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Chemical effects in secondary ion emission from metal surfaces

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It is shown that well-known chemical effects that result in a large enhancement of the positive secondary ion emission from metal surfaces coated with electronegative adsorbates can be explained in terms of the electron-tunneling model. The presence of adsorbed particles on a surface induces an electrostatic potential that causes a shift in the electronic level of the emitted atom, in addition to the shift caused by the conventional imagelike potential. This additional shift results in an increase in the effective neutralization distance and a decrease in the electron tunneling rate. As a consequence there is a drastic decrease in the neutralization probability of secondary ions.

When solid surfaces are bombarded with ion beams, atoms and molecules are ejected from the surface in various charge and excitation states. Of those ejected as ions, most are singly charged, either positively or negatively. The most comprehensive description of this secondary ion emission from clean metal surfaces is the electron-tunneling model in which the electron is resonantly transferred between an atomic state of the sputtered atom and a conduction-band state of the metal.[1-4] Secondary ion emission shows a high sensitivity to the surface chemical state with ionization probabilities increasing by as much as three orders of magnitude for metal surfaces covered by electronegative species.[5] Although this so-called chemical effect has been known for some time, the mechanism for this large enhancement is still unclear. One mechanism discussed in the literature is the bond-breaking model.[6] In this model, ions are produced in the collision cascade when atoms, bound to the surface by ionic (alkali halides) or partially ionic bonds (metal oxides), are emitted after the bond breaking. Qualitatively this process can be described by a two-level-crossing Landau-Zener model.[7] A recent survey of different models for secondary ion emission can be found in Ref. 8.

When a pure metal surface is exposed to a gas of an electronegative species like oxygen, chemisorption takes place immediately but surface oxidation can require from minutes to hours.[9] However, the ion-yield enhancement can be observed as soon as the surface is exposed.[10] This indicates that the bond-breaking model mentioned above cannot explain the observed enhancement. For metal surfaces covered by electropositive elements (Cs, Li, K, Na) a large enhancement of negative ion emission[11] and a decrease of positive emission[4] are observed. These effects can be explained in the framework of the electron-tunneling model as a consequence of a decrease in the work function.[4] However, this model should also be applicable to work-function changes induced by electronegative adsorbates. Measurements show that electronegative adsorbates always lead to an enhancement of positive ions independent of the sign of the change in the work function.[8,12]

We consider the emission of secondary atoms from metal surfaces in the jellium model. In this model the metal is treated as a uniform positive potential containing a noninteracting Fermi gas of electrons with work function Φ. We show how an adsorbed atom alters the charge-exchange processes which gives rise to the secondary ions emitted from the surface.

Any charge placed on a metal surface induced an imagelike potential[13] that at distances of more than several a.u. (here and below the atomic system of units is employed: $m=\hbar=e=1$) from the surface can be approximated as $1/[4(z-z_{\rm im})]$, where $z_{\rm im}$ is the position of the image plane.[14] The ionization potential of the valence electron of the atom changes near the metal surface. For the ion-metal interaction we use a potential which takes into consideration the screening effect at small distances by multiplying the image potential by the factor $[1-\exp(-z/\lambda)]$.[15] At some distance z_0 from the surface the ionization potential and the work-function values coincide (Fig. 1). Hence, for $z>z_0$ the neutralization of

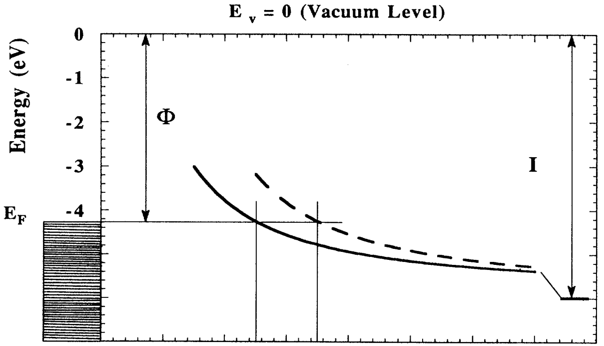

FIG. 1. Valence electron level energy (the ionization potential) as a function of the distance to the metal surface ($r_s=2$). $z=0$ corresponds to the jellium edge, which is half an interlayer spacing outside the first metal layer. Solid line, a pure surface; dashed line, a surface with an adsorbed O atom at the equilibrium position outside $z=1$ a.u. (Ref. 17) (the lateral distance is 3.5 a.u. from the O atom).

the emitted ion can take place. The ionization probability P^+ for an ion which moves along a classical trajectory can be calculated from

$$dP^+(t)/dt = -\Delta[z(t)]P^+(t) \;, \tag{1}$$

with the initial condition $P^+(t_0)=0$, where $\Delta(z)=\Delta_0 \exp(-\gamma z)$ is the width of the electron level, γ^{-1} is the characteristic decay length of the electron wave function,[3] and t_0 corresponds to z_0. By using the initial condition $P^+(t_0)=0$, we neglect the memory of the initial occupation. We justify this by noting that memory of any excitations is erased very rapidly by the resonance transition into unoccupied metal states much faster than typical emission time.[2] The solution of (1) is given by

$$P^+ = \exp[-\Delta(z_0)/\gamma v] \;, \tag{2}$$

where v is a constant velocity perpendicular to the surface. We now consider a metal surface with chemisorbed electronegative species. The affinity level for this species is a state below the Fermi level and is therefore occupied.[16] The electrostatic potential induced by the chemisorbed atoms has been calculated self-consistently within the local-density approximation and the jellium model.[17] The induced potential can be crudely approximated by a dipolelike potential with the dipole aligned perpendicular to the surface and having its negative charge pointing out. The potential induced by the chemisorbed atom will cause a change in the behavior of electron level in the vicinity of the chemisorption site.[18] This shifts the electron level upward. The level position as a function of the distance from surface is shown in Fig. 1 (dashed line) for a lateral distance 3.5 a.u. from a chemisorbed oxygen atom at its equilibrium position above the jellium edge. The induced potential value is taken from Ref. 17. In this case the effective neutralization distance, that distance at which the electron binding energy is equal to the work-function value, has a larger value of $z_1=7$ a.u. For Al, which is well described by the jellium model, known values of I and Φ yield $z_0=4.9$ and $z_1=7$ a.u. provided that $\Phi=\text{const}$. Assuming the ionization probability $P^+=0.007$ for clean surface and $\gamma=0.7$ Å^{-1},[4] formula (2) estimates the ionization probability for the coated surface to be $P^+=0.35$. In spite of the fact that it is an approximate estimate, it is clear that, by virtue of exponential falloff of metal electron wave functions away from the surface, even a slight increase of the effective neutralization distance may increase the ion survival probability by orders of magnitude.

The potential induced by the presence of an adsorbed atom causes a shift of the atomic level in addition to the conventional shift owing to the image potential. Though being necessarily accompanied by a change of the work function, the effect of this additional shift may be considered separately. The shift of the level is principally determined by the potential in the region of high electron density, that is, by the potential close to the atom, while the work function is determined by the integration over half-space.[19] Both factors affect the effective neutralization distance. However, when the additional shift of the atomic level is large enough, slight changes in the work function alter only the extent of the increase of the secondary ion yield. The presence of electronegative species usually increases the work function but in the case of the oxygen-coated Mg surface the work function is decreased; nevertheless the enhancement of positive ions takes place in both cases.[12]

Calculations of the broadening and energy shifts of atom levels near impurity-covered metal surface were performed for hydrogen using the complex scaling technique.[18,20] These calculations account for the observed formation of excited hydrogen atoms in electron-stimulated desorption from alkali-metal-promoted surfaces.[20] The excited states were found for work functions that are larger than their binding energies. This indicates that the levels are downshifted near the alkali-metal-promoted surfaces as predicted by their calculation instead of the conventional upshift predicted by the image potential.

For metal surfaces covered with electropositive elements a large enhancement of negative ion yield is observed.[11] This enhancement is usually explained in the electron tunneling model as a result of the substantial work-function decrease (up to 3 eV). However, the presence of electropositive atoms also induces a potential which causes an affinity level shift in addition to the imagelike potential. This results in an additional increase in the effective neutralization distance (Fig. 2). As a result of simultaneous action of these two factors we expect an even larger enhancement of negative ion emission than the one observed for positive ion emission. The experimental yield of Ni^- from Cs-coated nickel shows an increase of up to five orders of magnitude over that for the pure surface.[11]

In this work we have not dealt with the effects of the velocity change during the emission from the surface[3] or the finite time for electron diffusion in solids.[21] These and other effects are bound to modify the quantitative results to some extent. However, we feel we have shown the basic mechanism responsible for the huge changes in

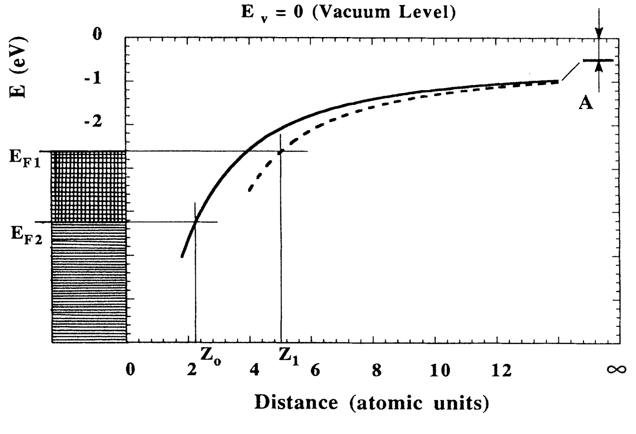

FIG. 2. Affinity level energy as a function of the distance to the metal surface ($r_s=2$). Solid line, a pure surface; dashed line, a jellium surface with an adsorbed Li atom at the equilibrium position outside $z=2.3$ a.u. (Ref. 17) (the lateral distance is 5 a.u. from the alkali metal).

ionization probability in chemical effect.

In conclusion, the model presented here explains the large enhancement of positive secondary ion yield from electronegative-coated metal surfaces. Chemisorbed electronegative elements induce an electrostatic potential that causes an extra shift upward of the valence electron level of the emitted atom, thus reducing the electron tunneling rate. As a result, the neutralization of emitted ions takes place at a greater distance from the surface and consequently with exponentially lower efficiency. The effect of the work-function change in this case, although present, does not play a dominant role in the large enhancement of positive secondary ion yield.

In the case of negative secondary ion emission from the alkali-metal-promoted surfaces, we have the analogous effect of increasing the effective neutralization distance (neutralization now is the electron tunneling from affinity level to metal band) but the work-function decrease now contributes much to the enhancement, resulting in a greatly enhanced negative ion yield.

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