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Formation of metastable excited states during sputtering of transition metals

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We propose a simple model which treats the formation of metastable excited neutral atoms during sputtering of a transition metal as a two step process. First, the energy deposited into the electronic system of the solid by electronic energy losses of all moving particles in the collision cascade is considered to lead to a locally altered equilibrium electronic state of the solid. It is found that this step is dominated by collective interaction with the conduction band electrons rather than by electron promotion in binary atom-atom collisions. Second, sputtered excited atoms are assumed to be formed by resonant neutralization of excited ions (reflecting the altered equilibrium state) while crossing the surface. It is shown that this model explains the total as well as the velocity dependent excitation probability observed in recent experiments on sputtered neutral silver atoms, which cannot be understood in terms of existing theories describing the formation of excited states in sputtering. [S0163-1829(97)07046-4]

I. INTRODUCTION

The formation of excited atoms during sputtering has been a subject of long standing interest in sputtering physics. Although a large amount of experimental data has been collected for atoms emitted in short lived excited states,[1] it is of interest to look at *metastable* particles which preserve their excitation state generated during the sputtering event until detection far away from the surface. A number of experiments have therefore been carried out using laser spectrometric methods for the state resolved detection of sputtered neutral atoms, a review of which can be found in Refs. 1 and 2. In earlier experiments (conducted before approximately 1985), data on the total population and the velocity distribution of excited metastable neutral Fe,[3,4] Zr,[5] Ba,[6] Ca,[7] and Ti (Ref. 8) atoms sputtered from the respective metallic surfaces have been collected which indicated that the total population of metastable states decreases with increasing excitation energy. As for the velocity distribution, two limiting cases were identified, in which the velocity distribution was either *identical*[4,5] or *significantly broader*[3,6–8] than that of the respective ground state atoms. For a long time, it was assumed that the former holds for states belonging to the ground state multiplet (with correspondingly low excitation energies), while the latter was characteristic for higher lying metastable states.

Data collected later for sputtered Rh atoms, however, showed significant broadening also for a state belonging to the Rh ground state multiplet,[9] thus implying that the excitation energy is not the essential parameter determining the velocity spectrum of sputtered metastable atoms. In the pending model, the broadening of the measured velocity distribution was interpreted in terms of a deexcitation mechanism[6,9] which assumed metastable states produced at some time during the collision cascade to be more or less efficiently quenched in a shallow region above the surface due to the electronic coupling to the electronic states of the solid. In this picture, atoms with higher emission velocity (perpendicular to the surface) cross the interaction region faster and will therefore be less efficiently deexcited, thus leading to an apparent broadening of the normalized velocity distribution of atoms sputtered in excited states. The question remained of why some states show broadening and others do not. Winograd and co-workers[10] proposed a model which related the deexcitation efficiency to the electronic configuration of the sputtered atom rather than to the excitation energy of its electronic state. Using the nomenclature developed in Ref. 10, states corresponding to ''shielded'' cases, i.e., cases in which the electronic interaction between the hole state of the sputtered particle and the surface is screened by a closed outer shell configuration of the outgoing atom, will show less broadening than ''exposed'' cases where no such screening occurs. It was shown that this model was consistent with the experimental data available at the time of publication.

Later, data collected by the same group[11] and others[12,13] on sputtered Ni atoms ejected in metastable states of three different low lying multiplets belonging to different electronic configurations at first seemed to confirm this model: states corresponding to a so-called ''open *s*-shell'' configuration exhibit a significantly broader velocity distribution than those corresponding to a ''closed *s*-shell'' configuration. However, for reasons outlined in detail in Ref. 14, the authors claim that it should be the *broader* energy spectrum which represents the ''normal'' sputtering case, while the *narrower* spectrum must apparently be influenced by electronic processes, a finding which would be inconsistent with the deexcitation model. In their most recent work,[11,14] the authors therefore propose a different interpretation of these data, which relates the observed velocity distributions to differences in the effective surface binding energy of atoms sputtered in different electronic configurations. In the framework of the same model, the total population distribution among the different electronic states of sputtered Ni atoms was interpreted in terms of the band structure of the nickel solid.[14] In particular, the pronounced population inversion between excited metastable states belonging to the ${}^3D_J$ manifold and the ${}^3F_4$ electronic ground state which was detected experimentally[11] was explained by the fact that the conduction band of solid nickel corresponds more to a $3d^94s$ configuration than to the $3d^84s^2$ electronic ground state configuration of an isolated Ni atom.

We have recently obtained experimental data on sputtered metastable Ag atoms[15] which are clearly not consistent with the deexcitation model. More specifically, here a case is observed in which the velocity distribution of sputtered metastable excited atoms is *narrower* than that of the respective ground state atoms, a finding which obviously cannot be explained by velocity dependent deexcitation processes occurring above the surface. The analysis of the excitation probability P^* as a function of the particle emission velocity v revealed that P^* is constant in the regime of low velocity and decreases approximately with v^{-1} at high values of v. This indicates that here the *excitation* mechanism itself must in some way depend on the velocity of the outgoing particle. To the best of our knowledge, no model has been published so far which would be consistent with this type of data. In the present work, we therefore develop a simple semiquantitative description of a scenario of electronic processes which lead to the ejection of a neutral metastable atom in sputtering. It will be shown that the model developed here provides an explanation of the data presented in Ref. 15.

II. MODEL CALCULATION

The formation of metastable excited neutral atoms in sputtering will be treated as a two step process. For simplicity as well as in view of the experimental data available to test the model we restrict ourselves to the description of atoms released from a transition metal. As a first step, it is assumed that electronic excitations in the band structure of the solid are created during the collision cascade leading to the sputtering event. For the case of transition metals, most of these excitations will manifest in form of d-band holes. Although any excitation created within the solid will be rapidly shared among the target atoms (as has been frequently pointed out in the literature), it will be shown that for a limited time these holes may remain localized within the cascade volume, i.e., the volume of the solid which is disturbed by the collision cascade initiated by the impinging primary ion. This leads to a locally altered ''equilibrium'' electronic state in the region from which sputtered atoms originate. Upon ejection, i.e., when crossing the surface, sputtered particles will reflect this modified equilibrium state and will therefore with a certain probability carry a d hole. We further assume that at this point the emitted particle is a positively charged ion due to the electron deficiency in its d shell. As a second step, on its path away from the surface, the sputtered particle strongly interacts with the electronic system of the solid. Therefore, most of the ions created this way will pick up an electron and become neutralized. Due to the limited range of the electronic interaction, only in a shallow region above the surface the transition matrix element is large enough to allow an efficient electron transfer. It is apparent that particles with higher emission velocity (along the surface normal) cross this region faster and are therefore less efficiently neutralized than slower particles.

The basic idea of the model is as follows. Due to the electronic excitation in the course of the collision cascade, a certain fraction of the emitted atoms carries a d hole and may therefore pick up an electron to become neutralized. If this occurs at a certain distance from the surface, electrons will be captured much more likely into an s orbital than into a d orbital of the outgoing atom. Far away from the surface, this leads to the detection of neutral metastable atoms with a one-electron deficiency in the d shell and a closed s shell. In the following subsections, the two main steps mentioned above will be described in more detail.

A. Electronic excitation during the collision cascade

We consider two different mechanisms as a source of electronic excitation within the collision cascade. First, the impinging primary ion as well as all moving target recoil atoms may directly interact with the *conduction band electrons* and therefore transfer energy into the electronic system of the solid. Second, inelastic collisions between two moving target atoms may lead to electronic excitation by *electron promotion* from an occupied atomic orbital into a higher lying empty state. Both mechanisms will be briefly discussed in a semiquantitative manner below. Where target specific numbers are needed in the calculation, data of silver as a target material will be inserted in order to allow a comparison of the results with experimental data collected for sputtered Ag atoms.

1. Valence electron excitation and d-hole localization

The energy transfer between a heavy particle moving across the electron gas of a solid and the electron gas itself may in principle be described by the Lindhard electronic energy loss formula[16]

$$\left.\frac{dE}{dx}\right|_e = k'v, \tag{1}$$

where $(dE/dx)|_e$ denotes the electronic part of the stopping power, k' is a material specific constant, and v the velocity of the moving particle. Transferring this into the energy loss per unit time, we obtain

$$\frac{dE}{dt} = \frac{dE}{dx}\,v = k'v^2 = kE_k, \tag{2}$$

where E_k, denotes the kinetic energy corresponding to v. In order to calculate the total energy transferred to the electronic system per unit time, we sum over all moving particles

$$\left(\frac{dE}{dt}\right)_e^{\text{tot}} = \sum_i \left(\frac{dE}{dt}\right)_e^i = k\sum_i E_k^{(i)} = kE_k^{\text{tot}}. \tag{3}$$

From a number of molecular dynamics simulations of the particle movement within the collision cascade, it is inferred[17] that during a time interval of several 100 fs after the primary ion impact—i.e., the time during which most of the sputtered particles are ejected—the total kinetic energy within the target crystal is approximately given by

$$E_k^{\mathrm{tot}} \cong \frac{2}{3} E_B , \tag{4}$$

where E_B denotes the kinetic energy of the impinging primary ion. The exact value of the numerical constant entering Eq. (4) is not critical. In the limiting case $t \to 0$ (i.e., directly upon impact of the primary ion) it must obviously be unity, while the other limiting case for large values of t (where the energy is completely thermalized) would correspond to a value of 1/2. Inserting Eq. (4) into Eq. (3) yields

$$\left(\frac{dE}{dt} \right)_e^{(\mathrm{tot})} \cong \frac{2}{3} k E_B . \tag{5}$$

This energy will be stored in form of electron-hole pairs, part of which correspond to d-band holes. The mean energy E_d needed to create a d hole is determined by the band structure of the target and can be roughly estimated from the energetic distance between the d-band maximum of the electronic density of states and the Fermi edge. For silver, this yields $E_d \sim 5$ eV.[18] Hence an upper limit of the number of d holes which can be created per unit time is given by

$$\frac{dN_d}{dt} = \frac{1}{E_d} \left(\frac{dE}{dt} \right)_e^{\mathrm{tot}} \cong \frac{2}{3} k \frac{E_B}{E_d} . \tag{6}$$

It should be noted that the step described by Eq. (6), which is based on purely energetic arguments, is essentially similar to the approach often adopted in semiquantitative theories of electron emission.[19] The problem how the electronic energy is equipartitioned in the system is not addressed in this approach.

In general, the electronic excitations produced by the above mechanism will be rapidly shared among all atoms and, hence, dissipate into the bulk of the crystal. Sputtered atoms, on the other hand, can only originate from a limited volume within the solid which is roughly determined by the range of the collision cascade generated by the primary particle. To proceed further, it is therefore important to consider the time τ_L during which a generated d-band hole may remain localized within the cascade volume. We estimate this localization time by means of a simple diffusion approach

$$\frac{\partial p}{\partial t} = D \Delta p , \tag{7}$$

where p describes the probability of finding a hole at a certain position in the solid and D denotes the diffusion coefficient which is relevant for d-band holes. Inserting a δ-distribution centered at $r=0$, $t=0$, we find

$$p(r,t) = \frac{1}{(4\pi D t)^{3/2}} \exp\left(- \frac{r^2}{4Dt} \right) \tag{8}$$

and identify τ_L by equating the diffusion length $\sqrt{4Dt}$ with a characteristic dimension of the cascade volume. The latter, in turn, can be roughly estimated from the mean range R of the primary particles within the solid, yielding

$$\tau_L = \frac{R^2}{4D} . \tag{9}$$

Due to the atomic disorder generated during the collision cascade, the diffusion coefficient D to be inserted into Eq. (9) will be significantly lower than that of an undisturbed solid. In general, D can be expressed by

$$D = \tfrac{1}{3} \lambda \overline{v} . \tag{10}$$

where λ denotes the mean free path and $\overline{v}$ the average velocity of the diffusing species. If we assume a complete randomization of the atom positions within the cascade volume, λ will be of the order of one atomic distance. The value of $\overline{v}$, on the other hand, can be roughly estimated from the width Δ_d of the d band. For silver, $\lambda \sim 0.25$ nm and $\Delta_d = 5.5$ eV,[18] leading to $\overline{v} \sim 1.2 \times 10^8$ cm/s and $D \sim 1.0$ cm^2/s.

It is of interest to calculate the number of d holes created during the localization time and relate it to the total number of atoms $N \cong nR^3$ present in the cascade volume, n being the number density of atoms in the solid. Since a sputtered atom can only ''remember'' excitation processes which occur within τ_L before its emission time, the resulting number must be identified with the probability P^{exc} that a sputtered atom carries a d hole. Combining Eqs. (6), (9), and (10), we find

$$P^{\mathrm{exc}} = \frac{\frac{2}{3} k E_B \tau_L}{n R^3 E_d} = \frac{\frac{2}{3} k}{4 n D E_d} \frac{E_B}{R} \cong 1.8 \times 10^{-5} \, \frac{\mathrm{nm}}{\mathrm{eV}} \frac{E_B}{R} . \tag{11}$$

Again, data of solid silver were used to evaluate the numeric constant in Eq. (11). It should be stressed again that due to the uncertainties discussed in the context of Eq. (6) the values calculated this way represent upper limits of P^{exc}.

2. Collisional excitation

A frequently used frame to describe the electronic excitation of atoms during sputtering is that of *electron promotion* due to energetic binary atom-atom collisions within the cascade. In this picture, as two atoms collide, the individual atomic orbitals combine to form quasimolecular orbitals, the energy of which depends on the distance between the two atoms. In an energetic collision, the energy of a certain occupied orbital may thus be promoted to higher values and can in a diabatic picture ''cross'' that of an unoccupied higher orbital at a critical distance r_c. For a detailed description of the process the reader is referred to the comprehensive treatment by Wille and Hippler[20] and references therein. In order to estimate the role of this excitation mechanism, we use an approach similar to that given earlier by Sigmund.[21] The most stringent parameter of the electron promotion process is the crossing distance r_c which can be estimated from an *ab initio* calculation of the quasimolecular orbital (MO) energies as a function of interatomic distance. Figure 1 shows such a correlation diagram for a collision of two Ag atoms. The levels are calculated by the Hartree-Fock method using the GAUSSIAN 92 code. At the right side of the figure, the levels are labeled with their isolated atomic names, while the relevant molecular levels are labeled inside the figure by corresponding MO names. It is seen that the $10\sigma_u$ and the $9\sigma_u$ orbitals can be viewed to diabatically cross at an internuclear distance of about 2.2 a.u. corresponding to 0.12 nm. Since in the limit of large distances these orbitals converge to the $5s$ and $4d$ states of the isolated atoms, respectively,

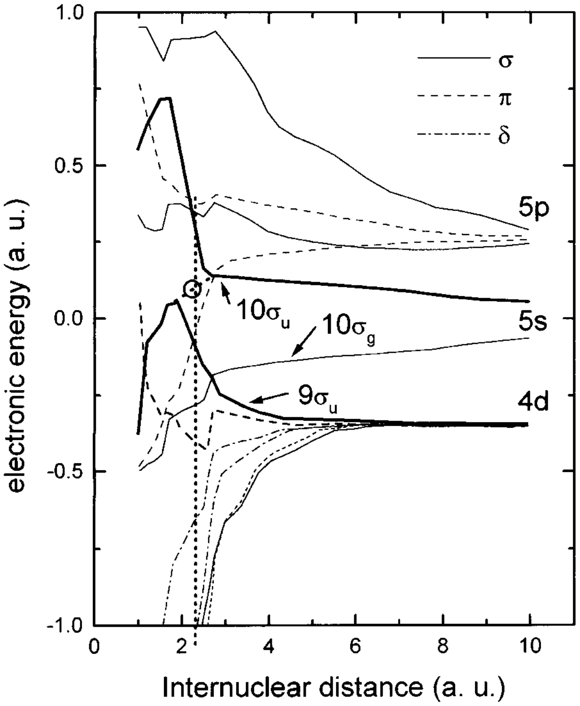

FIG. 1. *Ab initio* calculation of molecular orbital energies vs interatomic distance corresponding to a quasimolecule consisting of two Ag atoms. The dotted line indicates a diabatic interpolation to determine the crossing distance r_c of the $9\sigma_u$ and $10\sigma_u$ orbitals. (Data courtesy of J. Lorencic.)

this distance must be identified as the critical distance r_c for the production of a d hole by collisional promotion of an electron from the $4d$ to the $5s$ shell. The minimum collision energy needed to reach r_c can be estimated, for instance, using the Moliere potential[22] which is frequently employed as a repulsive internuclear potential in sputtering calculations. Performing the calculation described in detail in Ref. 22, we arrive at a minimum center-of-mass energy of around 135 eV which is necessary to permit the collisional generation of a d hole by a binary collision between two Ag atoms. In the linear cascade regime of sputtering, it is generally assumed that every binary collision involves a moving recoil atom and a target atom which is initially at rest. Therefore, the minimum recoil energy needed to allow collisional excitation is about $E_k^{\min}=270$ eV.

To proceed further, we estimate the cross section for electron promoting collisions by calculating the maximum impact parameter $b_{\max}$ which ensures that r_c is reached as the distance of closest approach during the collision. From simple kinematic considerations, we obtain

$$\sigma=\pi b_{\max}^2=\pi r_c^2\left\{1-\frac{E_k^{\min}}{E_k}\right\}, \tag{12}$$

where E_k denotes the kinetic energy of the recoil atom hitting another target atom initially at rest. If, as an upper limit, we assume that every collision capable of d-hole production actually generates such an excitation, the number of d holes a particle moving with E_k can generate per unit time is given by

$$\nu n\sigma=\sqrt{2E_k/M}n\pi r_c^2\left(1-\frac{E_k^{\min}}{E_k}\right). \tag{13}$$

At this point, the treatment deviates from that of Ref. 21, since for simplicity we neglect the energy loss of the recoil in a promoting collision. The next step is to estimate the number of recoil atoms with energy E_k present in the cascade volume. According to analytic sputtering theory, the distribution of kinetic energies within a fully developed collision cascade is given by[23]

$$f(E_k)=\text{const}E_k^{-2}. \tag{14}$$

The normalization constant in Eq. (14) can be calculated by evaluating the total kinetic energy in the cascade as

$$E_k^{\text{tot}}=\int_{\check{E}_B}^{\hat{E}_k}E_kf(E_k)dE_k\cong\tfrac{2}{3}E_B. \tag{15}$$

The choice of the integration boundaries is somewhat tedious. While the upper limit is easily identified as the bombarding energy E_B, the lower bound is more critical due to the divergence of the integrand at $E_k=0$. Here, we take a typical phonon energy as the lower limit and estimate $\check{E}_k$ from the Debye frequency ω_D of the solid. This yields

$$\text{const}\approx\frac{2}{3}\,\frac{E_B}{\ln(E_B/\hbar\omega_D)}. \tag{16}$$

By combining Eqs. (13), (14), and (16), the total number of electron promoting collisions and, hence, of d holes which may be produced per unit time within the cascade can be calculated as

$$\begin{aligned}\frac{dN_d}{dt}&=\int_{E_k^{\min}}^{E_B}f(E_k)\sqrt{2E_k/M}n\pi r_c^2\left(1-\frac{E_k^{\min}}{E_k}\right)dE_k\\&=\frac{8}{9}\sqrt{2/ME_k^{\min}}n\pi r_c^2\,\frac{E_B}{\ln(E_B/\hbar\omega_D)}.\end{aligned} \tag{17}$$

Using the same formalism as in Sec. II A 1, we calculate the excitation probability per cascade atom as

$$\begin{aligned}P^{\text{exc}}&=\frac{(dN_d/dt)\tau_L}{N}\\&=9.6\times10^{10}\ \text{s}^{-1}\,\frac{R^2}{4DnR^3}\,\frac{E_B}{\ln(E_B/\hbar\omega_D)}\\&\cong4.1\times10^{-6}\,\frac{\text{nm}}{\text{eV}}\,\frac{1}{\ln(E_B/\hbar\omega_D)}\,\frac{E_B}{R}.\end{aligned} \tag{18}$$

The numerical constants in Eq. (18) were evaluated using the atomic mass M of Ag atoms. Inserting the Debye frequency of silver,[24] we obtain $\hbar\omega_D\approx0.2$ eV. In connection with primary ion energies between 5 and 15 keV as used in Ref. 15, this yields

$$P^{\text{exc}}\cong3\times10^{-7}\,\frac{\text{nm}}{\text{eV}}\,\frac{E_B}{R}. \tag{19}$$

B. Resonant neutralization

The neutralization of d-hole ions during their flight away from the surface can be described by the formalism originally introduced by Hagstrum.[25] The process we wish to consider is a resonant electron capture from the Fermi electron gas within the solid into the s orbital of the departing ion. As usual, we approximate the dependence of the corresponding transition matrix element on the distance z above the surface as exponential and write the width of the s level (which is broadened due to the interaction with the solid electronic states) as[26]

$$\Delta(z)=\Delta_0 \exp(-\gamma z). \tag{20}$$

Assuming a constant particle velocity along the path, the occupation probability P of the s state is determined by

$$\frac{dP}{dt}=[1-P(t)]\,\frac{2\Delta(z=v_\perp t)}{\hbar}, \tag{21}$$

which can be integrated in a straightforward manner yielding the neutralization probability

$$P^{\mathrm{neutr}}=P(t\to\infty)=1-\exp\left[-\frac{2\Delta_0}{\hbar\gamma v}\right] \tag{22}$$

at a distance far away from the surface. In Eqs. (21) and (22), $v_\perp$ denotes the particle velocity component perpendicular to the surface.

The resonant neutralization of a d-hole ion by electron transfer into the s shell of the departing particle results in a neutral atom still containing a d hole. In the case of silver, this would, for instance, correspond to the metastable ${}^2D_J$ states of the Ag atom with a $4d^9 5s^2$ configuration and excitation energies of about 3.75 eV (${}^2D_{5/2}$) and 4.30 eV (${}^2D_{3/2}$) above the ground state. We can therefore take Eq. (22) to describe the probability for conversion of an ejected d-hole ion into a neutral metastable atom far away from the surface. In principle, resonant electron capture from the conduction band into the d shell and, hence, neutralization by directly filling the d hole of the departing ion are, of course, also possible. Compared to resonant transfer into the s shell, however, this process seems to be highly improbable for the following reason. Already within the solid, but significantly more pronounced at some distance above the surface, the d states of the departing atom are much stronger localized than the s states.[27] In addition, resonant transfer into the s state requires electrons from higher energetic states within the conduction band, the wave functions of which extend further into the vacuum above the surface than those of lower lying states which are required for resonant transfer into the d state. As a consequence, the overlap between conduction band and atomic states—and, hence, the transition matrix element—will be much larger for s-state than for d-state filling.

III. DISCUSSION

In this section, the results of the model calculation presented in Sec. II will be compared to experimental data on neutral metastable Ag atoms sputtered from polycrystalline silver under bombardment with rare gas ions of 5 and 15 keV which have been published recently.[15,28] On the experimental side, two major sources of information are present, namely the *total abundance* and the *velocity distribution* of metastable atoms within the flux of sputtered particles. According to the model developed above, the probability P^* for emission of an excited neutral atom is given by the product of P^{exc} and P^{neutr}. The basic characteristics with respect to the total population of a metastable state are, however, mainly determined by P^{exc}, since this quantity includes the influence of experimental parameters such as the type and energy of the impinging primary ions. The velocity distribution of the sputtered metastables, on the other hand, will be basically determined by P^{neutr}, since no dependence on the emission velocity is included in P^{exc}.

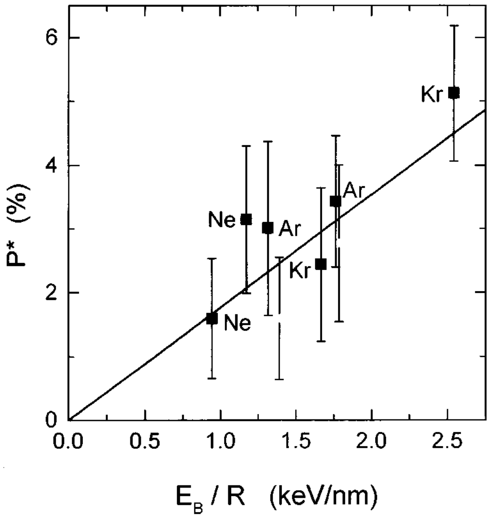

FIG. 2. Experimental excitation probability, i.e., the population ratio between the metastable ${}^2D_{5/2}$ state and the ${}^2S_{1/2}$ electronic ground state of neutral Ag atoms sputtered from polycrystalline silver by rare gas ions of 5 and 15 keV (data from Refs. 15 and 28). The solid line represents the theoretical prediction of the quantity P^{exc} calculated by Eq. 11 in the text.

A. Total excitation probability

According to the predictions of Eqs. (11) and (19), the total population of a metastable state should roughly scale with E_B/R. Figure 2 shows a corresponding plot of the experimentally determined total excitation probability, i.e., the population of the metastable ${}^2D_{5/2}$ state normalized to that of the ${}^2S_{1/2}$ ground state of sputtered neutral Ag atoms as given in Refs. 15 and 28. In order to evaluate the data plotted on the abscissa, the range R of the primary ions as a function of the bombarding energy E_B and the type of the impinging ion was calculated from the SUSPRE code[29] based on the projected range algorithm[30] yielding the values given in Table I. It is apparent that a correlation of the expected type exists.

TABLE I. Primary ion range in silver calculated by the SUSPRE code[29] as a function of the ion species and bombarding energy. Values are given in nm.

	Ne^+	Ar^+	Kr^+	O_2^+
5 keV	5.3	3.8	3.0	3.6
15 keV	12.8	8.5	5.9	8.4

Moreover, the prediction of P^{exc} as given by Eq. (11) has been included in the figure as a straight line. It is seen that the experimental data are described surprisingly well, i.e., almost quantitatively by the model calculation presented in Sec. II A 1. In view of the simplicity of the model as well as the fact that Eq. (11) represents the energetically possible upper limit of the excitation probability, this degree of agreement is certainly fortuitous. However, two important conclusions can be drawn from the figure. First, it is shown that the mechanism of collective electronic excitation described in Sec. II A 1 is in principle capable of producing excitation probabilities of the order of those observed in the experiment. This finding is of particular interest, since the relatively high excitation energy of 3.75 eV prohibits any noticeable population of this state by mechanisms resulting in a Boltzmann-like population distribution with population ''temperatures'' of the order of about 1000 K (which have been frequently reported in the literature[2]). Second, and probably most important, it is seen that the prediction of Eq. (19), which must also be regarded as an upper limit, results in excitation probabilities significantly below the experimental values. As a consequence, we are forced to conclude that the mechanism underlying Eq. (19), i.e., the promotion of electrons from occupied to empty atomic states during binary collisions between target atoms *cannot* be responsible for the production of metastable Ag atoms in sputtering of silver. Although the numerical constants in Eqs. (11) and (19) were evaluated using explicit data of solid silver, the results are not expected to change appreciably for other transition metals. We therefore conclude that at least for the metallic targets and high excitation energies discussed here the electron promotion mechanism is negligible and the observed excitation must be primarily generated by collective electronic excitation effects as described in Sec. II A 1.

B. Velocity distribution

The kinetic energy distribution of sputtered atoms as described by analytic sputtering theory is given by the well known expression[23]

$$f(E) \propto \frac{E}{(E+U)^3}. \tag{23}$$

In general, the surface binding energy U is approximated by the sublimation energy of the ion bombarded solid. Then, Eq. (23) provides a reasonable description of the velocity distribution of sputtered ground state Ag (Ref. 15) and other transition metal[3–5,8,31] atoms. The velocity distribution of metastable atoms, on the other hand, is described by Eq. (23) multiplied by the neutralization probability P^{neutr}. The spectral variation of the excitation probability $P^*(E)$, which is evaluated as the ratio between the experimentally determined normalized velocity distributions of metastables and ground state atoms, will therefore reflect the energy dependence of P^{neutr} and, hence, should be described by Eq. (22). In principle, it is of interest to discuss two limiting cases. For low emission energies, P^* is expected to be independent of E. At high energies, on the other hand, the value of P^* decreases with increasing energy. The model developed here therefore predicts a *narrower* energy (or velocity) distribution of the metastable excited atoms than that of the respective ground state atoms, a finding which is in pronounced contrast to other model calculations published to date. At sufficiently high energies, the expression on the right-hand side of Eq. (22) becomes proportional to the inverse of the emission velocity and P^* is thus expected to vary as $E^{0.5}$. This is consistent with our experimental data on sputtered metastable silver atoms,[15] where the experimental arrangement was such that only particles emitted along the surface normal were detected and, hence, the emission energy E directly corresponds to the velocity component perpendicular to the surface. From the data of Ref. 15, we can define a critical energy E_c at which P^* starts to deviate from the constant value at low energies and estimate the parameter Δ_0 entering the model calculation. With $E_c \sim 1.5$ eV and a typical value of $\gamma \sim 0.1\ \mathrm{nm}^{-1}$,[1] we obtain $\Delta_0 \sim 10^{-2}$ eV. This value is very low, typically this parameter should be of the order of an eV.[1] The reason may be that at very small distances from the surface, where the particle is still in close contact with the electronic system of the solid, the electron transfer picture is not appropriate. At those distances, the electronic state of the departing atom still reflects the equilibrium state of the solid, which in turn is described by P^{exc}. The integral of Eq. (21) may therefore be evaluated only for distances above a critical value z_c, where the d level of the departing atom becomes localized and, hence, essentially decoupled from the electronic system of the solid. In this picture, the apparent value of Δ_0 would correspond to $\Delta(z_c)$, the resulting value of z_c would be of the order of a few Å.

IV. CONCLUSION

We propose a simple model describing the formation of metastable electronic states during sputtering of transition metal atoms from the respective pure metallic solids. The main idea of the model is that a sputtered atom ''copies'' the equilibrium electronic state of the solid—which may be modified due to collisional excitation—to the vacuum above the surface. In this sense, the picture is very similar to that developed in Ref. 14 for the ejection of sputtered metastable Ni atoms.

Two different mechanisms are considered as a primary source of excitation within the collision cascade initiating the sputtering event. It is shown that electron promotion in binary collisions between target atoms, which has been frequently assumed as the major source generating the excitation, is presumably of only minor importance and, in particular, cannot explain the high excitation probabilities observed for sputtered metastable Ag atoms. We therefore conclude that the primary source of excitation is the creation of d-band holes within the collision cascade by collective electronic excitation induced by the direct interaction between moving atoms and conduction band electrons.

We assume that sputtered metastable excited neutral atoms are formed by resonant neutralization of ions containing a d hole. It is shown that this mechanism predicts a velocity distribution of sputtered metastable atoms which is narrower than that of the respective ground state atoms. The model developed here therefore explains the kinetic energy distributions measured for sputtered metastable Ag atoms which otherwise cannot be interpreted in terms of existing theoretical descriptions. We wish to stress, however, that the experimental data presently available is by no means sufficient to provide conclusive evidence for the excitation mechanism proposed here. Future experiments can test the model by experimental detection of sputtered metastable d-hole *ions*. The model predicts that these species constitute a precursor of the metastable neutrals discussed here and therefore should exhibit a velocity dependence which is complementary to that of the respective excited neutrals.

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