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Does local disorder influence secondary ion formation?

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The ionization probabilities of particles sputtered from a clean metallic single crystal surface bombarded under self-sputtering conditions (i.e. with projectiles of the same atomic species as the target material) are calculated using a hybrid computer simulation model based on a combination of molecular dynamics and excitation dynamics. The simulations reveal an apparent correlation between the ionization probability of a sputtered particle and the local lattice disorder at the point in space and time when it is being emitted from the surface. By examining cross correlations between emission time, local order and the local surface electron temperature, however, we find that particles exhibiting the highest ionization probability are being emitted in an early stage of the collision cascade, where the surface is still practically intact. Atoms emitted at later stages of the cascade can _in principle_ benefit from an effective excitation energy confinement induced by the local disorder; the resulting ionization probability, however, is too low to significantly contribute to secondary ion formation. Copyright © 2014 John Wiley & Sons, Ltd.

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Introduction

Secondary ion formation induced by ion bombardment of solid surfaces is still an important question in secondary ion mass spectroscopy that has only partly been solved.[1] For the conceptually simplest case of a metal ion emitted from a clean metal surface, the prevailing mechanism determining the charge state of a sputtered particle is resonant electron transfer between its valence state and the metal conduction band states. Although there are an abundant number of analytical models describing this scenario, it has been pointed out that the assumption of a quiescent substrate surface underlying most of the published model descriptions is highly questionable.[2] For instance, it is well known that the collision cascade following the ion impact strongly disturbs the local crystallographic order, thereby altering the band structure of the solid. In addition, electronic stopping of projectile and recoiling target atoms generates electronic excitation of the substrate, which must be taken into account in a realistic model description. In an attempt to include substrate excitation, Šroubek [3] has proposed a model based on the assumption of a locally elevated electron temperature, which is taken as a (constant) parameter of the model. Because of the vivid dynamics in a collision cascade, however, it is clear that such a parameter must be strongly time and space dependent. Over the recent years, we have therefore developed a hybrid computer simulation model describing secondary ion emission from a clean metal surface, which combines a molecular dynamics (MD) simulation of the collision cascade with kinetic excitation via the electronic energy loss of each moving particle.[4–7] The model is different from previous approaches to include kinetic excitation processes into an MD simulation,[8–13] where only the production of d-band holes in close binary collisions was considered, which were then assumed to stay localized on one of the colliding atoms, thereby neglecting both the generation of hot electrons as well as the fast transport of electronic excitation away from the point of its generation. In contrast, our model includes the direct excitation of hot electrons via the electronic friction experienced by the projectile and recoiling target atoms as well as autoionization following electron promotion in close atomic collisions as an additional source of excitation and incorporates the transport of excitation energy by means of a diffusive treatment. As a result, the model yields a time and space dependent electron temperature profile $T_e(\vec{r}, t)$ around the projectile impact point, which is then employed to calculate individual ionization probabilities for each sputtered atom using a simple rate equation tunneling model.[14,15]

Based on this model, it has been established that the local and temporary electronic substrate excitation induced by the projectile impact significantly influences the ionization probability of particles emitted from such a surface.[15–17] In the present work, we have expanded on this finding by investigating the correlation of the electron temperature 'seen' by a sputtered particle with its emission velocity and particularly the role of this correlation in secondary ion formation. In addition, the correlation of the local electron temperature with the local lattice disorder at the emission point of a sputtered particle is discussed with respect to its influence on the secondary ion formation process.

Model

The hybrid model employed in this study consists of four parts:

- MD simulation describing the particle dynamics,
- kinetic excitation via the electronic stopping of all moving particles using (i) Lindhard-type electronic friction and (ii) electron promotion in close binary collisions,

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- a nonlinear diffusion equation to calculate the transport of the excitation energy away from the point of its generation, where the electronic energy loss of each moving particle is treated as a source of excitation energy and
- numerical integration of a rate equation to calculate an individual ionization probability for each sputtered particle.

The parameters entering the model were chosen to represent the bombardment of a silver single crystal with an atomic silver projectile. More specifically, the interatomic forces entering the MD simulation were calculated by employing a many-body Monte Carlo-MD/corrected effective medium potential fitted to the bulk properties of solid silver,[18] and the Lindhard friction constant was calculated from the conduction band electron density of silver as well. The key parameter in this treatment is the electronic heat diffusivity D, which is calculated as

$$D = D_0(T_e, T_l) = \frac{1}{3} v_F \lambda \qquad (1)$$

For a perfect crystalline material, the electron mean free path is taken as

$$\lambda = \frac{v_F}{aT_e^2 + bT_l} \qquad (2)$$

with parameters $a = 1.2 \times 10^7\,K^{-2}s^{-1}$, $b = 1.2 \times 10^{11}\,K^{-1}s^{-1}$,[19,20] T_e and T_l being the local electron and lattice temperature, respectively.[1] For an amorphous crystal, on the other hand, the mean free path is assumed to be essentially restricted to an interatomic distance, corresponding to $D = D_{am} = 0.5\,cm^2/s$. To account for the local crystallographic disorder at a point $\vec{r}$ within the cascade volume, the diffusivity is interpolated between these limits by means of a local order parameter defined by examining the crystal atoms located within a sphere of radius $r_{cut} = 6.5\,Å$ around $\vec{r}$ using

$$\Lambda(\vec{r}, t) = \frac{1}{3N} \left| \sum_{i=1}^{N} \sum_{j=1}^{3} \cos\left(\frac{2\pi r_i^j}{a^{(j)}}\right) \right| \qquad (3)$$

where r_i^j is the jth component of the position vector of the ith atom and the parameters $a^{(1)}$, $a^{(2)}$ and $a^{(3)}$ represent the periodicity of the lattice in each of the three dimensions.[5,21] The outer sum loops over all $N = N(\vec{r})$ atoms that are within the cutoff radius $\vec{r}$.

The detailed information about the time-dependent local electron temperature determined this way allows the calculation of an individual ionization probability for each sputtered particle. For that purpose, we integrate the rate equation

$$\frac{dn_a(t)}{dt} = -\Gamma(z(t)) \cdot \left(n_a(t) - f\left(E_a(z(t)), T_e\left(\vec{r_p}, t\right)\right)\right) \qquad (4)$$

for the occupation of the outgoing particle's valence level $n_a(t)$ as proposed in Šroubek's model.[3] In Eqn (4), $f(E_a, T_e)$ denotes the Fermi–Dirac function at the energy E_a of the valence level at a distance z from the surface. As an important feature of the model, we follow the trajectory of each emitted particle and insert the electron temperature $T_e\left(\vec{r_p}, t\right)$ at the projection of the particle's momentary position onto the surface $\vec{r_p}$ into Eqn (4).

The transition rate $\Gamma(z)$ is calculated by $\frac{2\Delta(z)}{\hbar}$ where $\Delta(z)$ is the broadening of the atom's valence level at the surface. The exact parameterization of the functions $E_a(z)$ and $\Gamma(z)$ has been discussed in an earlier publication.[14] As an initial condition, we chose $n_a(t=0) = 0.5$ corresponding to the occupation of the conduction band states at the Fermi level.

Results and discussion

The calculations were performed for the bombardment of an Ag (111) surface with 5-keV silver atoms using a set of 120 impact points distributed equally within an irreducible zone on the surface.

In order to visualize the physical interpretation of the local order parameter, we plot in Fig. 1 the pair correlation function of all atoms within a volume of ($4.2 \times 4.2 \times 4.2\,Å^3$). The data were calculated as an average over all calculated trajectories at different times following the projectile impact.

It is evident that the crystallographic order quickly disappears in the course of the collision cascade. Already at 200 fs after the projectile impact, the sharp features indicative of the perfect crystal become significantly broadened and superimposed to a randomized background; until at 700 fs, the long range order has practically disappeared, indicating complete amorphization of the solid. The corresponding values of Λ calculated using Eqn (3) are also displayed in the figure, thus allowing judging of the amount of disorder described by a certain value of this parameter.

In order to examine a possible correlation between the ionization probability of a sputtered atom and the local crystallographic order, we calculate the local order parameter Λ at its emission site and time at the surface. In this context, the problem arises on how to define the exact time when a particle is considered to be emitted from the surface. Here, we use the time when the particle crosses a plane located at an interatomic distance (2.5 Å) above the initial surface, the height of which is defined by the center of the uppermost atomic layer within the undisturbed crystal. Taking the time when the particle crosses the surface plane itself is problematic as many sputtered particles originate from the uppermost atomic layer and therefore would be counted as sputtered immediately at the beginning of the simulation. Figure 2 shows the probability distribution
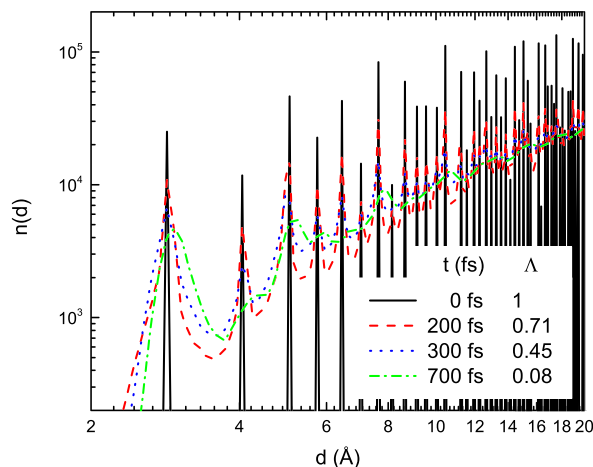

Figure 1. Pair correlation function for atoms located in a volume of about **42 × 42 × 42 Å³** around the projectile impact point at different times after the impact. The legend shows the corresponding values of the local order parameter Λ.
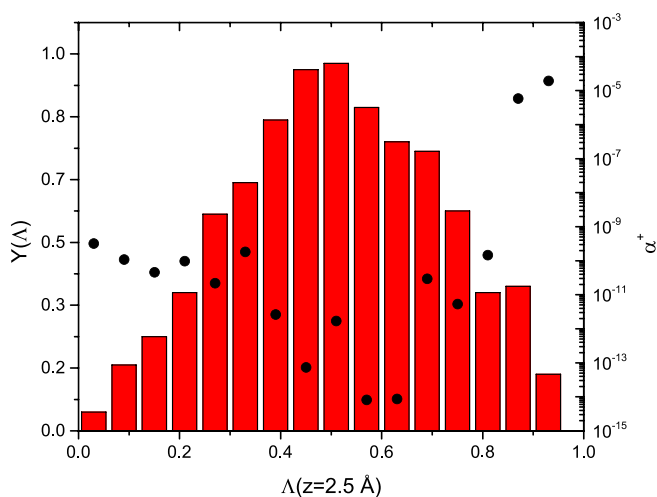
Figure 2. Number of emitted atoms per incident ion *versus* local order parameter Λ at the atom's emission point as defined in the text (red bars and left axis). Black dots and right axis: average ionization probability of the n atoms binned in a specific interval $\Delta\Lambda$.

of different local order parameter values among the sputtered atoms determined that way.

It is seen that only few particles are sputtered from an intact $\Lambda \approx 1$ or from a completely randomized ($\Lambda \approx 1/\sqrt{N}$) crystal. Most of the sputtered particles originate from a local environment that is described by $\Lambda \sim 0.5$, indicating severe disturbance of the perfect lattice order as described by the blue curve in Fig. 1. The implication of this finding is evident: Any secondary ion formation model that treats the substrate as an ideal crystal with its corresponding intact electronic band structure must fail to describe the ionzation probability of most of the sputtered material. While this is not too problematic for a metal (where the substrate is mostly treated as a Fermi electron gas anyway), it has strong consequences for semiconductors and insulators. In fact, Šroubek *et al.* have calculated the band structure of silicon following the impact of a 0.6-keV Argon ion and found a complete disappearance of the band gap on the subpicosecond time scale, leading to a practically metallic behavior of the substrate at the point and time when sputtered atoms leave the surface.[22]

The average ionization probability α^+ calculated for the atoms binned in each bar of Fig. 2 is presented as the black data points. If averaged over all emitted atoms, the calculation yields a mean ionization probability of $<\alpha^+>=5\times10^{-7}$, which underestimates the corresponding experimental value ($\alpha^+=3\times10^{-5}$) measured under 5-keV Ar$^+$ bombardment of a clean polycrystalline silver surface.[23] As discussed in detail elsewhere,[14] this difference can be attributed to the fact that the simulations were performed for a perfectly clean single crystalline target, whereas the experimental data were taken on a sputter cleaned polycrystalline surface that will inevitably be disturbed by bombardment-induced defects. In fact, if the simulation is repeated on a preamorphized crystal, the calculated mean ionization probability becomes comparable with the experimental value.[24]

From Fig. 2, it is obvious that the ionization probability shows a completely opposite behavior as compared with the distribution of Λ, indicating the highest ionization probability for those atoms sputtered from an intact region of the surface (note the logarithmic scale of the axis). In fact, the data indicate that local disorder does not favor the ionization of a sputtered atom unless the surface is completely amorphized. At first sight, this finding appears surprising because amorphization should lead to a decrease of the electronic heat diffusivity and therefore effectively trap the electronic excitation within the cascade volume. As a consequence, one would have expected an increase of α^+ with decreasing Λ. It is seen that this trend is indeed observed for $\Lambda > 0.5$, while it is clearly turned around at larger values of Λ.

In order to examine the physics behind the apparent anticorrelation between ionization probability and local order, the time structure of sputtering, electron temperature and crystal disorder must be considered. As a first step, we look at the emission time distribution among the sputtered atoms. In Fig. 3, the ionization probability of each sputtered atom is plotted *versus* the local order parameter calculated at the time and place of its emission. In addition, the emission time is presented by the color of the data points according to the color bar on the right hand side. As expected, there is a significant correlation between the degree of local order at the area the atoms are emitted from and the time the particles are sputtered. To complement the information, Fig. 2 shows the same ionization probability distribution with the color coding of the data points now indicating the
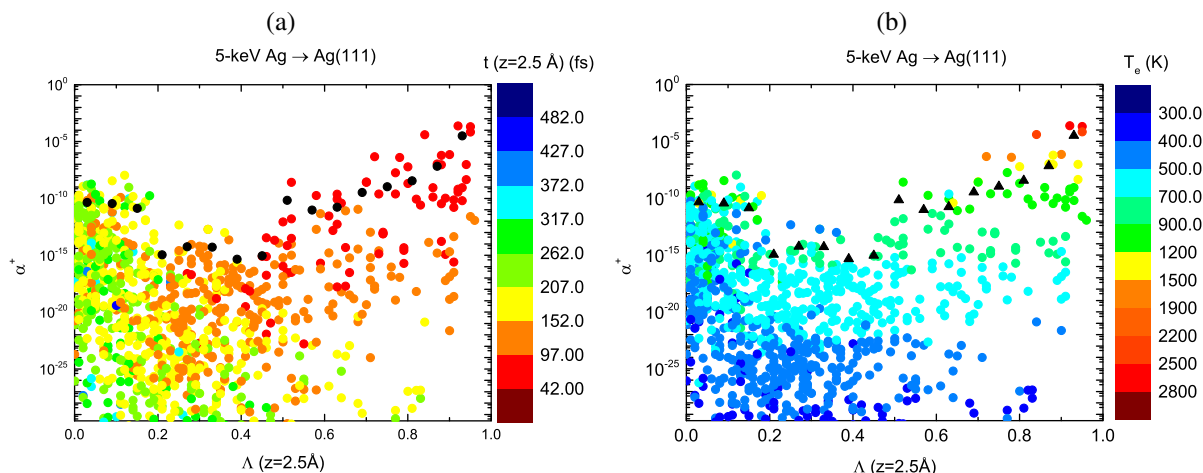

Figure 3. Ionization probability α^+ of a sputtered atom *versus* local order parameter Λ at the atom's emission site with color coding according to (a) emission time and (b) local electron temperature at the emission site.

surface electron temperature 'seen' by the sputtered atom during its emission.

As already pointed out earlier,[16,17] those atoms that exhibit the highest ionization probability are emitted during the very early stages of the collision cascade, when the surface has not yet been altered very much and most crystal atoms still reside at their original lattice sites. In this situation, the transport of excitation energy away from the surface is very fast, leading to an efficient cooling of the electronic system. On the other hand, the surface is strongly heated electronically by the fast projectile entering the solid, thereby transferring kinetic energy into excitation via both electronic friction and electron promotion. As shown previously, this leads to a sharp peak of the surface electron temperature at times of the order of 10 fs after the impact, followed by a strong decrease in time. Therefore, those atoms sputtered first 'see' the surface at a higher electron temperature, leading to a relatively high ionization probability. Atoms exhibiting the lowest average ionization probability, on the other hand, are being emitted at times around 100 fs after the projectile impact, where the collision cascade has spread to involve more atoms at deeper layers, and the crystallographic order becomes significantly altered. However, the corresponding value of $\Lambda \approx 0.5$ is still large enough to facilitate relatively rapid transport of excitation energy, thereby still efficiently cooling the electronic system, while the heating source right at the surface becomes strongly reduced because the kinetic energy is being distributed over more atoms moving with slower speed within a larger volume. As a consequence, we find a minimum of the surface electron temperature at that stage, leading to very low ionization probability of the emitted atoms. At times of the order of 300 fs and above, the surface becomes almost completely amorphized, thereby strongly reducing the electronic heat diffusivity and effectively trapping the excitation. Because the surface is still being heated electronically by the now fully developed collision cascade, the electron temperature rises again. This is clearly visible in Fig. 2, which shows that electron temperatures between 1000 and 1500 K are reached at that stage, leading to a corresponding increase of the average ionization probability.

Conclusion

The ionization probability of atoms sputtered from a single crystal Ag(111) surface after bombardment with 5-keV Ag was examined with respect to the local lattice order at the spot and time of their emission from the surface. It is found that the particles with the highest ionization probability are sputtered from an almost undisturbed surface, as they are emitted during the first 100 fs after the projectile impact. Ionization probabilities of particles sputtered at later stages of the collision cascade, when the crystallographic order of the solid is almost completely destroyed, may benefit from the confinement of excitation energy induced by the strong reduction of its transport away from the surface, but the resulting ionization probabilities are still orders of magnitude below those of the particles sputtered in the first 100 fs. As a consequence, we conclude that those atoms contribute only negligibly to the measured secondary ion yield. The apparent correlation between local order and ionization probability can be fully understood in terms of the calculated electron temperature dynamics at the surface, indicating that substrate excitation is the essential parameter determining the efficiency of secondary ion formation at a clean metal surface.

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