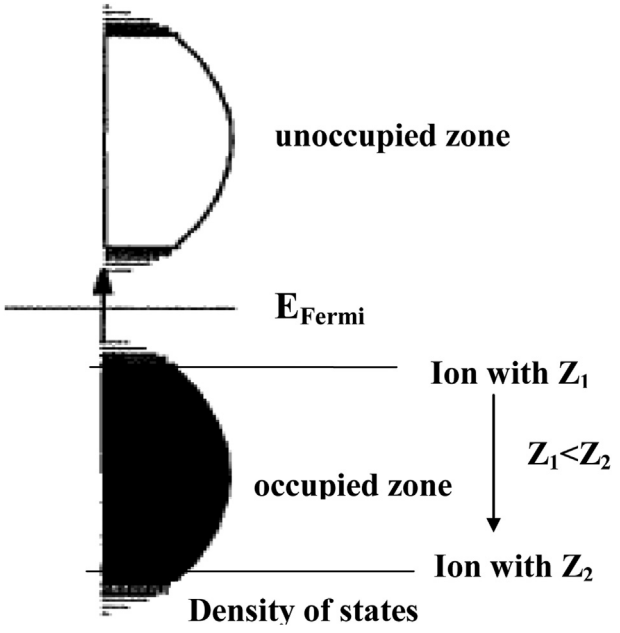

Fig. 1. Scheme of electron density of states of cluster and localization of ion electron state with multiple holes; black region is electron continuous occupied zone, white region is the unoccupied zone.

2. Cluster sputtering in the framework of the mechanism of thermal spike

Among the various regularities describing the process of cluster sputtering of solids under ion bombardment the very important one is the universal power law of cluster intensity decay with the increase of the number of atoms in them [8]:

$$Y(n) \sim n^{-\delta} \tag{5}$$

Here the exponent δ can be interpreted within the thermal spike model [9]. According to this concept, the clusters are sputtered from the "hot spots". These spots are formed at the "instant" energy release during the interaction of ions with the near-surface region and are characterized by a cylinder form of radius ρ_0 and the initial temperature T_0. For the total sputtering coefficient Y it has been found [10]:

$$Y = 0.1 f_n \frac{\lambda_0 \tilde{a}^2 F_{D,1}^2}{U_n^2}\exp\left(-\frac{U_n}{kT_0}\right) \tag{6}$$

Here $\lambda_0 \approx 24$, $\tilde{a} = 0.5(\tilde{Z}_1^{2/3} + \tilde{Z}_2^{2/3})^{1/2}$ Å, $F_{D,1} \sim F_D$, and F_D are the specific energy losses of ion in the atomic subsystem, U_n is the binding energy of the n-atomic protocluster, $\tilde{Z}_1$ and $\tilde{Z}_2$ are the nuclear charges of the bombarding ion and surface atom.

Defining the barrier as $U_n = U_1 ln(en)$, it has been obtained in [9]:

$$Y(n) \sim \frac{F_D^2}{U_1^2} n^{-\delta}, \tag{7}$$

where

$$\delta = \frac{U_1}{kT_0} = \frac{2\pi N\rho_0^2}{F_D}, \tag{8}$$

and N is the concentration of the surface atoms.

Let us consider how the Eq. (8) is modified if the ion enters the surface of the nanocluster embedded into the matrix. We assume that the embedded nanocluster has a hemisphere shape. Let the interface be neutral and the atomic densities of the neighbouring areas of the nanocluster and the matrix are N_n and N_m. The heat propagates in both structures with the velocities, v_n and v_m, respectively. If the nanocluster radius is larger than the track radius, $\rho_n > \rho_0$, then the heat released in the nanocluster spreads radially and confronts at the interface the wave resistance (phonons) with the coefficient R_r of reflection [11] (see Fig. 2):

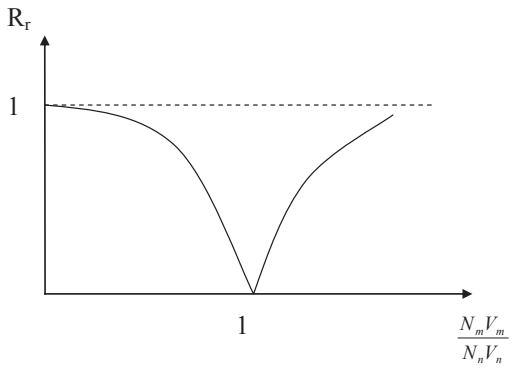

Fig. 2. Dependence of the efficiency of the phonon reflection of the "nanoparticle-matrix" interface on the ratio of wave impedances of neighbouring phases.