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The influence of crater formation for electron excitation processes in cluster induced collision cascades

B. Weidtmann *, A. Duvenbeck, A. Wucher

Fakultät für Physik, Universität Duisburg-Essen, 47048 Duisburg, Germany

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ABSTRACT

The interplay between electronic energy loss and the excitation of electronic degrees of freedom accompanying the bombardment of a silver crystal with 7-keV Ag and 20-keV Ag_3 particles is investigated by molecular dynamics simulation. Two kinetic excitation processes – the friction of moving atoms in a free electron gas and autoionization in close, binary collisions – are considered, as to describe the electronic stopping. In order to accommodate the massive transient morphology changes following a cluster impact, the electronic friction is described by a modified Lindhard/Scharff model, where the friction coefficient is scaled to the local environment of a moving atom. It is shown that this approach is capable of reproducing both the measured sputter yields and the degree of electronic excitation as manifested by measured electron and secondary ion yields.

1. Introduction

A single atom impinging onto a solid surface initiates a complex collision cascade due to which some atoms may overcome the surface barrier and be emitted into the vacuum. In addition, electronic degrees of freedom may be excited by the moving projectile and recoil atoms. This electronic stopping not only drains energy from the atomic motion but also is important for kinetic electron emission [1] and secondary ion formation [2,3]. The particle dynamics following the bombardment of a surface with clusters differ significantly from those following a single atom impact. Due to its greater cross section, a cluster impinging onto the surface deposits more energy close to the surface, thereby producing a collisional spike where nearly all atoms in a specific volume are set in motion. As a consequence, an overcritical pressure develops in the subsurface region which results in a rapid expansion of material into the vacuum. This "phase explosion" [4] leads to the emission not only of more sputtered particles, but also larger intact clusters and molecules, thereby making the cluster bombardment an important tool for molecular chemical surface analysis [5].

From a theoretical point of view, the description of cluster bombardment raises some problems. The collision dynamics following a projectile impact can in principle be described by classical molecular dynamics, with the electronic stopping being implemented as a friction force acting on all moving atoms [6]. In such an approach, the electronic system is approximated as a free homogenous electron gas formed by the conduction band electrons, thus yielding a constant friction coefficient which can be derived, for instance, from dielectric response theory [7]. The collisional spike following a cluster impact, however, causes a severe temporal deformation of the surface, which often manifests as a disruption producing a crater of several nanometers in size [8]. It is clear that the assumption of a constant electronic friction coefficient can no longer be valid in this case, as the electronic stopping force must in some way be corrected for the varying sample density in the crater region. Moreover, most theoretical models describing electron transfer processes following ion bombardment of solids are based on the assumption of the original, undisturbed surface as a boundary of the electronic system, which must also be violated under cluster bombardment conditions.

In a series of publications [1,9,10], we have developed a strategy to describe inelastic emission phenomena like kinetic electron emission and secondary ion formation in terms of the transient local and temporal electronic excitation induced by electronic stopping of all moving particles in the collision cascade. In such a model, there is a complex interplay between the amount of electronic excitation and the particle kinetics, leading to a strong correlation between predicted quantities like sputter yields on one hand and electron emission yield or secondary ion formation probability on the other hand. While the model allows a satisfactory prediction of both sets of experimental observables under linear cascade conditions typical for atomic projectile bombardment, it has been shown that the model fails under spike conditions typically following a cluster impact. In the latter case, it was found that

* Corresponding author.

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the assumption of an undisturbed surface as a boundary of the electron gas leads to a significant overestimation of the electronic energy loss, thereby draining too much energy from the particle kinetics, which in turn leads to a significant underestimation of the sputter yield. In order to fix this problem, we have tried to scale the electronic friction by the local electron density according to the model proposed by Caro and Victoria [14], where the local electron density is calculated as a superposition of atomic orbitals. Following this approach, Sandoval and Urbassek [15,16] have found that the unrealistic reduction of the sputter yield induced by cluster impacts onto a metal surface – which is caused by the overestimation of electronic stopping via Eq. (1) – is significantly reduced if the local electron density is included in the calculation of electronic stopping. Implementing a similar scheme here, we find that – at least for a metallic system as studied here – this approach now severely underestimates the electronic energy loss, since the atomic wave functions decrease exponentially with a decay length of about 0.43 Å, whereas the conduction band electrons are delocalized in form of a free electron gas. In the present work, we therefore implement a different strategy to scale the electronic stopping according to the local *atom* density of the sample. The sputter yield as well as the secondary ion formation probability predicted by this approach are compared to corresponding experimental data. In particular, we will show that the sputter yields calculated this way appear quite realistic, provided the experimental data are corrected for variations in the velocity distribution of the emitted particles.

2. Model

The kinetic excitation/emission model used here consists of four parts. The particle dynamics are followed by classical molecular dynamics using a parametrized force field based on the MD/MC-CEM interaction potential fitted to the properties of solid silver [17]. Electronic stopping of all moving particles is implemented via two different excitation mechanisms, namely (i) in form of an electronic friction force using the Lindhard/Scharff formalism and (ii) via the promotion of inner shell states to energies above the Fermi level in close binary collisions [11,12]. The resulting loss of kinetic energy is fed into the electronic subsystem, where it acts as a time and space dependent source of excitation energy, which is then inserted as a source term into a nonlinear diffusion equation describing the rapid spread of excitation away from the point of its generation. A numerical solution of this equation then yields a transient excitation energy density profile, which is parametrized by a space and time dependent electron "temperature". The resulting temperature profile then forms the basis for the prediction of inelastic emission phenomena such as electron or secondary ion emission as described in detail elsewhere [1,13].

As outline above, we assume the collision cascade to be embedded into a free electron gas which exerts a friction force onto every atom moving with velocity v as

$$\frac{dE}{dx} = -k \cdot v \tag{1}$$

where the constant k is calculated according to the Lindhard/Scharff formula [18,19]

$$S_e = \zeta_e \times 8\pi e^2 a_0 Z_1 Z_2 \left(Z_1^{2/3} + Z_2^{2/3}\right)^{-3/2} (v/v_0), \tag{2}$$

where the Z_1 and Z_2 denote the atomic numbers of projectile and target atoms, a_0 is the bohr radius, and $v_0 = e^2/\hbar$ and $\zeta_e \approx Z_1^{1/6}$. The stopping cross section S_e is defined via

$$\frac{dE}{dx} = n_a S_e, \tag{3}$$

where n_a denotes the atom density of the target. In this context, it is of note that the Lindhard model considers all electrons of the target atom via the atomic number Z_2. In a nearly undisturbed bulk volume, the atom density is that of the solid material, and the corresponding value for silver ($n_a = 0.0585$ Å^{-3}) results in a friction coefficient $k = 258.9$ kg fs^{-1}. In a collisional spike, the surface will be radically deformed as seen, for instance, in Fig. 1 of Ref. [20]. This affects the atom density inside the crater and at its boundaries as schematically depicted in Fig. 1(b). In this situation, less electrons contribute to the friction, which manifests as a reduced effective friction constant. In order to account for this effect, we calculate a *local* atom density by counting the number of target atoms inside a sphere of radius r_{cut} around the position of each moving atom. The resulting value is inserted into Eq. (3), leading to an individual friction coefficient for each atom in the target. The cutoff distance r_{cut} is a parameter of the model determining the spatial resolution of the density calculation. It is obvious, that r_{cut} may not be lower than the nearest neighbors distance. In the present work we chose $r_{cut} = 3.0$ Å which for the crystalline silver includes the twelve nearest neighbors.

Note that the second excitation mechanism included in our model is not affected by the density correction, since it is based on the direct binary collision between two atoms and, hence, fully described by the MD simulation.

3. Results

To simulate cluster bombardment, an Ag_3 projectile was realized as an equilateral triangle with a side length of 2.64 Å. The bombardment was simulated for ten impact points with the triangle oriented parallel to the surface and for ten additional impact points with the triangle face perpendicular to the surface. For the case of Ag atom impact, a total number of 120 trajectories were simulated. All impact points were chosen inside an irreducible zone on the Ag(1 1 1) surface. The impact energies of 20 keV and 7 keV for cluster and single atom bombardment, respectively, were chosen in order to facilitate direct comparison to experimental data [21] (note that these energies ensure nearly constant impact velocity in both cases). In all cases, the calculations were performed for (i) simple Lindhard friction (k = const), (ii) electronic friction scaled with the local electron density via the model of Caro and Victoria ($k = k(n_e)$) and (iii) Lindhard friction scaled with the local atom density ($k = k(n_a)$). In this paper, we focus our attention on the discussion of the calculated sputter yields which are listed in Table 1. These values can now be compared with published experimental data derived from secondary neutral mass spectroscopy (SNMS) measurements on a polycrystalline silver surface bombarded with Ag_n^+ projectiles [21].

For the 7-keV atom bombardment, all friction models result in a similar sputter yield which is almost equal to the experimental value. In the case of the cluster bombardment, on the other hand, the calculated sputter yield varies significantly depending on the way the friction is treated. At first glance, the electron density scaling appears to provide the best agreement with the experimental data.

An additional observable correlated to the prediction of inelastic emission phenomena (secondary ion emission, electron emission, ...) is the total amount of excitation energy transferred to the electronic subsystem. This quantity is depicted in Fig. 2 as a function of time after the projectile impact for the three different implementations of the electronic friction constant. The 5-keV results are plotted here since a detailed calculation of ionization probabilities [22,3,23,24] and kinetic electron emission yields [1,25] has been performed for these bombardment conditions. However, we do not expect significant differences between 5 keV and 7 keV impact energies.