Formation of excited Ag atoms in sputtering of silver

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A model is presented for the formation of excited Ag* ($4d^9 5s^2$) atoms during sputtering of Ag metal by energetic Ar$^+$ ions. The essential part of the formation process is the slow diffusion of $4d$ holes in the collision cascade from the sites of violent Ag-Ag collisions to the emitted Ag atoms. A computer simulation of Ag cascades and of the $4d$-hole transport allows us to quantify the model and to describe all characteristic features of the available experimental data, in particular the fact that the sputtered Ag* atoms exhibit a narrower kinetic energy distribution than those ejected in the electronic ground state.

I. INTRODUCTION

When an atomic particle collides with a solid surface, the incident particle can scatter from the surface by either single or multiple binary elastic collisions, or the projectile impact can generate a cascade of quasielastic collisions in the near-surface region that leads to the ejection of surface atoms into the gas phase (sputtering). In principle, inelastic processes that alter the excitation or ionization states of the backscattered projectile and sputtered particles accompany all of these collisions. For scattering, an analysis in terms of one-electron transfer often provides a sufficient description of charge and excited state formation of the emitted particles.[1-3] For sputtering, however, multiple electronic excitations and their transfer in the cascade may significantly influence the charge and excitation states of the emitted atoms,[4-6] although the experimental evidence is not yet conclusive.

In this paper, we analyze experimental results on excited silver atoms Ag* sputtered from clean silver surfaces by impact of energetic (>3 keV) Ar$^+$ ions. We chose this system because the experiments, based on laser postionization secondary neutral mass spectroscopy,[7-9] give precise information on the energies and intensities of both neutral ground-state and excited-state sputtered silver atoms. The relatively simple electronic structure of silver, with only two relevant excited states, facilitates the comparison with theoretical models and the analysis provides quantitative information on electronic processes in cascades. The most salient features of the experimental results, which must be explained by any realistic model, are the high probability with which excited atoms are emitted (about 0.1–1 % of the total flux) and the observation that the Ag* ($4d^9 5s^2$, $^2D_{5/2}$, and $^2D_{3/2}$) kinetic energy distribution is narrower than that of Ag atoms emitted in the ground state ($4d^{10}$, $^2S_{1/2}$), i.e., the ex-

citation probability decreases as the kinetic energy of sputtered silver atoms increases. In addition, the excitation probability is independent of the emission angle. It should be stressed that these features are not unique for Ag, but have been observed in Cu and other d metals,[7] as well. Ag, however, has a higher excitation energy ($^2D_{5/2}$ at 3.75 eV and $^2D_{3/2}$ at 4.3 eV) so that the narrowing of the Ag* kinetic energy distribution and the high excitation probability are particularly striking.

Previous attempts[10,11] to explain the experimental data were based on two-step models describing the formation of excited neutrals as a combination of the emission of an ionic precursor, produced by various excitation mechanisms, followed by its resonant neutralization above the surface. In these models, the final energy distribution of excited atoms, and thus the narrowing of that distribution, is ascribed to the surface neutralization process. It is difficult, however, to find a physically acceptable, angular independent neutralization process based on resonant electron transfer[10] that correctly describes the experimental results.

In contrast, we present a model of excited atom emission that does not use the concept of surface excitation and neutralization. It is instead assumed that d holes are created by energetic collisions at the beginning of the cascade, and that they are immediately screened by conduction electrons, thus forming excited atoms. The excitations propagate through the solid, and are then transferred to an atom as it is sputtered from the surface, forming neutral excited Ag*. By computer simulation of Ag collision cascades, and by the fitting of calculated and observed Ag and Ag* energy distributions, we obtain quantitative information on the d-hole transport. Our model provides a physical understanding of the major features of the experiments, and the results are in good numerical agreement with the experimental data.

II. COMPUTER SIMULATIONS

The simulation of cascades was carried out on an HP workstation J7000 using a Molecular Dynamics code originally developed by Garrison and co-workers. The basics of these calculations have been described in great detail earlier,[12–15] and therefore only the parameters and modifications relevant to the present work will be mentioned here. In short, the motion of all target atoms is followed simultaneously by numerically solving the classical Newton equations of motion with electronic energy loss included as a friction mechanism using the Lindhard formalism.[16] The Ag solid is modeled by a fcc crystallite containing $12\times12\times6$ atoms with an unreconstructed (001) surface. It was tested that the use of larger crystallites does not significantly change the results. The interatomic Ag-Ag interaction was described using the MD/MC corrected effective medium potential developed by Kelchner *et al.*,[17] and free boundary conditions were applied to all sides of the crystallite. The bombarding projectile is represented by a 3-keV Ar atom moving along the surface normal and hitting the crystallite at different surface locations ("impact points"). The Ar-Ag interaction was described by a purely repulsive Moliere potential.[18] In order to obtain averaged quantities with sufficient statistics, a total of 20 000 individual cascades ("trajectories") were simulated using different impact points that were uniformly distributed within an irreducible triangular zone located in the center of the (001) surface. Target (Ag) atoms that are set in motion are counted as sputtered if they move in a direction away from the surface and cross a plane situated 7 Å above and parallel to the surface. Note that this distance is matched to the cutting distance of the Ag-Ag interaction potential used. Since the surface can be heavily deformed in the course of the cascade, it is checked at the end of the simulation that no residual interaction with other crystallite atoms is detected.

To simulate the excitation we assume, in the spirit of the preceding discussion, that a $4d$ vacancy is created with unit probability in the course of the collision cascade whenever the interatomic distance between two target atoms becomes smaller than a critical distance R_c. In that sense, the collisional excitation process is treated in the same way as has been employed earlier.[19–22] For the case of Ag-Ag collisions, R_c was taken as 1.2 Å.[9] For collisions between Ar and Ag, on the other hand, R_c must be significantly smaller, thus leading to a relatively high center-of-mass energy threshold of about 1400 eV for a d-hole generating collision.[23] We therefore neglect the contribution of Ar-Ag collisions to the excitation mechanism, as the critical collision energies are one order of magnitude higher than for Ag-Ag.

In order to examine the localization behavior of the resulting excitation, it is assumed that the d hole is created with a delta shaped probability function peaked at the point $\mathbf{r}_i$ and the time t_i when the excitation criterion is fulfilled, where $\mathbf{r}_i$ refers to the coordinates of one of the colliding atoms. We would like to stress that, although the actual excitation process in violent collisions is more complex, it is highly localized in space and time. Thus, the delta function approximation is sufficient in this case as the transfer processes have

much longer temporal and spatial scales. Note that we do not take into account any possible influence of electron promotion excitations on the particle trajectories because the energy losses are small (about 4 eV) compared to the particle kinetic energies involved in such collisions (>270 eV).

III. RESULTS AND DISCUSSION

Ag* may be produced during the rapid passage of a Ag atom through the surface region. According to the theory of nonadiabatic transitions, the probability for excitation P is approximately given by

$$P_{\mathrm{exc}} = A \exp\left(\frac{-\Delta E}{B\hbar\,\gamma\nu}\right), \tag{1}$$

where A and B are constants of the order of one, with their precise values dependent upon the electronic structure of the system. ΔE is the separation between the ground and the excited states, ν is the velocity of the emitted atom perpendicular to the surface, and γ is the inverse value of the characteristic interaction distance of the system. Using typical values of $A=B=1$, $\Delta E=3.75$ eV, $\gamma=2$ Å^{-1}, and $\nu=3\times10^5$ cm/s (corresponding to an emitted Ag atom with 5 eV of kinetic energy), a value of $P_{\mathrm{exc}}=3\times10^{-43}$ is obtained.

Much larger excitation probabilities than the values predicted by Eq. (1) are expected at higher Ag kinetic energies, however, when promotion of electrons from deeper levels can take place during a close collision.[24,25] If the $4d$ level of a Ag atom is promoted to an energy above the Fermi level, the electron may escape, leading to a semilocalized d hole.[25] According to a calculated *ab initio* correlation diagram for the Ag-Ag interaction,[10] such a promotion of semilocalized $4d$ levels can occur when the internuclear separation is below a critical distance of $R_c=1.2$ Å, which is attained during a collision in which the center-of-mass energy is above 135 eV. Thus, if a Ag atom in the cascade hits a surface Ag atom originally at rest from below with a kinetic energy of 270 eV or higher, the surface atom can be sputtered into the $4d^9 5s^2$ excited state with a high probability. In this scenario, however, the excited atoms would be preferentially ejected with a relatively high kinetic energy, which is at variance with the experiment. To explain why most of the sputtered Ag* atoms have kinetic energies below 5 eV,[8] the excitation must be transferred from the sites of violent Ag-Ag collisions to the surface emission sites. A relatively slow transport of $4d$ holes in the cascade is the essential feature of the model that has been incorporated into these computer simulations.

To determine the number of excited atoms initially produced by deep level promotion, we calculated the number of collisions with $R_c<1.2$ Å per unit time (fs), averaged over 20 000 collisions. The result is shown in Fig. 1 by the full line. For the transfer of the excitation from the cascade to the sputtered atom it is essential to define the time t_e and the position r_e when the sputtered particle no longer electronically interacts with the substrate atoms. Because the physics of the hole transfer is not elaborated in detail, the distance
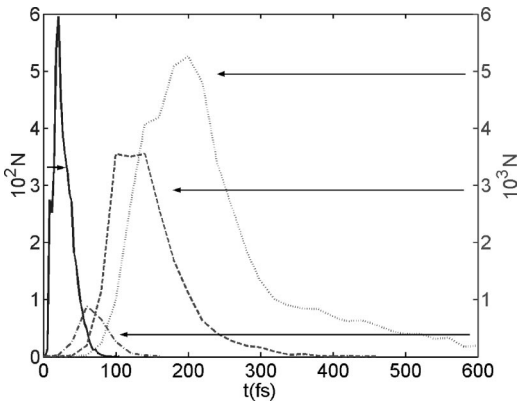
FIG. 1. The calculated numbers N of Ag atoms sputtered from Ag metal per unit time (fs) under the impact of 3-keV Ar$^+$ ions as a function of ejection time. The time $t=0$ corresponds to the initial Ar$^+$ impact, and t represents the time when the sputtered particle has just separated from other atoms by 3 Å. The numbers are averaged over 20 000 cascades. The dotted, dashed, and dash-dotted lines correspond to atoms with kinetic energies in the 0.4–4, 10–15, and 80–100 eV ranges, respectively. The solid line denotes the number of collision events per unit time (fs) with minimum collision distances smaller than 1.2 Å.

between two atoms that defines r_e is not precisely known. It is reasonable to assume, however, that this distance is approximately twice the $4d$ orbital radius, which in the present case is about 3 Å. The values of r_e and t_e are therefore calculated when the atom to be sputtered has just separated by at least 3 Å from any of the substrate atoms. Using this definition of t_e, we calculated, as shown in Fig. 1, the number of atoms sputtered per unit time with kinetic energies in the intervals of 0.4–4 eV (dotted line), 10–15 eV (dashed line), and 80–100 eV (dash-dotted line) as a function of their ejection time. The important feature apparent from the graph is the time lag between the generation of excitations in violent binary collisions and the emission of slower atoms. Obviously, the excitation can influence the state of slower sputtered atoms only if it stays localized in the cascade region for a sufficiently long time.

The time-space development of the excitations in the cascade is described as a relatively slow diffusion process in which the excitations spread from the site of the violent collision to the surface emission sites. Such a process would be governed by the diffusion equation,

$$\frac{\partial p(\mathbf{r},t)}{\partial t} = D\nabla^2 p(\mathbf{r},t) - \frac{p(\mathbf{r},t)}{\tau_h} + \sum_i \delta(t-t_i)\delta(\mathbf{r}-\mathbf{r}_i),$$
(2)

where $p(\mathbf{r},t)$ is the density of the excitation probability at $\mathbf{r}$ and t, defined as a continuous quantity, D is the diffusion constant, and τ_h is the lifetime of the d holes. The use of the continuous excitation density is one of the possible approximations that can be used to treat the transport of d holes in the solid. Another possible approximation would be to ascribe the holes to individual atoms and the transport to a hopping process, which would certainly be appropriate in the limit of a very small diffusion constant D. As an approximate

criterion of a critical diffusion constant separating the applicability of both approaches, we compared the average diffusion velocity of d holes to the average velocity of moving atoms in the cascade. Even for the smallest diffusion constant used in our model, both velocities are of the same order, and thus the diffusion approximation should still be applicable. This approximation also reduces the number of free parameters to the diffusion constant D and the lifetime τ, thereby greatly simplifying the mathematical treatment.

The source term on the right side of Eq. (2) is a sum of δ functions at the positions $\mathbf{r}_i$ and the times t_i of violent collisions. To further simplify the solution we assume that the lifetime of the hole τ_h is longer than the time needed for the hole to be transported from the excitation spot to the emission spot (i.e., several hundred fs). If this assumption is not fulfilled and the value of τ_h would be comparable to the dwelling time at individual atoms, its characteristic features would still be the same, although the excitation probability will be lower. We should also stress that Eq. (2) describes only the space-time development of $4d$-hole excitations, since the diffusion constant of excitations in the s-p band may be very different.

For each collision cascade, the number of sputtered atoms with kinetic energies between E and $E+\delta E$ was calculated, where δE is 0.4 eV and E varied from 0 to 100 eV. Also calculated were the time t_e of the emission and the location $\mathbf{r_e}$ on the surface from which the atom was emitted. Moreover, in each cascade $\mathbf{r}_i$ and t_i was determined for all violent collisions with $R_c<1.2$ Å. The excitation probability density $p(\mathbf{r},t)$ was determined numerically from Eq. (2). The probability P_{exc} that the sputtered atom is excited is then equal to $p(\mathbf{r_e},t_e)$ multiplied by the atomic volume. The number of sputtered Ag* atoms in the kinetic energy interval between E and $E+\delta E$ is the sum of probabilities $P_{\text{exc}}^{(i)}$, where $P_{\text{exc}}^{(i)}$ is calculated for each sputtered atom i in this energy interval. The final results were obtained by again averaging over 20 000 cascades, and are presented in Fig. 2. For comparison, the energy distribution calculated for sputtered ground state atoms is also included in the figure. Note that these distributions are normalized to 1 at the maximum.

The experimentally measured distributions of ground state Ag atoms and of excited Ag* atoms in the $^2D_{5/2}$ state are also shown in Fig. 2, and are indicated by black squares and open circles, respectively.[8] As apparent from the figure, the simulated distribution of ground state atoms is in good agreement with the experimentally observed one. The calculated energy distribution of excited Ag* atoms is shown for two different values of the diffusion constant, namely $D=0.002$ cm^2/s (solid gray line) and $D=1$ cm^2/s (dotted line). It is clearly seen that for $D=0.002$ cm^2/s the energy distribution calculated for Ag* is narrower than that of Ag, whereas the distribution calculated for $D=1$ cm^2/s is considerably broader than that of ground state atoms. This means that the experimentally observed narrowing of the Ag* energy distribution is at least qualitatively reproduced by the simulation if the lower value of the diffusion constant is applied. The ratio of the absolute values of the calculated distributions of Ag* and Ag at lowest kinetic energies is
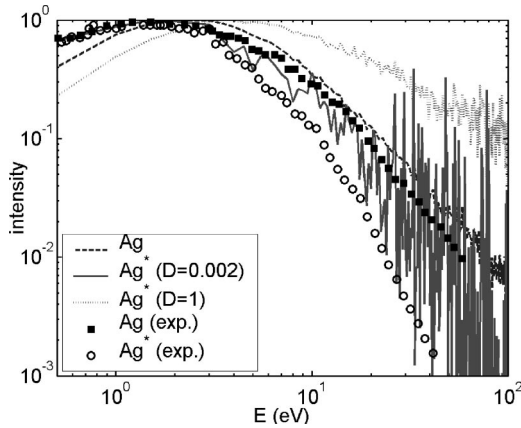
FIG. 2. Calculated and measured kinetic energy distributions of Ag atoms sputtered from Ag metal by 3-keV Ar$^+$ bombardment. All distributions are averaged over 20 000 impacts, and normalized to equal peak heights. The dashed line marks the calculated intensity of Ag atoms emitted in the ground state ($4d^{10}5s^1$); the solid and dotted lines correspond to the distributions of excited Ag* ($4d^95s^2$) calculated with diffusion constants $D=0.002$ and 1 cm^2/s, respectively. The black squares and the open circles denote the experimental data of ground state and excited atoms, respectively, taken from Ref. 8. The critical interatomic distance for the $4d$ electron transfer was set equal to 3 Å (see the text).

1.5×10^{-3} for $D=0.002$ cm^2/s and 3×10^{-5} for $D=1$ cm^2/s respectively. These ratios represent the theoretical value of the probability of Ag* ($^2D_{5/2}$) formation during the sputtering of silver with 3-keV Ar$^+$ ions. The values are orders of magnitude higher than the excitation probability predicted by nonadiabatic processes via Eq. (1). The probability $P_{exc}=1.5\times10^{-3}$ for $D=0.002$ cm^2/s is reasonably close to the experimental value of $P_{exc}=0.01$.[8] Hence, we conclude that the small value of the diffusion constant yields both the narrowing of the energy spectra and the correct order of magnitude of the excitation probability.

The agreement with experiment can be improved further by using smaller values of D, but for smaller D the numerical solution of Eq. (2) becomes more difficult and the calculated energy distributions are very noisy. We can, however, demonstrate the effect of a further reduction of the rate of electronic transport by increasing the interaction distance from 3 to 5 Å, which leads to a shift of the distributions in Fig. 1 to the right, i.e., to larger t. In the simulation of the excitation of sputtered atoms, this has the same effect as if the interaction distance remained 3 Å, but the propagation of the excitation in the substrate slowed down by a decrease of D. An approximate estimate of how much yields $D=0.001$ cm^2/s. The result of the simulation of the Ag* energy distribution in this case is shown in Fig. 3 and is found to be in good quantitative agreement with the experiment. The value of D, though rather small, must be finite. As $D\rightarrow0$, the concept of diffusion must be replaced by hopping from one atomic site to another. In the limit of $D=0$, the excitations would become localized at the sites where $4d$ excitations take place and the energy distribution of the sputtered Ag* atoms would be very broad.

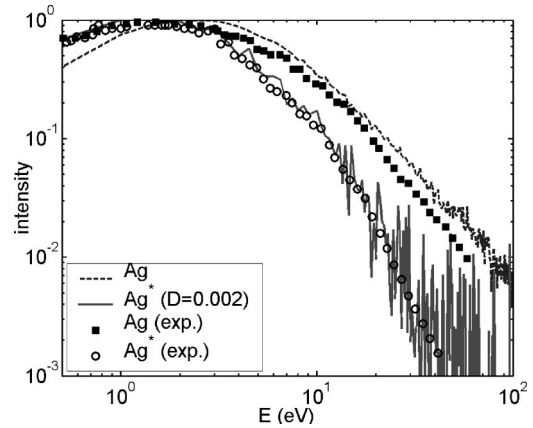The small value of D deduced from the experimental data

FIG. 3. Similar to Fig. 2, but the critical interatomic distance at the surface was set to 5 Å (see the text). The simulation was performed for a diffusion coefficient $D=0.002$ cm^2/s.

indicates that the transport of the $4d$ hole excitation across the collision cascade region is slower than one would predict from the width of the $4d$ band in bulk Ag.[26] We can estimate the time Δt needed for the transfer of a hole from one atomic site to the neighboring one from the relation $D=\frac{1}{3}(d^2/\Delta t)$, where d is the average interatomic distance, which can be assumed to be equal to the mean free path of the excitation. By substituting $d\sim3$ Å, the value of Δt is equal to approximately 120 fs. On the other hand, from the width of the $4d$ band in silver [about 2 eV (Ref. 26)] the dwelling time of the d hole at an atomic site in bulk Ag metal can be estimated to be around 1 fs. One of the possible reasons for the very low mobility of d excitations in the cascade is the strong temporary dynamic amorphization of the cascade region, which may lead to the formation of localized d states below the conduction band. In fact, photoemission measurements show that even in perfect bulk Ag some k states in the Ag $4d$ band can have a lifetime as long as 50 fs.[26] Other experiments using ultrashort pulse pump-probe techniques[27] indicate that the transport of the d holes in undisturbed metals can be significantly slower than expected from simple band structure arguments. In this context it should be mentioned that in ionization of particles sputtered from metals, where the conduction s-p electrons rather than d electrons play the decisive role, the excitations in the cascade region seem to be also more localized than expected for a quasifree electronic system.[28]

IV. CONCLUSIONS

The model presented here consistently explains all of the characteristic features of excited Ag* atoms sputtered from Ag metal by energetic Ar$^+$ ions: (i) The narrow energy distribution of sputtered Ag* atoms as compared to the energy distribution of sputtered ground state atoms, (ii) the relatively large probability of Ag* formation, and (iii) the observation that the formation of Ag* does not significantly depend upon the exit angle.[8] The model is based on the assumption that $4d$ holes in Ag are formed by promotion

processes during violent Ag-Ag collisions in cascades, and that the excitations are subsequently transferred to sputtered slow Ag atoms. The comparison of the model with the experiments provides information on $4d$-hole transport in Ag collision cascades. This transport is slow, and the slowness actually helps to accumulate the holes in the cascade region. This process differs from transport in undisturbed metals, thus suggesting that the physical mechanism of d level excitation of atoms sputtered from collision cascades is different from the excitation of atoms scattered from the surface by a single collision event.

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