Quantum effects in the trajectories of sputtered ions

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Recent experimental results of Yu have shown remarkable behavior of the sputtering yield as a function of ion velocity. The usual assumption that the sputtered ions desorb as classical particles with a constant velocity is clearly incorrect at low velocities. We have tried a simple model based on a conjecture that the ion follows a quantum rather than a classical trajectory. The results, which are based on quasiclassical and quasistationary final-state ion trajectories (WKB wave functions with a complex potential), are in excellent agreement with the experiment. However, the imaginary part of the complex force necessary to achieve this agreement is at least an order of magnitude larger than typical interatomic forces. The conclusion therefore is that these quantum effects on the ion trajectory are not the cause of the nonlinearity of Yu's data.

Yu[1] has shown experimentally that there exists a correlation between the ionization probability of ions sputtered from metal surfaces, the outward normal velocity $v_\perp$, and the ionization potential I or affinity level A of the desorbing atom. The probability $\alpha^{+(-)}(E)$ that the sputtered particle comes out as a positive or negative ion was calculated by Nørskov and Lundquist[2] and shown to be proportional to $\exp[-(I-\phi)/\epsilon_0]$ or $\exp[-(\phi-A)/\epsilon_0]$, respectively, $\epsilon_0=\epsilon_0(v_\perp)$ being a function of $v_\perp$. These results suggest that during the process of sputtering there is an ion-surface interaction operative rather than an ion-atom binary interaction.

Direct verification of the $v_\perp$ dependence of ϵ_0 has been given by Yu[1] for sputtered O^- from chemisorbed oxygen layers of vanadium (V) and niobium (Nb) surfaces. In Yu's work the exponential dependence of α^- on the work function ϕ is utilized to determine the parameter ϵ_0 for various combinations of emission velocity and emission angle θ measured with respect to the surface normal. The ion-yield data for various angles were used to calculate ϵ_0 as function of $v_\perp$. The results for vanadium are shown in Fig. 1. At high velocity it is seen that ϵ_0 is linear with $v_\perp$ for various angles of sputtering but both these graphs begin to deviate from linearity at $v_\perp$ near 1×10^6 cm/sec. The most striking feature of the graphs is the upward curvature of the data points for velocities less than 1×10^6 cm/sec which also seems to have some θ dependence.

The low-energy upturn of ϵ_0 cannot be attributed to experimental errors and is not predicted by any theoretical model of $v_\perp$ dependence. Yu suggests that $v_\perp$ may vary along the secondary-ion trajectories as the ions have to overcome both the image and surface binding potentials. This may well explain some of the deviations from linearity at low velocity. However, a purely classical model of these effects due to Lang,[3] while successful in giving a deviation from linearity in the right direction, fails to give the proper upward curvature in the data (as shown in Fig. 1). We have tried a simple quantum model for the ion trajectory which does indeed predict such an upward curvature of the ϵ_0 vs $v_\perp$ data. However, in order to do so requires the use of a dissipative force that is many times larger than one might expect on intuitive as well as on computational grounds.

In treating the velocity dependence of ϵ_0, we will assume the same model as a number of workers (Lang,[3] Blandin, Nourtier, and Hone,[4] and Nørskov and Lundquist[2] and at a later stage introduce our correction to the ionization probability. The metal, according to previous work, is thought of as a noninteracting Fermi gas of work function ϕ, where the motion of a single atom in the vicinity of the metal is treated classically. The atom is supposed to have an affinity level $|a\rangle$ with energy $\varepsilon_a(t)$ which lies in the conduction band of the metal. The atom interacts with the metal via the "hopping" matrix element $V(z)=\langle a|V|k\rangle$. $V(z)$ is the tunneling interaction potential which is a function of time through the classical trajectory $z(t)$ of the ion. In particular, for an exponential model with constant velocity,

$$V_{ak}(z)=V_{ak}^0\exp(-\gamma z/2)=V_{ak}^0\exp(-v_\perp\gamma t/2)\quad z>0\,, \tag{1}$$

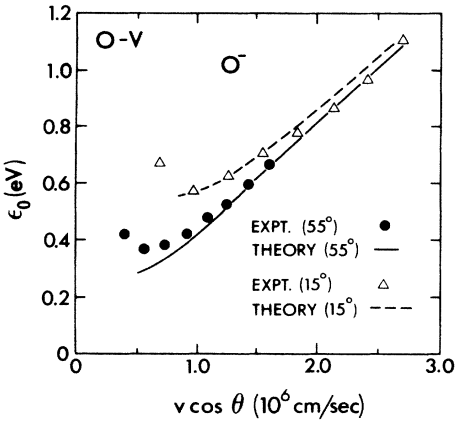

FIG. 1. Lang's theoretical values of ϵ_0 compared to Yu's experimental values for O^- from V. Lang's theory is based on a purely classical and initial-state modification of the $z=v_\perp t$ trajectory. (Taken from Ref. 3.)

where z is measured perpendicular to the surface and γ^{-1} is the range of the potential.

The ionization of the atom takes place because there is a charge transfer between the Fermi sea and the broadened level $|a\rangle$ with a resonance width Δ. The one-electron resonance width is given by

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

For $\varepsilon_a(t)$ Lang uses $\varepsilon_a(t)=C\exp(-\alpha v_\perp t)-A$. First-order time-dependent perturbation theory for the electron tunneling yields the ionization probability (in the adiabatic limit) in the form previously discussed, i.e.,

$$\alpha^{-1}(E)=\exp[-(\phi-A)/\epsilon_0] , \tag{3}$$

where

$$\epsilon_0=\hbar\gamma(\phi-A+E_0)v_\perp/2\Delta_0 , \tag{4}$$

and

$$E_0=\varepsilon_f-\varepsilon_a(0) .$$

This result is consistent with the linear portion of the data in Fig. 1.

A more detailed treatment of the classical ion trajectory using a Morse potential leads to the Lang improvement also shown in Fig. 1. However, the upturn is not reproduced. In what follows we try a model that does explain the upturn but at the expense of nonphysical forces. We suppose that at low velocities the assumption of classical ion motion is the most damaging. Thus we assume the marked deviation of ϵ_0 from linearity and especially the upturn is principally due to deviations from classical behavior. In order to test this conjecture we replace $v_\perp$ in Eq. (4) with $\langle v_{\perp\mathrm{op}}\rangle$, a quantum expectation value of the velocity to be discussed in what follows. Our results require certain empirical parameters involving dissipative forces to achieve a best fit to the data of Yu. These forces turn out to be anomalously large. We therefore conclude that the conjecture must be rejected unless one can provide a realistic calculation that shows such forces are possible.

We use a quasiclassical and quasistationary model for the ion motion. In the classical limit there is a small region of z which provides the main contribution to the integrand appearing in the expectation value $\langle v_{\mathrm{op}}\rangle$. That is, since the quasiclassical wave function is peaked near the classical turning point the expectation value of the velocity operator will be evaluated somewhere near this peak, i.e.,

$$\langle v_{\perp\mathrm{op}}\rangle=\frac{\int dz\psi^* v_{\perp\mathrm{op}}\psi}{\int dz\psi^*\psi}\approx\left.\frac{v_{\perp\mathrm{op}}\psi}{\psi}\right|_{z=z_0} . \tag{5}$$

The precise point where it is evaluated must for the present be determined empirically.[5]

An equally important quantum modification to $v_\perp$ arises from the fact that the potential must be taken to be complex due to the decay process itself. Thus, as pointed out Brenig,[6] because the atom is decaying via the electron tunneling process, then the quantum velocity will also be effected by the wave packet changing its shape. We can conveniently treat this effect in the quasistationary approximation in which E is replaced by $E-i\Gamma$ and $V(z)$ is replaced by $V(z)-iW(z)$. We can then use a realistic value for V and allow W to be a semiempirical parameter. Specifically, we take the real part of the z component of the force, $F_R=-V'(z)$, evaluated at z_0, to have a value in agreement with that used by Lang[3] and then use $F_I=-W'(z_0)$ to be the adjustable parameter.

For the wave function we use

$$\psi_{\mathrm{WKB}}(z)=[1/p(z)^{1/2}]\exp\left[\frac{i}{\hbar}\int_s^z p(z')dz'\right] , \tag{6}$$

with the local momentum given by

$$p(z)=\{2M[E-V(z)-i\Gamma+iW(z)]\}^{1/2} . \tag{7}$$

In addition, because the potential is complex, the usual derivation of the velocity operator is also modified. That is, we now must have

$$V_{\perp\mathrm{op}}=\left[\frac{\hbar}{iM}\right]\frac{d}{dz}+W(z)(z-\langle z\rangle)/\hbar . \tag{8}$$

Using this result in Eq. (5) we have

$$\langle v_{\perp\mathrm{op}}\rangle=(\hbar/iM)[(d/dz)\psi_{\mathrm{WKB}}/\psi_{\mathrm{WKB}}]|_{z_0}+W(z_0)(z_0-\langle z\rangle)/\hbar . \tag{9}$$

Further, the second term in $\langle v_{\perp\mathrm{op}}\rangle$ will be small since again the integrand is peaked near z_0 and hence $\langle z\rangle=z_0$. Therefore,

$$\langle v_{\perp\mathrm{op}}\rangle\approx\frac{\hbar}{Mi}\left.\left[\frac{d}{dz}\psi_{\mathrm{WKB}}/\psi_{\mathrm{WKB}}\right]\right|_{z=z_0} . \tag{10}$$

When Eq. (10) is used in place of the classical velocity only the real part enters into ϵ_0. Thus we need

$$\mathrm{Re}\langle v_{\perp\mathrm{op}}\rangle=|v_\perp(z_0)|\left[\cos\phi_v+\frac{\hbar F_I\cos(2\phi_v)}{2M^2|v_\perp(z_0)|^3}+\frac{\hbar F_R\sin(2\phi_v)}{2M^2|v_\perp(z_0)|^3}\right] , \tag{11}$$

where $v_\perp(z)=\{2[E-V(z)-i\Gamma+iW(z)]/M\}^{1/2}$ is the local classical velocity and ϕ_v is the phase angle of the complex velocity. Clearly $\langle v_{\perp\mathrm{op}}\rangle$ is a function of $v_\perp=(2E/M)^{1/2}$ which corresponds to the velocity of the ion at the detector and therefore the value measured and referred to in the experiment by Yu.

It is evident from Eq. (11) that because of the $1/|v_\perp(z_0)|^3$ terms $\mathrm{Re}\langle v_{\perp\mathrm{op}}\rangle$ can exhibit the proper experimental behavior, i.e., the low-velocity dramatic increase of ϵ_0 vs $v_\perp$. *Our conjecture, which is that* $v_\perp$ *in Eq.*

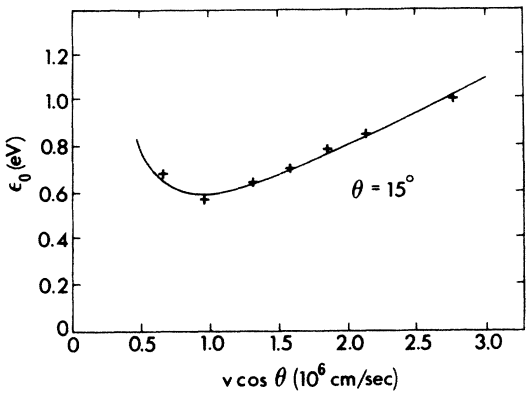

FIG. 2. Theoretical quantum (quasiclassical) values of ϵ_0 (solid lines) compared to Yu's experimental values (crosses) for vanadium (O^-). $F_I = 5.16 \times 10^2$ eV/Å.

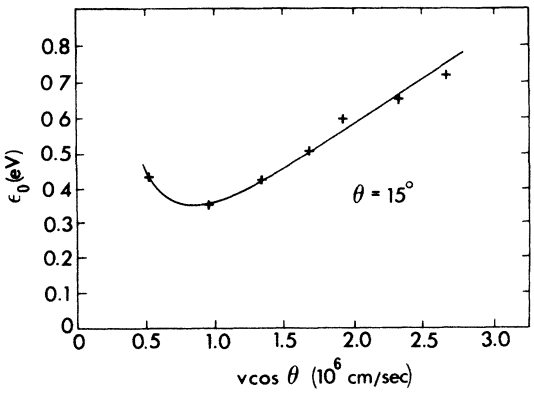

FIG. 3. Theoretical quantum (quasiclassical) values of ϵ_0 (solid lines) compared to Yu's experimental values (crosses) for niobium (O^-). $F_I = 3.42 \times 10^2$ eV/Å.

(4) be replaced by the quasiclassical velocity given by Eq. (11), therefore has the proper semiempirical behavior.

The parameters in Eq. (11) are determined as follows: we choose a value of F_I and ϕ_v so as to optimize visually the agreement with experimental curves of Yu. We have found that if we take $V(z_0)=0$ and $W(z_0)=\Gamma$, then we obtain a very good fit to the data. These choices make $\phi_v = 0$ and Eq. (11) simplifies to

$$\mathrm{Re}\langle v_{\perp \mathrm{op}} \rangle = v_\perp (1 + \hbar F_I / 2M^2 v_\perp^3) . \tag{12}$$

The best fit is not entirely sensitive to the parameters F_I and ϕ_v and therefore we discuss only this simpler expression. We note that $F_R(z_0)$ does not enter into Eq. (12) because of the previous choices. Other values of z_0 would lead to a contribution from F_R via Eq. (11).

In Figs. 2 and 3 we display the experimental data (+) compared to our theoretical curves (solid lines). We note that the agreement is excellent in all cases—probably well within the error inherent in the experimentally reported values of ϵ_0. The values of $F_I(z_0)$ used to determine the graphs in Figs. 2 and 3 are indicated in the figure captions.

We note that F_R using Lang's potential[3] when evaluated at the cross-over point $V(z_0)=0$ is approximately equal to 73 eV/Å. This should be compared to the values of F_I in Figs. 2 and 3 which are quite a bit larger. *It is these values that seem to make our conjecture incorrect or at best dubious.* Indeed one might expect the imaginary part of the force to be small compared to the real force.

We therefore conclude that although treating the ion motion with a quantum optical potential might be useful in some applications[6] it is probably not large enough to give rise to such a radical effect as observed in the nonlinear dependence of ϵ_0 on velocity observed by Yu. Nonetheless there exists a challenging theoretical problem embodied in the data and theory curves of the figures reported herein. On the one hand, a purely classical model involving only a single desorbing ion cannot explain the data. On the other hand, a simple quantum model, while giving the correct experimental behavior, requires an anomalously large force to explain the data. It seems worthwhile to search for other simple models that can explain this dramatic upturn in Yu's experimental data.

ACKNOWLEDGMENT

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[4]A. Blandin, A. Nourtier, and D. W. Hone, J. Phys. (Paris) **37**, 369 (1976).

[5]One can of course calculate $\langle v_{\perp \mathrm{op}} \rangle$ usng a properly joined Wentzel-Kramers-Brillouin or the exact wave function for an exponential potential, for example. However, the calculation reported here is far simpler and, we feel, contains the essential elements of our model.

[6]W. Brenig, in *Desorption Induced by Electronic Transitions, DIET I*, edited by N. H. Tolk, M. M. Traum, J. C. Tully, and T. E. Madey, Chemical Physics, Vol. 24 (Springer-Verlag, New York, 1983), p. 90.