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Velocity Dependence of the Ionization Probability of Sputtered Atoms

Ming L. Yu
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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The velocity dependence of the ionization probability of sputtered O^- from chemisorbed oxygen layers on V and Nb is studied. The ionization probability is found to depend on the normal component of the emission velocity, which suggests that the ionization process is an ion-surface interaction and not an ion-atom binary interaction. For $v_\perp > 1\times 10^6$ cm/sec, the ionization probability shows an exponential dependence on $v_\perp$. However, this velocity dependence fails at lower velocities.

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By considering the time-varying potential experienced by the sputtered particle leaving the surface as the origin of the excitation, Blaise and Nourtier[1] and, independently, Nørskov and Lundquist[2] calculated the ionization probability P of secondary ions emitted during sputtering. They both arrived at a similar exponential dependence of P on the component $v_\perp$ of the emission velocity v normal to the surface. According to Ref. 2, P is directly related to the ionization potential I, electron affinity A of the secondary ion, and the work function φ of the substrate surface:

$$P \propto \exp[-(I-\varphi)/\epsilon_0] \text{ or } \exp[-(\varphi - A)/\epsilon_0] \qquad (1)$$

for positive and negative ions, respectively. Here the parameter ϵ_0 is velocity dependent. In fact,

$$\epsilon_0 = \hbar\gamma v_\perp / C_1\pi, \qquad (2)$$

where γ and C_1 are defined in Eq. (12) of Ref. 2 and are related to the electronic configurations of the secondary-ion–substrate combination. The exponential dependence of P on φ was observed for the emission of negative secondary ions.[3] However, the $v_\perp$ dependence of P through the parameter ϵ_0 is still under dispute. Published experimental data[4,5] seem to show a certain consistency with an exponential dependence on the emission velocity v. However, in these experiments, the conclusions are based on a comparison of the ion energy distributions (IED) of the secondary ions with the energy distributions of the sputtered neutral atoms which were taken from theory[4] or measured with great difficulty.[5] In addition, so far there has been no reported experiment to demonstrate that both v and the emission angle θ are pertinent in determining the magnitude of the ionization probability. This test is crucial to establish the ionization process as an ion-surface interaction. Recently, Šroubek, Žďánský, and Zavadil[6] argued against such a velocity dependence. They used a computer simulation of the whole sputtering process for a small (six-atom) atomic cluster to show that P for positive secondary ions is quite independent of the emission energy up to about 100 eV ($v \sim 3\times 10^6$ cm/sec for their twenty-proton-mass atoms).

I have studied the sputtering of O^- from chemisorbed oxygen layers on vanadium and niobium surfaces. In this Letter, I report the first direct evidence that the ionization of sputtered atoms can indeed be an ion-surface interaction where $v_\perp$, rather than v, is the more relevant quantity. The exponential dependence of P on $v_\perp$ is observed but only for $v_\perp > 1\times 10^6$ cm/sec.

The novelty of this experimental approach is that the exponential dependence of P on the work function φ is utilized to determine the parameter ϵ_0 for each combination of emission velocity v and emission angle θ measured with respect to the normal to the surface. The change in φ was induced by the deposition of submonolayers of Li on the target surface. Then ϵ_0 was compared to $v_\perp$ $(=\mathbf{v}\cos\theta)$. ϵ_0 should be directly proportional to $v_\perp$ according to Refs. 1 and 2. Since only ion yields within the same narrow velocity interval were compared each time, the necessity of accurate measurements of the energy distributions of sputtered ions and neutral atoms was completely bypassed.

The experiment was performed in an ion-pumped ultrahigh vacuum (UHV) system with a base pressure of about 2×10^{-10} Torr. Both V and Nb samples are Marz-grade polycrystalline foils. The V surface was cleaned by repeated cycles of heating and 400-eV Ne^+ bombardment in the UHV system to remove sulfur and other contaminants as determined by *in situ* Auger electron analysis. The Nb surface was cleaned by a heat treatment of the sample to 1900 °C for a few minutes. A differentially pumped ion gun provided 500-eV, 1-nA, 3-mm-diam Ar^+ and Ne^+ beams for sputtering in the static mode condition. The sample was at ground potential. The secondary ions were first energy analyzed with a modified Bessle Box energy filter.[7] A ground plane was put in front of the energy filter to eliminate any extraction voltage which might have perturbed the angular distribution of the secondary ions. Apertures on both the ground plane and the entrance plate of the Bessel Box were covered with very fine high-transparency grids to minimize lens effects during the entrance of the ions into the energy filter. The constant bandpass was adjusted to about 0.5 eV full width at half maximum as calibrated by a surface-ionization K^+ source. The emission velocity v was selected by adjusting the pass energy of the energy filter. The secondary ions were then mass filtered by a quadrupole mass spectrometer. The mass spectrometer axis was always maintained at a constant potential with respect to the pass energy to maintain constant transmission for ions of different energies. The assignment of zero energy is always difficult for electrostatic energy filters because of the work function difference between the sample and the detector. The "zero" energy in this experiment was assumed to be the point on the low-energy end of the IED where the ion yield was 50 times below the peak yield. This assignment may cause an error of ±1 eV on the energy scale. The energy filter axis and the primary ion gun axis were at right angle to each other. The angle of emission θ of the detected ion was changed by rotating the sample surface normal at the bombardment spot on the plane defined by these two axes. To ensure sufficient signal strength, the angular resolution was compromised. Geometrically, the entrance aperture subtended a cone of about 19° semiapex angle at the bombardment spot.

Li was applied to the sample surfaces by thermal evaporation from a thoroughly outgassed Li getter (SAES Getters). The electron-beam retarding-field method[8] was used to measure the work function change $\Delta\varphi$ to an accuracy of about ±0.05 eV. About $\frac{1}{4}$ to $\frac{1}{2}$ of a monolayer[9] of Li is required to obtain the maximum lowering of the work function ($\Delta\varphi \sim -3$ eV). The use of the light and small Li atoms minimizes the perturbation on the momentum transfer of the sputtering process.

The ion yield data in Fig. 1 were taken at a fixed emission angle of 55°. The work-function dependence of the O^- emission from a vanadium surface which was exposed to 1 L (10^{-6} Torr sec) of oxygen is shown for two emission energies, 8.3 and 65 eV. These emission energies correspond to $v_\perp$ values of 5.7×10^5 and 1.6×10^6 cm/sec, respectively. The O^- yield is enhanced exponentially by the decrease in φ for a $\Delta\varphi$ range of about 2 eV, in accordance with Eq. (1). The O^- yield starts to deviate from this exponential behavior at higher Li coverages. An explanation of this behavior is offered in Ref. 2. In this paper we shall limit our interest to the exponential region. Figure 1 clearly shows that the O^- ions emitted with a smaller $v_\perp$ have smaller ϵ_0 value as shown by a larger slope ($=\epsilon_0^{-1}$) in this semilogarithmic plot, in qualitative agreement with Eq. (2). However, the best evidence that the O^- formation is an ion-surface interaction comes from the angular dependence. The ion yield data

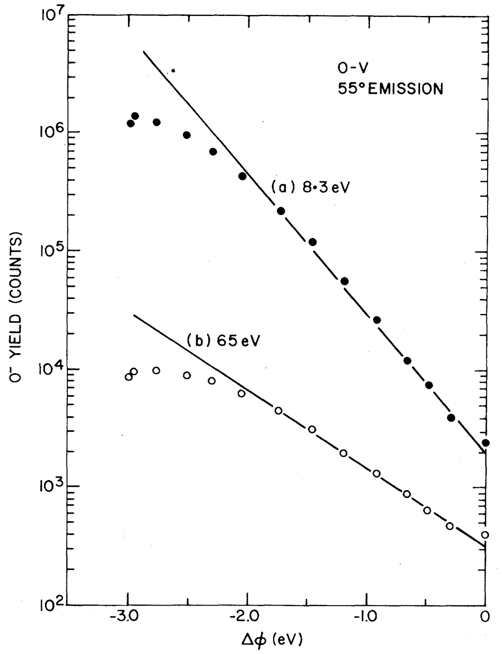

FIG. 1. The work-function dependence of the O⁻ yield at two different emission energies 8.3 and 65 eV but for the same angle of emission, 55°. Notice that the exponential dependence on $\Delta\varphi$ for $-\Delta\varphi < 2$ eV and the smaller slope at higher energy are both in good agreement with Refs. 1 and 2.

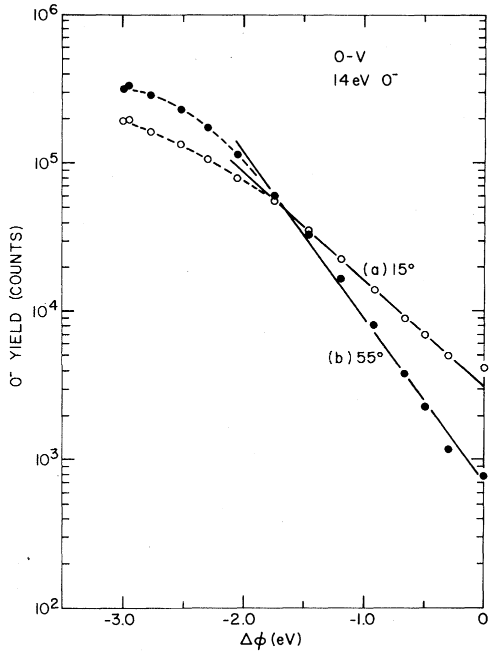

FIG. 2. The work-function dependence of the O⁻ yield at two different emission angles, 15° and 55° but for the same emission energy, 14 eV. The strong dependence on the emission angle suggests the ion-surface nature of the ionization process.

in Fig. 2 were taken at a fixed emission speed (1.3×10^6 cm/sec at 14 eV) but at two different emission angles, 15° and 55°. The corresponding values of $v_\perp$ are 1.26×10^6 and 7.6×10^5 cm/sec, respectively. Again, the O⁻ ions emitted with a smaller $v_\perp$ have a smaller ϵ_0 value.

The final test of Eqs. (1) and (2) is presented in Fig. 3. ϵ_0 was determined by fitting the $\Delta\varphi$ dependence of the O⁻ yield at low Li coverages ($-\Delta\varphi \lesssim 2$ eV) for a large number of combinations of v and θ. When ϵ_0 is plotted against $v\cos\theta$ ($=v_\perp$), all the ϵ_0 values converge to a fairly general behavior. ϵ_0 is approximately proportional to $v_\perp$ only for $v_\perp > 1\times10^6$ cm/sec. The straight line drawn in Fig. 3 to go through the data points has a slope of 4×10^{-7} eV cm^{-1} sec. Below 1×10^6 cm/sec, ϵ_0 deviates from this proportionality with $v_\perp$ and tends to stay roughly constant.

These general features are also confirmed in the sputtering of O⁻ from an oxygenated (1-L O_2 exposure) Nb surface by 500-eV Ar⁺. Figure 4 shows the ϵ_0 vs $v\cos\theta$ plot for this system. The slope of the straight line that fits the data points with $v_\perp > 1\times10^6$ cm/sec is about 2.9×10^{-7} eV cm^{-1} sec. The deviation from the exponential dependence on $v_\perp$ for $v_\perp < 1\times10^6$ cm/sec cannot be accounted for by errors in the $v_\perp$ measurement. The kinetic energy of an O⁻ ion with ve-

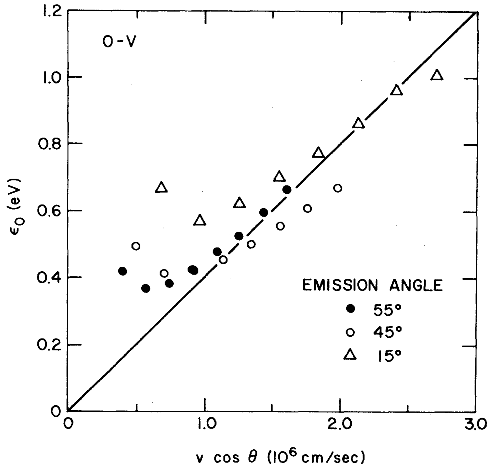

FIG. 3. The dependence of the ϵ_0 defined in Eq. (2) for O⁻ sputtered from oxygenated (1-L) vanadium surfaces on the normal component $v_\perp$ of the emission velocity. The approximate proportionality between ϵ_0 and $v_\perp$ for $v_\perp > 1\times10^6$ cm/sec is in agreement with Refs. 1 and 2.

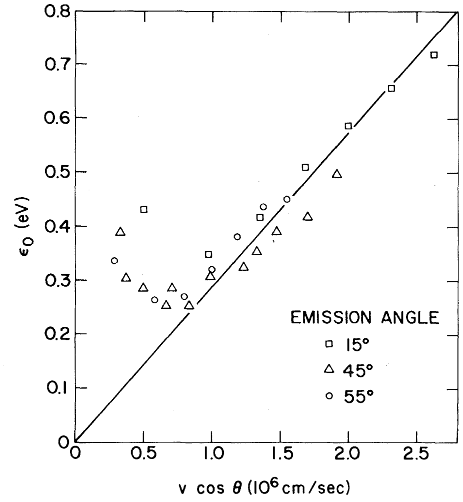

FIG. 4. The dependence of ϵ_0 for O^- sputtered from oxygenated (1-L) Nb surfaces on the normal component $v_\perp$ of the emission velocity. The behavior is similar to that of the O-V system.

locity 1×10^6 cm/sec is 8.3 eV, close to the peak energy ($\lesssim 10$ eV) of the O^- IED. That ϵ_0 remains fairly constant in the velocity region containing most of the secondary ions explains why velocity-integrated negative-ion yields always show good exponential dependence on $\Delta\varphi$ in spite of the lack of $v_\perp$ resolution.[3,10] That ϵ_0 is relatively insensitive to changes in $v_\perp$ in this region resembles the conclusion of Ref. 6. According to the authors of Ref. 6, it is conceivable that the extension of the theory to larger clusters may shift the region of high velocity dependence toward higher escape velocities.

The implications of the experimental results can be summarized as follows. (i) The strong emission angle θ dependence and the correlation with $v_\perp$ show that the ionization process in O^- formation is an ion-surface interaction. This phenomenon is similar to the previously reported data on the angular dependence of the neutralization of fast (>10 keV) positive ions during scattering on solid surfaces.[11] But it contrasts with the ion-atom binary interaction during nonadiabatic neutralization of scattered ions on solid surfaces where no angle of scattering dependence was observed.[12] (ii) For $v_\perp > 1\times10^6$ cm/sec the ionization probability follows reasonably well the exponential dependence on $v_\perp$ as predicted by Refs. 1 and 2. It is sometimes convenient to write the exponential dependence in this form[1]:

$$P \propto \exp(-v_0/v_\perp). \qquad (3)$$

Taking the slope in Fig. 3 to be 4×10^{-7} eV cm^{-1} sec, and assuming that $\varphi - A \simeq 2$ eV, v_0 of Eq. (3) would have a value $\simeq 5\times10^6$ cm/sec, only slightly lower than the estimate of Ref. 1 ($1-3\times10^7$ cm/sec). (iii) For $v_\perp < 1\times10^6$ cm/sec, the dependence of ϵ_0 on $v_\perp$ is weak. This result resembles the prediction of Šroubek, Žďánský, and Zauadil. I also suspect that $v_\perp$ may vary along the secondary-ion trajectory since the secondary ion has to overcome the surface binding energy and the image potential. The energy of an O^- ion with velocity 1×10^6 cm/sec is 8.3 eV and is comparable with the bond energy of oxygen on refractory metals (~ 10 eV). $v\cos\theta$ as measured may not be a good representation of $v_\perp$ at the most important near-surface region at low emission velocities. However, more theoretical work is required to understand the implications on the data presented in Fig. 3 and 4.

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