Computer simulation of cluster impact induced electronic excitation of solids

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

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

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We present a computational study of electronic excitation upon bombardment of a metal surface with cluster projectiles. Our model employs a molecular dynamics (MD) simulation to calculate the particle dynamics following the projectile impact. Kinetic excitation is implemented via two mechanisms describing the electronic energy loss of moving particles: autoionization in close binary collisions and a velocity proportional friction force resulting from direct atom–electron collisions. Two different friction models are compared with respect to the predicted sputter yields after single atom and cluster bombardment. We find that a density dependent friction coefficient leads to a significant reduction of the total energy transferred to the electronic sub-system as compared to the Lindhard friction model, thereby strongly enhancing the predicted sputter yield under cluster bombardment conditions. In contrast, the yield predicted for monoatomic projectile bombardment remains practically unchanged.

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1. Introduction

The bombardment of solid surfaces with cluster ions has become an important tool in surface analysis and sputter depth profiling, where the investigated surface is analyzed by means of Secondary Ion Mass Spectroscopy (SIMS) [1]. Therefore, a detailed understanding of the fundamental processes underlying the formation of sputtered ions under cluster ion bombardment is of utmost interest. A microscopic model of secondary ion formation under these conditions, however, is currently not available.

In the past, we have described the ion formation process in sputtering by means of a hybrid computer simulation model combining a molecular dynamics (MD) treatment of the collision dynamics with a simple analytical model of the transfer of kinetic energy into the electronic sub-system and a nonlinear transport mechanism for the generated excitation energy [2]. This model yields a space- and time-dependent electron temperature profile within the bombarded solid, allowing us to calculate an individual ionization probability for every sputtered particle. Due to the complex interplay between electronic energy loss of the moving atoms, the sputtering yield and the resulting ionization probabilities, an accurate description of electronic stopping is essential for the success of such a model.

For the bombardment with atomic projectiles, the energy loss due to atom–electron collisions of particles moving through a quasi-free electron gas of constant electron density can successfully be described by a constant, space-independent friction coefficient in terms of the Lindhard–Scharff model [3]. The transport of excitation energy away from the point of its generation is essential and may be described by a non linear diffusion equation with a simple Neumann-type boundary condition at a static and planar surface. In case of cluster bombardment, on the other hand, the target crystal becomes strongly disturbed during the cascade evolution (crater formation, defects, voids, etc.). As a consequence, the assumption of a constant electron density as well as a planar surface appears questionable. In this paper, modifications of the electronic friction mechanism necessary to take into account fluctuations of the local electron density as well as the consequences of these modifications with respect to the predicted sputter yield and the amount of kinetically generated excitation energy will be discussed.

2. Model

The hybrid model employed to calculate the ionization probability of sputtered particles has been described in detail elsewhere [2,4,5]. It consists of an MD simulation to obtain detailed information about the particle dynamics following a projectile impact, which is combined with a description of kinetic electronic excitation induced by each moving particle, a transport model for the generated excitation energy and a rate equation model for charge exchange between the surface and the sputtered atoms. As outlined above, the extension of the model towards cluster bombardment requires extensive modifications of the description of the excitation process and the transport. Here, we will focus on the MD and the excitation mechanism which will be described in the following.
2.1. Particle dynamics

A standard MD-code developed for the simulation of sputtering is employed to describe the collision dynamics following the impact of the projectile. The interatomic forces are described by a parametrized many-body interaction potential fitted to the properties of solid silver [6].

2.2. Electronic excitation

The atomic collision cascade is assumed to be embedded in a free electron gas, where moving atoms can lose their energy in direct atom–electron collisions (electronic friction) or due to close inelastic binary collisions between two atoms (electron promotion).

Electronic friction is described by means of a friction force proportional to the particle’s velocity according to [3]

\[ \frac{dE_{\text{kin}}}{dt} = -k \cdot v, \]

which yields a kinetic energy loss rate of particle moving with kinetic energy \( E_{\text{kin}} \) as

\[ \frac{dE_{\text{kin}}}{dt} = -\frac{2k}{m} E_{\text{kin}} = -A \cdot E_{\text{kin}}. \]

In the previous version of the model, all moving atoms are assumed to be embedded in a free electron gas of constant, space-independent electron density. Thus, the friction coefficient \( k \) is assumed to be constant and is calculated from the Lindhard–Scharff formula [3].

Cluster bombardment, however, yields strong perturbations of the target, resulting in the formation of transient craters and defect clusters reaching down to depths of several nanometers below the original surface [7]. As an example, Fig. 1 shows a snapshot of the collisional spike induced by the impact of a 20-keV Ag3 cluster onto an Ag(111) surface.

It is immediately evident that under these conditions the concept of a free, homogeneous electron gas and, hence, a constant electron friction coefficient becomes questionable. In particular, it appears insensitive to assume those particles moving within the practically empty crater volume to experience the same electronic stopping as they would in an intact solid. Moreover, it is obvious that the assumption of a flat, static Jellium edge at the position of the original surface can no longer constitute a proper boundary of the electron gas. In order to tackle the first problem, we therefore introduce an electron density \( \rho_e \) dependent friction coefficient \( k = k(\rho_e) \), which is calculated as a replacement of the constant Lindhard–Scharff value \( k_0 \) via

\[ k(\rho_e) = k_0 \log \left( \frac{z \rho_e}{\sqrt{2}} \right) + b, \]

as proposed by Caro and Victoria [8]. The parameters \( z = 3.090 \) and \( b = 0.65 \) are directly taken from Ref. [8], while the parameter \( k_0 \) is chosen such that the average electronic energy loss experienced by a 100-keV Ag projectile penetrating a 9 nm thick silver foil equals that calculated from the Lindhard–Scharff model. The philosophy behind this scaling is that – in this configuration and energy range – the Lindhard–Scharff model is known to correctly describe experimentally measured electronic stopping powers [9]. For the local electron density \( \rho_e(\mathbf{r}) \) at each position, a superposition of the electron densities induced by the surrounding atoms was calculated using atomic wave functions taken from Hartree–Fock calculations [10] of the respective atoms. It should be noted that this approach neglects the influence of electronic excitation on electron density, since the consideration of such a relationship would require TD-DFT calculations for the electronic system which – at least for the size of the crystal necessary to describe the entire collision cascade initiated by 20-keV Ag3 bombardment – are still computationally too expensive.

As a second excitation mechanism, we consider close inelastic binary collisions. When two colliding atoms approach each other, their orbitals overlap and form quasi molecular orbitals (Q-MO), the eigenenergies of which depend on the interatomic distance. Calculations show that the 9σo orbital originating from the 4d-level of silver shifts upwards with decreasing interatomic distance [11] and, if the collision occurs in the environment of a silver solid, energetically crosses the Fermi level at an interatomic distance of \( r_{\text{cross}} = 1.5 \AA \) [11]. Thus, for interatomic distances below \( r_{\text{cross}} \) free conduction band states are accessible and transitions between the Q-MO and the conduction band may occur, thereby generating a quasi-free electron with an excitation energy depending on the particular interatomic distance at which the electronic transition takes place. Details of the numerical implementation of this process have been described elsewhere [12].

3. Results

The particle dynamics induced by the impact of a 20-keV Ag3, a 7-keV Ag, and a 5-keV Ag projectile are simulated for both the constant friction coefficient \( k_0 \) and the electron density dependent friction coefficient \( k(\rho_e) \). In the case of Ag3, bombardment, the angular orientation of the projectile upon impact constitutes an additional bombarding parameter. Disregarding the complex influence of the projectile orientation on the sputtering process [see Ref. [13]] for a

![Fig. 1. Snapshot of the atoms in a collision cascade induced by the impact of a 20-keV Ag3 Cluster onto Ag(111). The colors of the particles indicate their original position. Red colored particles have been part of the projectile, yellow particle originate from the very surface layer. Blue and green particles are from layers below the surface. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
detailed analysis), we restrict the present calculation to two different choices, where the first one corresponds to a flat impact geometry where all three constituents of the cluster simultaneously hit the surface, whereas the second one corresponds to a perpendicular impact geometry where the plane spanned by the three projectile atoms is perpendicular to the surface. In the following, all results presented for Ag3 bombardment constitute the average of ten impacts for each of the two orientations of the cluster using randomly chosen impact points. For the single atom bombardment with 5-keV, there are ten impact points calculated with the modified model as opposed to 120 impact points calculated with the previous model.

As a first step of the analysis, the calculated sputter yields are listed in Table 1. For comparison, corresponding published experimental data obtained under self-sputtering conditions for polycrystalline silver are also shown. First, one should note that for atomic projectiles, both descriptions of the electronic friction lead to nearly the same predicted sputter yield, which appears to be in good agreement with the experimental value. For the cluster bombardment, on the other hand, the sputter yield calculated with a constant friction force is less than half of that calculated with the electron density dependent friction force. Moreover, the constant friction model appears to significantly underestimate the experimental value, while this discrepancy almost disappears if an electron density dependent friction coefficient is employed, thereby suggesting that the underestimation of the calculated sputter yield may be caused by an overestimation of the electronic energy loss in the constant electron density model.

In order to further unravel the cause of this effect, Fig. 2 shows the total excitation energy transferred to the electronic sub-system as a function of time after the impact of a 5-keV Ag and a 20-keV Ag3 projectile onto an Ag(111) surface, respectively, as calculated with both implementations of the electronic friction force. Obviously, for both the 5-keV Ag and 20-keV Ag3 bombardment the modification of the friction model yields a strong decrease of the generated excitation energy. While the Lindhard friction model predicts that about 75% of the original kinetic energy imparted to the solid is transferred to electronic degrees of freedom at 2.5 ps after the projectile impact, the electron density dependent friction model predicts only about half that amount (40%) for both projectiles and energies. This finding is surprising for two reasons:

- the pre-factor of the electron density dependent friction mechanism was scaled such that the energy loss experienced by a single 100-keV atom was the same for both models. Therefore, why is the amount of excitation energy now different for low-energy single atom bombardment?
- Why does the sputter yield for 5-keV bombardment not increase in spite of the apparently significant decrease of the amount of electronic energy loss?

To clarify the first point, the dependence of the electron density on the distance to an atom as well as the repulsive part of the atomic interaction potential must be considered, which is shown in Fig. 3. Due to the steeply rising repulsive wall for small interatomic distances, a particle with 100-keV initial kinetic energy can get much closer to another particle than a particle with 5-keV or even less energy (note that the most energy transferred into electronic degrees of freedom at the later times originates from low energy recoils with energies of just a few eV). At smaller
internuclear distance, the local electron density described by Eq. (3) is much higher, thereby yielding a much higher average friction coefficient for high energy atoms.

The second point is that with almost the same reduction of the friction energy loss, the sputter yield calculated for cluster bombardment increases by a factor of three, whereas the sputter yield calculated for single atom bombardment remains practically unchanged. This effect can be understood by considering the time at which particles are being sputtered. For single atom bombardment, sputtered atoms are mostly emitted during the first 400 fs after the projectile impact as a consequence of the well known linear collision cascade mechanism. In case of cluster bombardment, on the other hand, many particles are ejected at later times – up to several ps after the impact, where the difference in the amount of kinetic energy lost to the electronic sub-system between the two models is significantly larger. This enhanced energy loss results in a lower probability for these particles to overcome the surface barrier, thereby effectively reducing the sputtering yield.

4. Conclusion

Modeling the flux of sputtered particles following the bombardment of a solid silver surface with atomic and cluster silver projectiles, it is shown that different assumptions regarding the electronic friction force may lead to significantly different predictions of the sputter yield. For the specific case of cluster bombardment, we show that an electron density dependent friction coefficient calculated, for instance, according to the formalism suggested by Caro and Victoria leads to a significantly enhanced predicted sputter yield as compared to the Lindhard description of electronic friction. At first sight, this finding seems understandable, since less kinetic energy is transferred to the electronic sub-system as compared to the Lindhard friction mechanism. The sputter yield calculated for 5-keV Ag bombardment, on the other hand, is the same for both models of the friction force, although the excitation energy dynamics and particularly the reduction of the total electronic energy loss appear to be the same. In order to rationalize this discrepancy, one needs to consider the different sputtering mechanisms prevailing in both cases, leading to vastly different ejection times and energies of the sputtered particles under atomic and cluster projectile bombardment, respectively. Comparing the calculated sputter yields with corresponding experimental data, one finds that the modified friction model reproduces published yield values obtained under 7-keV Ag⁺ and 20-keV Ag⁺ bombardment of a polycrystalline silver surface rather well, while the Lindhard friction model appears to underestimate the yield measured under cluster bombardment.

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