Secondary-ion emission probability in sputtering

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It is shown that the experimentally observed correlations between the ionization probability of the ejected particles of a sputtered metal surface and the substrate work function ϕ, the outward velocity v, and the ionization potential I or affinity A of the departing atom, can be accounted for by considering the probability that the initial occupation of the ionization or affinity level survives during the nonadiabatic passage of the surface. With reasonable models for the variation of the position and width of the ionization or affinity level with distance from the surface, the ionization probability is shown for a large class of systems to be roughly proportional to $\exp[-(I-\phi)/cv]$ (positive ions) or $\exp[-(\phi-A)/cv]$ (negative ions), where c is a constant.

An important quantity in the description of the sputtering process is the probability $\alpha^{+(-)}(E)$ that the sputtered particle comes out as a positive (negative) ion. For instance, a knowledge of $\alpha^{+(-)}$ is crucial for the application of secondary-ion mass spectroscopy (SIMS) for chemical analysis,[1] and a recognition of the parameters determining $\alpha^{+(-)}$ is of great help in designing ion sources based on the sputtering technique.[2] The present paper addresses itself to the question how $\alpha^{+(-)}$ depends on the physical properties of the sputtered particle, and the ejecting substrate, and on the kinetic energy of the ejected particle. It is shown how an ionization mechanism for metallic substrates, which is based only on surface-physics experience of the behaviour of the valence level of the secondary ion during the nonadiabatic passage through the metal surface, is sufficient to explain the overall parameter dependencies of $\alpha^{+(-)}$ found experimentally.

Most experimental studies of the substrate and secondary-ion effects have been limited to a "total" ionization probability $S^{+(-)}$, which is an average of $\alpha(E)$ over a rather broad energy window, and often contains features due to the detection system.[3]

By varying the cesium coverage during the sputtering of Mo^-, H^-, D^-, and O^- from a Mo surface,[4] Yu has recently shown that, at least for small coverages, the substrate work function ϕ controls S^- through an exponential dependence on ϕ or $(\phi)^{1/2}$.[4] As for the secondary-ion parameters entering $S^{+(-)}$, a correlation with the affinity A (for negative ions) or the ionization potential I (for positive ions) is usually found.[1] Also this parameter dependence has been reported to be roughly exponential.[1]

So far, the least experimental work has been done on the kinetic energy (E) dependence. It seems that $\alpha(E)$ is an increasing function of E,[5] and it has been suggested that $\alpha(E) \propto \exp(-b/v)$, where v is the outward velocity normal to the surface.[6] For Cu^+ ions sputtered from a clean copper surface, a value for b of the order of 10^6 cm/sec has been found.[5]

In the theoretical description of the ionization process it is usually assumed that the occurrence of secondary ions is due to excitations (to ionic products or autoionizing states) during the atomic collisions producing the sputtered particle. By assuming a local thermodynamical equilibrium in the collision cascade, Anderson and Hinthorne[1] have arrived at a quantitative description, where $\Gamma(A)$ is introduced through a Boltzmann factor. For metals, an assumption that the excitation consists of a promotion of an electron to (or from) the Fermi level makes the $I(A)$ and ϕ dependence read

$$\exp[-(I-\phi)/kT] \quad \{\exp[-(\phi-A)/kT]\} \ ,$$

in accordance with the above-mentioned experimental trends. A serious problem is, however, that effective electronic temperatures T of the order of 10^4 K must be assumed in order to fit the experimental data.[3]

The central difficulty of any theory built on excitations within or close to the substrate is that the lifetime of the excitation would be much shorter than the time needed for the excited particle to get out of the metal. If $w(t)dt$ is the probability that the excited electron (hole) will hop back into the conduction band between the times t and $t + dt$, the probability $P(t)$, that an excitation made at time t, will survive

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until the excited particle gets out is

$$P(t) = \prod_{t'>t} [1 - w(t')dt']$$

$$= \exp\left[-\int_t^\infty w(t')dt'\right] . \tag{1}$$

The probability $w(t')$ is related to the one-electron width Δ of the electron level through

$$w(t) = \frac{2}{\hbar}\Delta(t) . \tag{2}$$

As will be discussed below, Δ falls off roughly exponentially outside the surface so that

$$\Delta(t) = \Delta_0 e^{-\gamma v t} , \quad t > 0 , \tag{3}$$

if a constant normal velocity v is assumed. This gives

$$P(t) = \exp\left[-\frac{2\Delta_0}{\hbar\gamma v}e^{-\gamma v t}\right] = \exp\left[-\frac{2\Delta(t)}{\hbar\gamma v}\right] . \tag{4}$$

While an expression like Eq. (4) is often included to account for the de-excitation during the passage of the surface,[3,6] it is usually not realized that early in the ejection process $\Delta(t)$ is typically of the order of 5 eV. For a typical outward velocity ($v \sim 4 \times 10^5$ cm/sec), $\hbar\gamma v$ is of the order of 0.1 eV and thus $P(t) \sim e^{-100}$!

Several groups have instead suggested the time-varying potential of the sputtered particle leaving the surface as the source of the excitation.[7,8] As such variations occur also in the outer part of the surface region, the excitation may happen so far out that the survival probability $P(t)$ becomes large. In this paper it will be shown how this approach, combined with a realistic model for the variation of the effective ionization potential I or affinity level A with distance from the surface is able to reproduce the above-mentioned trends.

To be specific, we will in the following discuss the negative ionization probability of an atom leaving a metal surface. As will become clear, the theory for the positive ionization is completely analogous.

In an adiabatic process the typical ejected particle should be a neutral atom, because most atomic affinities are smaller than typical metallic work functions. Away from adiabaticity, there is a certain probability n_a that the affinity level $|a\rangle$ will be occupied. The negative ionization probability α^- is equal to the value of n_a at $t = \infty$, if we neglect possible higher-excited states of the atom. During the ejection, the energy parameter $\epsilon_a(t)$ of $|a\rangle$ varies in time (or rather with position) due to the interaction with the substrate. The coupling between the substrate electron states $|k\rangle$ and the adsorbate state $|a\rangle$ is described by a "hopping" matrix element $V_{ak}(t)$, which is also time dependent. For a level $\epsilon_a(t)$, which is always above the Fermi level $\epsilon_F(=-\phi)$, the amplitude $a_{a,k}(t)$ at time t on $|a\rangle$ due to excitation from $|k\rangle$, can be obtained to first order by a straightforward extension of ordinary first-order time-dependent perturbation theory,[9]

$$a_{a,k}(t) = \frac{1}{i\hbar}\int_{-\infty}^t V_{ak}(t')\exp\left[-\frac{i}{\hbar}\int_{t'}^t [\epsilon_k - \epsilon_a(t'')]dt''\right]dt' . \tag{5}$$

In the present problem the electron may hop back to the substrate once it is excited. Therefore, the phase factor in Eq. (5) must be multiplied by

$$\exp[-(1/\hbar)\int_{t'}^t \Delta(t'')dt''] ,$$

which is the probability amplitude [cf. Eqs. (1) and (2)] that an electron excited to $|a\rangle$ at a time t' will survive in that state until the time t. From $a_{a,k}(t)$ we can get the occupation of $|a\rangle$ at a time t as

$$n_a(t) = \sum_{\epsilon_k < \epsilon_F} |a_{a,k}(t)|^2$$

$$= \frac{1}{\hbar^2}\sum_{\epsilon_k < \epsilon_F}\left|\int_{-\infty}^t V_{ak}(t')\exp\left[-\frac{i}{\hbar}\int_{t'}^t [\epsilon_k - \epsilon_a(t'') - i\Delta(t'')]dt''\right]dt'\right|^2 . \tag{6}$$

Although the proof of Eq. (6) is only indicated here to first order in V_{ak}, it is valid through any order of V_{ak}. This has recently been shown by Blandin et al.,[8] using an extension due to Keldysh of the diagrammatic Green's-function techniques.[10] In Ref. 8, Eq. (6) has also been solved for constant ϵ_a by as-

suming an exponential dependence of V_{ak} on position z outside the surface,

$$V_{ak}(z) = \begin{cases} V_{ak}^0 , & z < 0 \\ V_{ak}^0 e^{-\gamma z/2} = V_{ak}^0 e^{-\gamma v t/2} , & z > 0 . \end{cases} \tag{7}$$

The last equation expresses an assumption of a constant velocity $v = z/t$. In the present model, which can be regarded as a simplified version of the Newns-Anderson model for chemisorption[11] (the energy dependence of Δ being neglected), the resonance width Δ is related to V_{ak} through

$$\Delta(t) = \pi \sum_k |V_{ak}(t)|^2 \delta(\epsilon_a(t) - \epsilon_k) . \tag{8}$$

Therefore, Δ gets the exponential decay of Eq. (3) in this approximation. In the limit $\hbar \gamma v \ll \epsilon_a - \epsilon_F$, $n_a(\infty)$ has the analytical solution[8]

$$n_a(\infty) = \frac{2}{\pi} e^{-\pi(\epsilon_a - \epsilon_F)/\hbar\gamma v} . \tag{9}$$

We pause here for a moment to discuss the result (9) from a somewhat different standpoint. It is illuminating to look at the solution of Eq. (6) in the two extreme limits $v \rightarrow 0$ (adiabatic) and $v \rightarrow \infty$ (sudden). In the adiabatic limit the assumption $\hbar \gamma v \ll \epsilon_a - \epsilon_F$ is valid and the result $n_a^{ad}(\infty) = 0$ is readily obtained from Eq. (9), as would be expected. In the sudden limit, on the other hand, one must go back to Eq. (6) with a step function $\theta(-t)$ for $V_{ak}(t)$ and $\Delta(t)$:

$$n_a^{sud}(\infty) = \frac{\Delta_0}{\pi \hbar^2} \int_{-\infty}^{\epsilon_F} d\epsilon \left| \int_{-\infty}^{0} e^{(1/\hbar)[i(\epsilon - \epsilon_a)t' + \Delta_0 t']} dt' \right|^2$$

$$= \frac{\Delta_0}{\pi} \int_{-\infty}^{\epsilon_F} d\epsilon \frac{1}{(\epsilon - \epsilon_a)^2 + \Delta_0^2} = n_a(0^-) .$$

That is, in the sudden limit $n_a(\infty)$ is equal to the occupation of the Lorentz-broadened level $|a\rangle$ just before the coupling V_{ak} disappears. This suggests an alternative interpretation of $n_a(\infty)$ applicable also in the general case (arbitrary v): As the affinity level has a nonzero width near the surface, it has an initial occupation. This occupancy may in a nonadiabatic transition be retained in $|a\rangle$. Equation (9) then simply gives the probability for this in the small velocity region.

For an application of the above to the sputtering process, the low velocities involved should justify the approximation $\hbar \gamma v \ll \epsilon_a - \epsilon_F$ behind Eq. (9), except in cases with extremely low substrate work functions or with large secondary-ion affinities, where ϵ_a may be at or even below ϵ_F during the surface passage. These cases will not be discussed here although they can be treated from Eq. (6). Here it suffices to note that according to the preceding discussion, large ionization probabilities are expected for such systems as opposed to the usual situations for which the approximation $\hbar \gamma v \ll \epsilon_a - \epsilon_F$ should be valid.

Approximation (7) can be justified as a rough estimate, due to the exponential decay into the vacuum of the substrate states $|k\rangle$.

The assumption of a constant ϵ_a is quite inade-

quate, though, for Eq. (9) to be directly applicable as a negative ion probability. In principle we would require a full knowledge of the variation of $\epsilon_a(z)$ with z (or t) in order to be able to solve Eq. (6). In practice, however, only the values of $\epsilon_a(z)$ in a narrow z region are of importance. This can be seen by noting that the function containing ϵ_a in Eq. (6) is weighted by the matrix elements V_{ak} and the survival probability amplitude

$$(P)^{1/2} = \exp[-\frac{1}{\hbar} \int_{t'}^{t} \Delta(t'') dt''] .$$

The implications of this weighting can be drawn from the lower part of Fig. 1, where $\Delta(z)$ [which according to Eq. (8) can be regarded as an averaged $|V_{ak}|^2$] and P and their product ΔP are shown as functions of z. A value of 2.3 Å^{-1} for γ, a velocity corresponding to a kinetic energy of 5 eV and an atomic mass of 65 has been used. The width at $z = 0$, Δ_0, is chosen to be 1 eV. With these values, typical of an atom being sputtered out of a metal surface, the weight function ΔP is a rather narrow function peaked at 3–4 Å outside the first atomic layer. It is clearly seen how a balance exists between an excitation probability $(\sim |V_{ak}|^2)$ and the probability that the excitation will survive (P).

In deriving a rough dependence on the fundamental parameters of the problem, we may on this background use the value of the energy difference in this region as an effective $\epsilon_a - \epsilon_F$ in Eq. (9),

$$\alpha^-(E) = n_a(\infty)$$

$$= \frac{2}{\pi} e^{-\pi(\epsilon_a - \epsilon_F)_{eff}/\hbar\gamma v} . \tag{10}$$

The discussion above also indicates that the assumption of a constant normal velocity in Eq. (10) is
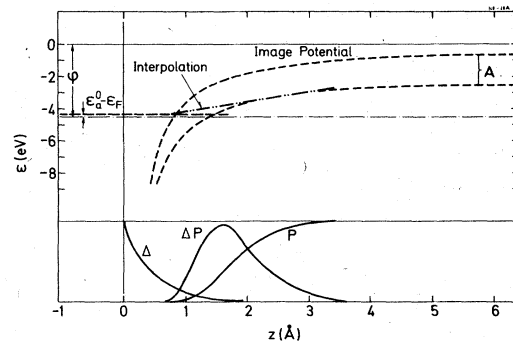

FIG. 1. Variation of the affinity level $\epsilon_a(z)$ of an atom outside a metal. The zero of the distance z is at the image plane, which is 1.5–2 Å outside the first atomic layer. Below is shown the one-electron width Δ, the survival probability P and their product. The parameters used are meant to be typical for a transition-metal atom being sputtered off a transition-metal substrate.

all right, provided v is chosen to be the velocity in the interesting region just outside the surface, and not the one inside or the one measured outside. For all but the smallest v the difference is not very significant, though.

While the determination of the parameter $(\epsilon_a - \epsilon_F)_{eff}$ is ultimately an experimental problem, it is possible to say something about how $(\epsilon_a - \epsilon_F)_{eff}$ should depend on parameters like the work function ϕ and the atomic affinity A. In doing this, we must rely on the increasing amount of knowledge of the adsorbate-induced electron structure coming from surface physics. Unfortunately, most available experimental and theoretical information concerns ϵ_a either at the equilibrium position or far outside the surface and not in the range of distance in between of interest in this work.

Near the surface the electron structure is determined by the interaction between $|a\rangle$ and the substrate, and ϵ_a will be fixed relative to, e.g., the substrate Fermi level. Therefore, changing the work function of the substrate, as in the experiment of Yu,[4] will alter the inner limit of $\epsilon_a(z)$. Far outside the surface, $\epsilon_a(z)$ will follow the classical image potential $-e^2/4z$,[12] so that asymptotically $\epsilon_a(z) = -e^2/4z - A$, where A is the atomic affinity. The outer limit of $\epsilon_a(z)$ is thus determined by A.

The variation of $\epsilon_a(z)$ between these limits has only been investigated in some detail in a few simple cases of light atoms (H, Li, Cl, O, ...) outside free-electron-like metals (Na, Mg, Al).[13,14] Here it has appeared that the affinity level follows the effective electron potential of the clean metal surface also close to the surface. For, e.g., Cl on Na a linear interpolation has been applied successfully[15] for the transition between the outer and the inner part. This suggests that also in the general case a first approximation to $\epsilon_a(z)$ would be an interpolation between an inner value ϵ_a^0 and the outer limit. Such an approximation will be able to account for the trends in the dependence of α^- on ϕ and A. An example of an interpolation is indicated in Fig. 1. The resulting $\epsilon_a(z)$ follows the image potential on the way in. In the region, where overlap with the substrate becomes important, $\epsilon_a(z)$ bends off and goes smoothly to the inner limit at ϵ_a^0. This is the region of the linear interpolation,

$$(\epsilon_a - \epsilon_F)_{eff} = c_1(\phi - A) + c_1 V_i + (1 - c_1)$$
$$\times (\epsilon_a^0 - \epsilon_F)$$
$$= c_1(\phi - A) + c_2 . \tag{11}$$

Here, c_1 is determined by the position where the effective energy difference is taken, i.e., roughly by the peak position of ΔP, relative to the position where the outer asymptotic (image) formula takes over. V_i is the size of the image potential at the latter point.

The take-over of the classical image potential is expected to take place when all the overlap effects with the substrate electrons have disappeared. This will be rather independent of the actual system in question.[16] The constant c_1 depends on the parameters γ, Δ_0 and v through its dependence on ϕ and P. This dependence is rather weak, though. A doubling of $2\Delta_0/\hbar\gamma v$ in Fig. 1 would, e.g., only change the peak position of ΔP by 0.3 Å. The v dependence must, however, be born in mind if a detailed account of the velocity dependence of α is wanted. The position of ϵ_a^0 relative to ϵ_F is thus the only parameter other than ϕ and A strongly affecting $(\epsilon_a - \epsilon_F)_{eff}$. In the present context this is a complication. It shows, on the other hand, that once the dependence of α^- on the other parameters involved is clarified, measurements of α^- can give information on adsorbate electron structures. It is seen that in Eq. (11), $(\epsilon_a - \epsilon_F)_{eff}$ has been divided into a part depending only on the parameters ϕ and A characterizing the substrate and the secondary ion, and a part containing information about their interaction. Similarly, $\alpha^-(E)$ can be written as a product,

$$\alpha^-(E) = \frac{2}{\pi} e^{-c_1\pi(\phi-A)/\hbar\gamma v} e^{-c_2\pi/\hbar\gamma v} . \tag{12}$$

It follows that for a class of systems having $\epsilon_a^0 - \epsilon_F$ independent of the actual secondary ion-substrate combination, all the rough experimental-parameter dependencies mentioned are reproduced. An example of secondary ion-substrate combinations belonging to this class is the systems where the secondary ion is sputtered off the element itself. Here the valence level of the atom at the surface must be pegged at the Fermi level in order to ensure approximate charge neutrality. Since this level includes the atomic affinity level, ϵ_a^0 must be pegged at ϵ_F, too.[17] For the transition metals this seems to be the case even if the adsorbate and substrate are different elements.[18] Other such cases may exist. One requirement will be that the difference in electronegativity between the adsorbate and the substrate should be small.

In the cases where c_2 cannot be regarded as constant, as for instance when comparing Mo^- and H^- or O^- ion yields in the experiment of Yu,[4] the experimentally found dependence of α^- on ϕ and v is still refound in Eq. (12) and there will obviously still be some correlation with A. It is, however, clear that when ϕ is changed by varying the Cs coverage θ, the exponential dependence of α^- on ϕ is only valid as long as c_2 or $\epsilon_a^0 - \epsilon_F$ is not affected by the Cs overlayer. This will be true for small θ, but for larger θ a dependence of α^- on θ other than through ϕ is expected. In the experiment of Yu,[4] this explains why the exponential dependence of S^- on ϕ stops at the higher coverages, and why two θ values giving the

same ϕ does not give the same S^-.

If we regard the positive-ion production as the excitation of a hole from above the Fermi level to the ionization level, it becomes completely analogous to the negative-ionization case above, where an electron from below the Fermi level is promoted to the affinity level. We get in the same way and under the same assumptions

$$\alpha^+(E) = \frac{2}{\pi} e^{-\pi c_1(I-\phi)/\hbar\alpha v} e^{-\pi c_2/\hbar\alpha v} \quad . \quad (13)$$

Again a term is included involving $\epsilon_a^0 - \epsilon_F$ through c_2, where ϵ_a^0 is now the position of the ionization level at the surface.

For Cu^+ sputtered off Cu, the experimental value $b \cong 10^6$ cm/sec quoted above[5] enables us to find a typical value for c_1. Since in this case we can assume $\epsilon_a^0 - \epsilon_F \cong 0$, we only need $I - \phi$ and a value for V_i. The former is 3.3 eV,[19] while a value of 1.4 eV is reasonable for V_i.[16] We find that $c_1 = 0.024$. This, in turn, can give the "effective temperature" T of the experiment $kT = \hbar\gamma v/\pi c_1$. Using an average velocity corresponding to an outward kinetic energy of 5 eV,

this gives $T \cong 9000$ K, which is of the right order of magnitude.[3]

It is thus seen that the theory presented does not only reproduce the experimental trends in the parameter dependencies, it is also internally consistent, as far as the orders of magnitude of the constants are involved. It must be stressed, however, that in a more detailed theory each system should be considered separately, and the integral (6) should be solved numerically. As mentioned above, there are a few adsorbate-substrate combinations where the variation of the adsorbate level $\epsilon_a(z)$ is known in some detail in the interesting range of z values. For such systems the more detailed theoretical predictions can be made once they are called for by relevant experiments.

ACKNOWLEDGMENTS

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