Influence of the polar angle of incidence on secondary ion formation in self-sputtering of silver

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The influence of the projectile impact angle on secondary ion formation was studied using a computer simulation model applied to the bombardment of an amorphous silver crystal by 5-keV Ag atoms. The model employs a molecular dynamics (MD) scheme for the description of particle dynamics within the atomic collision cascade. The electronic degree of freedom is treated within the framework of a free electron gas model incorporating kinetic excitation by electronic friction and electron promotion. Transport of the excitation energy away from the spot of generation is treated by a diffusive approach. In combination with a rate equation model for electronic charge transfer an individual ionization probability \( \alpha^+ \) is assigned to each sputtered particle. The results reveal that the average ionization probability of sputtered atoms increases upon the transition from normal to oblique incidence. The dependence of \( \alpha^+ \) on the emission velocity of ejected atoms is traced back to the temporal structure of the excitation profile induced after projectile impact.

**Keywords:** angle dependence; ion formation; sputtering; silver; collision

**Introduction**

The bombardment of a solid with atomic projectiles initiates an atomic collision cascade in a near-surface region. In the course of this collision cascade, particles may overcome the surface barrier and may be ejected (sputtered) from the surface into the gas phase. The flux of sputtered particles does not only consist of neutrals but also of ionized atoms. Because of the fact that only the ionized fraction of particles can be detected by means of secondary ion mass spectroscopy (SIMS), a detailed understanding of the ion formation process is of utmost importance for a quantitative analysis of experimental SIMS spectra.

The physical mechanisms underlying the secondary ion formation are still not fully understood. Although there exists a variety of adiabatic and nonadiabatic analytical models (see reviews Refs [4,5] and references therein), all these descriptions exhibit some principal drawbacks concerning their application potential. First, they neither involve the detailed particle dynamics in the atomic collision cascade nor do they take into account any space- or time-dependence of the electron temperature. Second, these models are not directly linkable to experimental bombarding parameters like the kinetic energy of the projectile, its nuclearity or its angle of incidence. Therefore, we have developed a model combining molecular dynamic (MD) simulations for the description of particle dynamics with a kinetic excitation model. The latter incorporates the transport of excitation energy away from the spot of generation and yields a space- and time-dependent electron temperature profile \( T_e(\vec{r}, t) \) in the cascade volume. Using this model, it is possible to individually analyze the emission process of each sputtered atom under consideration of the local, momentary electron temperature at the site the particle is emitted from. For each sputtered particle, this is then used as input for a simple rate equation model describing the charge transfer between the valence level of the sputtered atom and the conduction band of the solid. This way, it is possible to ascribe an individual ionization probability to every emitted atom.

In the present paper, this model will be applied to calculate ionization probabilities \( \alpha^+ \) for silver atoms sputtered from an amorphous silver crystal under self-sputtering conditions (5 keV: \( \text{Ag} \rightarrow \text{Ag}^+ \)) with different polar angles of incidence. The results will be discussed in terms of the influence of the angular degree of freedom on secondary ion formation.

**Model**

The computational model employed in this study consists of four parts: the calculation of particle dynamics within an atomic collision cascade, the description of electronic excitation mechanisms within the cascade, a model for the transport of electronic excitation energy away from the spot of generation and a model for secondary ion formation based upon an elementary charge exchange model. In the following, each part of the scheme will be briefly described.

**Molecular Dynamics (MD)**

A standard MD Code is employed to integrate the Newtonian equations of motion for the projectile and all 15 000 atoms of the amorphous Ag model target. The interatomic forces are derived from the MD/MC CEM potential fitted to bulk and cluster properties of silver. For further details, see Ref. [10].
Excitation mechanism

The atomic collision cascade is assumed to be embedded in a quasi-free electron gas with a Fermi energy $E_F$. According to the Lindhard model\cite{11} of electronic stopping, cascade atoms in motion experience an effective, velocity-proportional friction force originating from direct atom–electron collisions. This frictional energy loss is treated as a source of excitation energy fed into the electronic system.

In addition, we take into account autoionization processes in close binary collisions as originally proposed by Joyes\cite{12}. Briefly, it is assumed that in violent binary encounters quasi-molecular orbitals (MO) are transiently formed, the eigenenergies of which vary as a function of interatomic distance $r$. Calculations reveal\cite{16} that the diabatic $9\sigma_g$ MO evolving from the atomic 4d–4d level monotonously increases in energy such that it energetically crosses $E_F$ at $r_c = 1.5$ Å. Whenever the MO is energetically above $E_F$, autoionizing resonant electronic transitions into free conduction band states may occur with a transition rate given by the energetic width of the promoted orbital. Each transition at an energy $E^*$ corresponds to the generation of a hot electron with an excitation energy $(E^* - E_F)$ which is another source of excitation. Such processes leave a vacancy in the MO that on a time scale of femtosecond will manifest as a $d$-hole in the valence band. The $d$-hole energy amounts to approximately 5.4 eV. Both, the excitation energy of the hot electron and the $d$-hole energy are subtracted from the kinetic energy of the colliding atoms by means of an artificial shift of their positions directly following the electronic transition. For details, the reader is referred to Ref. [13].

Transport

We assume that the excitation energy is transported away from the spot of generation according to a diffusion equation for the excitation energy density $E(r, t)$ with a central parameter $D$ describing the rapidness of the transport. This diffusion model as well as the discussion of the physics and the appropriate numerical choice of $D$ has been discussed elsewhere\cite{14}. Therefore, we only note that for the amorphous crystal considered here, $D$ can be estimated as $1 \text{cm}^2/\text{s}$ corresponding to an electron mean free path reduced to the order of an interatomic distance due to the atomic disorder.

The numerical solution of the diffusion equation yields an excitation energy profile $E(r, t)$ that can be converted into an electron temperature profile $T_e(r, t)$. The parametrization of the excitation energy density via an effective electron temperature may be criticized due to the relatively short-time and length scales considered here. However, we note that recent ab initio calculations\cite{15} for similar model systems as considered here reveal – that at least for the electronic friction mechanism – the native excitation spectrum generated by the excitation mechanism itself already closely resembles a Fermi-Dirac equilibrium distribution, thereby justifying the concept of $T_e$.

Ion formation

For the calculation of the ionization probability, we apply the substrate excitation model of Stroube\cite{16} and numerically solve the rate equation

$$\frac{dn_a(t)}{dt} = -\Gamma(z(t))(n_a(t) - f(E_a(z(t)), T_e(t)))$$

for the occupation probability $n_a(t)$ of the atomic valence level $a$, of each individual particle on its path away from the surface. The distance of the particle to the surface $z(t)$ is directly taken from the MD. The time- and space dependent electron temperature $T_e(r, t)$ is evaluated at the projection of the particle position $r(t)$ onto the surface. The function $\Gamma(z)$ describes the electronic transition rate between the conduction band and the atomic valence level. The parameter $E_a(z)$ denotes the $z$-dependence of the energy of the atomic valence level. The $z$-dependence of both quantities is parametrized by means of simple functional forms as explained in detail elsewhere\cite{17}.

Results

For 5-keV Ag bombardment of an amorphous silver target consisting of 15 000 atoms, the presented model has been applied to simulate secondary ion generation for three different choices ($\Theta = 0^\circ, 30^\circ, 60^\circ$) of the polar angle of incidence. For each $\Theta$, 169 trajectories with different impact points have been calculated. In total, 1000 ($0^\circ$), 1400 ($30^\circ$) and 2100 ($60^\circ$) atoms are found to be sputtered from the surface.

Figure 1 shows the calculated individual ionization probability $\alpha^+$ for each sputtered atom as a function of its inverse velocity $v_z$ perpendicular to the surface.

We find that $\alpha^+$ varies within a range of almost 20 orders of magnitude depending on $(v_z)^{-1}$ and $T_e$. For all $\Theta$, we observe an initially exponential decrease of $\alpha^+$ with $v_z^{-1}$ that tends to saturate for inverse velocities above $4 \mu$s/cm. With decreasing emission velocity, $\alpha^+$ becomes more and more independent of $v_z^{-1}$ and the electron temperature $T_e$ increasingly adopts the role of the crucial parameter determining $\alpha^+$.

Interestingly, we find atoms with comparable $(v_z)^{-1}$ and $T_e$ (time average of $T_e$ along particle trajectory from the surface to the detection plane) can exhibit ionization probabilities that differ by orders of magnitude. This observation impressively demonstrates the crucial role of the detailed particle kinetics and electron temperature dynamics during the emission process. Owing to the fact that both pieces of information cannot easily be obtained from analytic theory, MD simulations as presented here appear to be the most promising tool to tackle the problem of secondary ion generation.

The variation of the angle of incidence mainly affects the ionization probabilities of fast particles with emission velocities $v_z > 1 \text{cm/\mu s}$. In that velocity regime the ionization probabilities increase with increasing $\Theta$ due to higher electron temperatures $T_e$ experienced by the emitted particles. In consequence, the average ionization probability $\alpha^+$ increases from $3.4 \times 10^{-4}$ for normal incidence and $1.5 \times 10^{-2}$ for $\Theta = 30^\circ$ up to $6.7 \times 10^{-3}$ for $\Theta = 60^\circ$. These values compare rather well with experimentally measured ionization probabilities for 5 keV $Ar^+$ bombardment of polycrystalline silver with an incidence angle of 30° ($\alpha^+ = 0.3 \times 10^{-4}$, see Ref. [17]).

In order to uncover the physics behind the $\Theta$-dependence of $\alpha^+$, we have analyzed the particle emission process for each particle in more detail.

Figure 2 shows $v_z$ versus the time of emission $t$ after the projectile impact. The emission time is defined as the time the projectile impact when the particle crosses a parallel to the surface plane 7 Å above the surface. From the obtained correlation between $v_z$ and $t$, which is naturally afflicted with statistical fluctuations, the physical origin of the angular dependence of $\alpha^+$ for $v_z > 1 \text{cm/\mu s}$
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Figure 1. Calculated ionization probabilities versus the inverse normal velocity of the sputtered particle. In addition, the electron temperature experienced by the emitted particles is shown using the indicated color map.

Figure 2. Normal emission velocity component \( v_z \) for each sputtered particle as a function of emission time \( t \) for three different polar impact angles. This can be traced back to the time slot from approximately 0 to 150 fs. For this time interval, Fig. 3 illustrates the trajectory average of the maximum local electron temperature at the surface for the different impact angles as a function of time. It is obvious that the first peak in \( T_e \) not only becomes more pronounced with larger \( \theta \) but also exhibits a slower temporal decay thereby leading to higher ionization probabilities. This increased kinetic substrate excitation under non-perpendicular incidence in the initial stage of the cascade may be attributed to the longer residence time of the projectile in a near-surface region compared to normal incidence.

Conclusion

Using a multistep computer simulation model, we have investigated secondary ion formation in 5-keV self-sputtering of amorphous silver for three different polar bombarding angles \( \Theta = (0^\circ, 30^\circ, 60^\circ) \). We find that the average ionization probability increases by a factor of 20 from normal incidence to \( \Theta = 60^\circ \). Unfortunately, no experimental data exist so far to test the effects predicted here. The present study therefore calls for an experimental investigation of secondary ion formation as a function of impact angle, preferably by detecting both secondary ions and their neutral counterparts under otherwise identical experimental conditions. Investigations of this kind are currently under way in our lab. A detailed analysis of the particle emission processes reveals that this effect originates from higher substrate excitations for larger \( \Theta \) within the first 150 fs after the projectile impact.

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References