# Ionization of low-energy atoms ejected from ion-bombarded solid surfaces

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A microscopic semiphenomenological theory of ionization is described and compared with newly available experimental data. The theory assumes that the substrate electrons around the point of ejection are excited by the collision process and have a very high effective temperature. Formally, the approach is similar to that developed by Overbosch *et al.* to interpret the Na scattering data.

The need for a comprehensive and detailed theory of ionization in sputtering has been stimulated by the recent experiments on well-defined surfaces[1–5] which allow a quantitative comparison of theoretical and experimental results. The hitherto proposed models[6–8] do not describe, in the present form, all aspects of the ionization process satisfactorily and the development of a precise microscopic description based on molecular dynamics[9] is still hampered by the complexity of the problem. In this paper I present a simple microscopic semiphenomenological theory of ionization which seems to describe qualitatively and in some instances quantitatively most of the available experimental data on ejected low-energy ions. The results may serve as guidance for the development of a more complete theory.

The theory is based on the assumption that the electrons in the collision cascade region are excited to the empty states of the energy $\epsilon$ above the Fermi level with the probability $\exp(-\epsilon/kT_s)$. Such assumption allows one to define the effective electron temperature $T_s$ in the cascade region. The existence of $T_s$ has been inferred previously from the computer simulation[8] and from experimental evidence.[10,11] Its value depends sensitively[8] upon the substrate atomic parameter $\gamma$, defined below. In the present treatment, $T_s$ is assumed to be an empirical parameter having a value between 1000 and 3000 K for clean metals as suggested by the computer simulation.[8]

The second assumption is that $T_s$ is constant during the ejection process and the ejected atoms interact with the excited substrate through the space and time-dependent hopping integral $V\exp(-\gamma x) = V\exp(-\gamma v t)$, where $x$ is the distance from the surface and $v$ is the velocity of the ejected particle perpendicular to the surface. The hopping integral is taken to be proportional to the overlap of valence wave functions. The parameter $\gamma$ is then the average value of $\gamma_a$ and $\gamma_b$, where $\gamma_a$ and $\gamma_b$ are defined from the valence wave functions of the ejected atom $A$ and the substrate atom $B$ as $\psi_a \propto \exp(-\gamma_a r)$ and $\psi_b \propto \exp(-\gamma_b r)$. The distance $r$ from the nucleus is assumed to be sufficiently large ($3 < r < 6$ Å) to allow the description of the wave functions in terms of one exponential. The numerical values of $\gamma$ can be calculated from atomic tables.[12] The energy $\epsilon_a$ of the valence level of the ejected atom also changes with time because the value of $\epsilon_a$ depends upon the distance from the surface due to space-varying surface potentials. The inclusion of the time dependence of $V$ and $\epsilon_a$ distinguishes the presented theory from the oversimplified "local thermal equilibrium" (LTE) theory.[10]

The time development of the positive change $p$ (the formation of negative ions is analogous) on the ejected atom satisfies then the following master equation[13]:

$$\frac{dp}{dt} = -\frac{p - p_0}{\tau} , \tag{1}$$

where

$$p_0 = \exp\left(\frac{\epsilon_F - \epsilon_a(t)}{kT_s}\right) ,$$

$$\tau = \frac{\hbar}{2\pi V^2(t)\rho} = \frac{\hbar}{2\Delta}\exp(2\gamma v t) .$$

The energies are positive quantities measured with respect to the vacuum level, $\rho$ is the substrate electronic density of states, and $\Delta$ is the half width of the $\epsilon_a$ level at $x = 0$.

The solution of (1) for the ionization coefficient $R^+ = p(\infty)$ is in good approximation given by

$$R^+ = \exp\left(\frac{\epsilon_F - \epsilon_a(x_0)}{kT_s}\right) , \tag{2}$$

where

$$x_0 = \frac{1}{2\gamma}\ln\left(\frac{\Delta}{\gamma\hbar v}\right) .$$

The results are formally equivalent to those developed by Overbosch *et al.*[14] and Brako and Newns[15] (the high-temperature limit) to describe the

ionization of hyperthermal Na atoms scattered by the externally heated tungsten substrate. In the present model, the substrate is not in thermal equlibrium but is electronically excited in the area of a few atomic distances around the emission point. The excitation can be described by a very high effective temperature $T_s$.

The energy $\epsilon_a(x)$ in (1) and (2) consists of the atomic ionization energy $I$, the energy shift due to the electron exchange with the surface, the image charge contribution, the Madelung energy (at polar surfaces), and of the dipolar field of adatoms (work function changes). To demonstrate the consequences of (2) we will first approximate $\epsilon_a(x)$ by the linear relation

$$\epsilon_a(x)=\begin{cases}\epsilon_a(0)+[\epsilon_a(\infty)-\epsilon_a(0)]\Gamma x & \text{for } x\leq 1/\Gamma\\ \epsilon_a(\infty) & \text{for } x>1/\Gamma\end{cases} . \tag{3}$$

Then,

$$R^+=\exp\left[\frac{\epsilon_F-\epsilon_a(0)}{kT_s}\right] \times\exp\left[\frac{[\epsilon_a(0)-\epsilon_a(\infty)]\Gamma}{2\gamma kT_s}\ln\left[\frac{\Delta}{\gamma v\hbar}\right]\right] \tag{4}$$

for

$$\Delta\exp\left[-\frac{2\gamma}{\Gamma}\right]<\gamma v\hbar<\Delta$$

and

$$R^+=\exp\{[\epsilon_F-\epsilon_a(\infty)]/kT_s\}$$

for smaller $\gamma\hbar v$. The velocity dependence of $R^+$ is obtained by rewriting (4) as

$$R^+\propto(v)^{[\epsilon_a(\infty)-\epsilon_a(0)]\Gamma/2\gamma kT_s} . \tag{5}$$

Similar functional dependence of $R^+$ on $v$ has been identified in recent experiments.[2,3]

The dipolar field of adatoms can be reasonably well described by the linear relation (3). This field causes an energy step $\delta\phi$ (the change of the work function $\phi$) within the distance $1/\Gamma'$ above the surface. Then, as follows from (4), $R^+$ depends upon $\delta\phi$ as

$$R^+\propto\exp\left[\frac{\delta\phi\Gamma'}{2\gamma kT_s}\ln\left[\frac{\Delta}{\gamma v\hbar}\right]\right] \tag{6}$$

and for smaller velocities as

$$R^+\propto\exp(\delta\phi/kT_s) . \tag{7}$$

The exponential dependence on $\delta\phi$ is in accordance with the recent experiments.[1,4] Furthermore, the experiments indicate that the coefficient by $\delta\phi$ in the exponent depends very specifically upon the size of the adatoms ($\Gamma'$), upon $\gamma$ of ejected atoms and upon $v$. These observed relationships are by (6) also well qualitatively reproduced.[13] More than a qualitative agreement cannot be expected because of the approximate expression for $\epsilon_a$.

In the case of emission from clean metals, $\epsilon_a(x)$ can be well described for larger $x$ by the image charge energy and one can thus test the validity of (2) quantitatively. Suitable experiments, allowing a comparison with the theory, are described in Refs. 2 and 3. The $Cu^+$ current, obtained in Ref. 2 by sputtering clean copper surface, can be converted into $R^+$ by dividing it by the experimentally verified expression $E(S+E)^{-3}$ for the neutral $Cu^0$ flux[16], where $E$ is the kinetic energy of emitted atoms and $S=4$ eV. The experimentally determined $R^+$ of Cu is plotted in Fig. 1 as a function of $E$ by the full line. The absolute value of $R^+$ at $E=5$ eV was taken from Ref. 17. The calculated values of $R^+$ are shown by black dots. In the calculation, the energy $\epsilon_a(x)$ was set equal to

$$\epsilon_a(x)=I-\phi-\frac{e^2}{4x}=3.52-\frac{3.37}{x} . \tag{8}$$

The value of $\gamma$ for Cu was estimated from atomic tables[12] to be $\gamma=1.33$ Å$^{-1}$. The good fit in the figure is obtained for $\Delta=5$ eV and $T_s=2400$ K. By changing $\Delta$ and $T_s$ within a realistic range, one can obtain

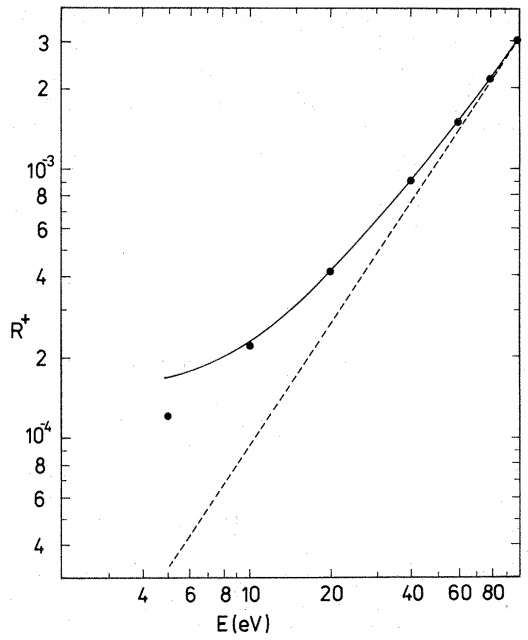


FIG. 1. Positive ionization coefficient $R^+$ of ejected copper atoms vs their kinetic energy. The theoretical values are shown by black dots, the experimental results by the full line. To obtain the experimental values of $R^+$ the measured intensity of sputtered $Cu^+$ ions (Ref. 2) is divided by the intensity of sputtered $Cu^0$ neutrals (Ref. 16). The tentative high-energy dependence $E^{3/2}$ is shown by the dotted line.

smaller or larger absolute values of $R^+$ but the $v$ dependence remains practically the same. For larger $v$, i.e., for smaller $x_0$, $\epsilon_a(x)$ is better described[7] by the linear relation and therefore, according to (5), $R^+$ depends on $v$ as $v^n$. The tentative $v^3$ dependence is shown in Fig. 1 by the dashed line.

Very similar experimental results as in the case of Cu have been obtained on beryllium.[3] Moreover, the authors in Ref. 3 have measured the influence of oxygen coverage on the velocity dependence of the Be ionization coefficient $R^+$ (Be). The measured velocity dependence is such that $R^+$ (Be) $\propto v^{3.06}$ for clean surfaces and $R^+$ (Be) $\propto v^{2.2}$ for oxygen-covered surfaces. The change of the exponent with increasing oxidation from the value of 3.06 to 2.2 is well accounted for by the relation (5). The values of the parameter $\gamma$ in (5) are given by $\gamma_{Be}=1.38$ for clean Be (Ref. 12) and by $\gamma=\frac{1}{2}(\gamma_{Be}+\gamma_O)=1.78$ for the oxidized Be surface, where $\gamma$ of oxygen is taken equal to $\gamma_O=2.18$.[12] Thus, if we assume that for the clean sample the exponent is 3, the calculated exponent for the surface covered by oxygen would be 2.32, in good agreement with the experiment.

The rapid increase of $R^+$ with the coverage of clean surfaces by reactive gases, the so-called "chemical ionization yield enhancement," is another experimentally documented effect which can be treated within the described theory. When we neglect the Madelung contribution to $\epsilon_a(x)$, the replacement of the surface substrate atom $A$ by the reactive atoms $B$ will manifest itself in Eq. (2) only through the change of $\gamma$. It is easy to show, in the way suggested in Ref. 13, that (4) leads to an ionization yield of the $A$ atoms which increases with the surface reactive gas concentration $c_B$ ($c_B \ll 1$) as

$$R^+ \propto \exp[c_B N(R_0^{-d}-1)] \ , \qquad (9)$$

where $N$ is the number of the nearest-neighbor sites at the surface, $R_0$ is the ionization yield of $A$ atoms emitted from the clean surface, and $d=(\gamma_B-\gamma_A)/2N\gamma_A$. $\gamma_A$ and $\gamma_B$ are the $\gamma$ coefficients of $A$ and $B$ atoms, respectively. Typically, $\gamma_A$ of metals and silicon is equal to 1.3, $\gamma_B$ of reactive gases (oxygen) is 2.2, and $N=4$, $R_0=10^{-6}$. The value of coefficient $N(R_0^{-d}-1)$ in (9) is then equal to 9 which is within the range of experimentally observed values.[18,19] It is interesting to note that the enhancement (9) works for negative ions as well[19] and is generally more important than is the variation of $R^+$ (or $R^-$) due to the work-function changes $\delta\phi$ [(6) and (7)].

In conclusion, one can say that the conceptually simple theoretical description of ionization based on (1) accounts surprisingly well for most experimental data gathered in recent years. The theory uses well-defined atomic and solid-state parameters except for the effective substrate temperature $T_s$, the existence of which is postulated and needs further justification.

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