ABSTRACT IONIZATION PROBABILITIES IN SECONDARY ION EMISSION FROM CLEAN METAL SURFACES

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The energy spectra of sputtered positive secondary ions and the corresponding neutral species have been measured for sputter-cleaned polycrystalline Ta, Nb, and Cu. By division of the measured energy distributions, the absolute values of the energy-dependent ionization probability \( \alpha^+(E) \) could be determined. The results are compared with predictions of current secondary-ion formation models. It is found that available analytical expressions for the dependence of \( \alpha^+ \) on the velocity of the ejected particles do not describe the experimental data.

Ion-induced ejection of atomic or molecular species from solids has become of great importance for surface analysis as far as the charged fraction of the flux of such particles is concerned. With respect to the analytical applications of Secondary Ion Mass Spectrometry (SIMS), detailed knowledge of the mechanisms leading to the formation of secondary ions is necessary in order to correlate SIMS intensities to the composition of the sample.

In the picture commonly used, the formation of secondary ions \( X^\pm \) is governed by two closely coupled processes: the collision kinetics leading to the sputtering of a species \( X \), and the electronic interactions determining the charge state of the sputtered particle. The latter is usually characterized by the ionization probability \( \alpha^+_X(E) \), which is a function of the kinetic energy \( E \) of the sputtered particle and which in addition strongly depends on the chemical environment (matrix) from which the particle is ejected.

Experimental Method and Results

An attempt to determine \( \alpha^+_X(E) \) experimentally requires a knowledge of the energy distributions of sputtered atomic and molecular secondary ions \( X^+ \) and the corresponding neutral species \( X \), which can be provided by energy-resolved in situ SIMS and SNMS measurements. In SNMS (Secondary Neutral Mass Spectrometry), the sputtered neutrals pass through a slab of a special low-pressure rf plasma, the electron component of which serves as a postionizing medium.²

In the present investigation, polycrystalline Ta, Nb, and Cu targets were sputter-cleaned in an ultrahigh-vacuum environment (base pressure \( 6 \times 10^{-8} \) Pa) by bombardment with 2keV, 45° Ar⁺ ions. The residual steady-state surface concentration of impurities and adsorbates was determined by SNMS and in situ Auger Electron Spectroscopy (AES) to be in the order of 1 at%. The SIMS and SNMS energy spectra of sputtered secondary ions Me⁺ and MeO⁺, or postionized secondary neutral particles MeO²⁺ and MeO²⁻, respectively, were measured under the bombarding conditions mentioned above. The experimental setup is described in detail in Ref. 2.

Since for clean metal surfaces the SIMS- and SNMS-intensities of a species \( X \) are given by

\[
I_{X^+}(E) = I_p K^+_X Y_X(E) \alpha^+_X(E)
\]

(1)

and

\[
I_{X^0}(E) = I_p K^0_X Y_X(E)
\]

(2)

where \( I_p \) primary ion current, \( K^+_X \) is the geometry and transmission factor for SIMS, \( K^0_X \) is the proportionality factor containing geometry, transmission, and postionization probability for SNMS,² and \( Y_X(E) \) is the energy differential partial sputter yield for species \( X \), we obtain

\[
\alpha^+_X(E) = \left[ \frac{I_{X^+}(E)}{I_{X^0}(E)} \right] (X^0_X/K^+_X)
\]

(3)

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Equation (2) is valid if the measured SNMS energy distributions are corrected for energy-dependent plasma influences such as the spatial distributions of plasma density and potential, as well as heavy-particle scattering, by a well-established procedure described elsewhere.\textsuperscript{2-4} For Ta, the absolute value of $K_{\text{SNMS}}/K_{\text{Ta}}$ can be taken from previous measurements.\textsuperscript{5} For Nb and Cu these values were obtained by a comparison of the energy-integrated SNMS and SIMS intensities with literature data for sputter yields and secondary ion yields taken from Refs. 6 and 7, respectively. Hence, according to Eq. (3), the absolute values of the spectral ionization probabilities $\alpha_x^+(E)$ could be obtained for $x = \text{Ta}, \text{Nb}, \text{Cu}$. The results are shown in Fig. 1.

Comparison with Theory

A large amount of theoretical work has been devoted to the formation of secondary ions emitted from clean metal surfaces.\textsuperscript{8-14} Most of the various models can be divided into two groups that essentially yield the expressions

$$\alpha_x^+(E) = \frac{2}{\pi} \exp\left(-\pi \frac{C(I-\phi)}{\hbar \gamma \nu_\perp}\right) = \frac{2}{\pi} \exp(\nu_0/\nu_\perp)$$

and

$$\alpha_x^+(E) = \left(\frac{\hbar \gamma \nu_\perp}{\Delta_0}\right)^{2n}$$

where $I$ is the ionization potential of the sputtered particle, $\phi$ is the work function of the bombarded metal surface, $\gamma$ is the characteristic decay length of the electron hopping integral between metal states $\epsilon_k$ and valence state $\epsilon_\sigma$ of the sputtered particle, $\Delta_0$ is the original width of $\epsilon_\sigma$ for distance $z = 0$ between sputtered particle and surface, and $\nu_\perp$ is the normal component of particle velocity $\nu$ corresponding to energy $E$.

Both types of predicted velocity dependences can be examined by logarithmic plots of $\alpha^+ \text{ vs } \log \nu$ or $\nu^{-1}$, respectively, as shown in Fig. 2. As can be seen, neither Eq. (4) nor Eq. (5) describe the experimental results in the entire velocity interval covered by the present investigations. The observed deviations in the low-velocity region in Fig. 2(b) have been reported previously\textsuperscript{15,16} and explained theoretically.\textsuperscript{17} The parameters $2n$, $\nu_0$, and $C$, as evaluated from the straight-line fits indicated in Fig. 2, are shown in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$2n$</th>
<th>$V_0$ (cm/s)</th>
<th>$C$</th>
<th>Validity interval of $\nu_\perp$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>0.9</td>
<td>$5.8 \times 10^5$</td>
<td>0.006</td>
<td>$5-10 \times 10^5$</td>
</tr>
<tr>
<td>Nb</td>
<td>0.9</td>
<td>$3.9 \times 10^5$</td>
<td>0.006</td>
<td>$5-8 \times 10^5$</td>
</tr>
<tr>
<td>Cu</td>
<td>1.9</td>
<td>$2.1 \times 10^5$</td>
<td>0.023</td>
<td>$7-14 \times 10^5$</td>
</tr>
</tbody>
</table>

For Cu the values for $2n$ and $V_0$ from Table 1 agree well with $2n = 2.1$ and $V_0 = 2.2 \times 10^6$ cm/s, which can be obtained from measurements in Ref. 18. If $2n$ and $V_0$ from Table 1 are inserted into Eqs. (4) and (5), respectively, the absolute order of magnitude of $\alpha_x^+(E)$ is theoretically estimated to be of the order of $10^{-2}$ for Cu and $10^{-5}$ for Ta and Nb. On the other hand, the absolute experimental values for $\alpha_x^+(E)$ have been found to be of the order of $10^{-8}$. As a consequence, we must conclude that analytical approaches yielding expressions similar to Eqs. (4) and (5) do not describe the experimental results in an appropriate manner.

However, reasonable agreement can be found with recent computer simulations of the secondary ion emission process that takes into account the dynamical disorder of the ion bombarded surface.\textsuperscript{19} This finding indicates that the concept of significantly altered electronic states during the emission of sputtered particles is more appropriate than the naive assumption of an undisturbed metal surface.
References

2. A. Wucher and H. Oechsner (to be published).

FIG. 1.--Ionization probability for atoms sputtered from polycrystalline Cu, Nb, and Ta as a function of particle emission energy E. Samples were previously cleaned by bombardment with 2keV, 45° Ar+ ions.

FIG. 2.--Velocity dependence of the ionization probability for atoms ejected from sputter-cleaned Ta, Nb, and Cu in two different logarithmic plots. The straight lines are obtained by least-square fits in the validity region indicated by (—).