Calculation of postionization probabilities as a function of plasma parameters in electron gas secondary neutral mass spectrometry

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Using the semiempirical cross-section functions for electron impact ionization developed by Lotz, we calculated the ionization rate constants for most elements as a function of the electron temperature in a low-pressure noble gas plasma typically employed in electron gas secondary neutral mass spectrometry (SNMS). After first-order corrections accounting for (a) the different mean energies of sputtered neutral particles and (b) signal losses due to heavy particle scattering by discharge gas particles (e.g., Ar), the neutral-to-ion conversion factors $\alpha_X^0$ are calculated for the Leybold INA 3 system for most elements $X$ across the Periodic Table. Assuming uniform (mass independent) transmission in the detection system the ratios $\alpha_X^0/\alpha_X^+$ are equivalent with the relative sensitivity factors $D_X^0/D_X^+$ in SNMS.

I. INTRODUCTION

Electron gas secondary neutral mass spectrometry (SNMS) has been proposed as a quantitative method for surface and bulk analysis of solids.\textsuperscript{1,2} In SNMS, neutral particles sputtered from the investigated sample surface are postionized for subsequent mass spectrometric analysis by traversing a special low-pressure noble gas rf discharge.\textsuperscript{3} The electron component of the rf plasma represents a hot electron gas with Maxwellian velocity distribution and serves as a postionizing medium. Electron temperatures $T_e$ in the range of $5$ to $15 \times 10^4$ K are achieved with the commonly used Ar working gas.\textsuperscript{5,6,7} The corresponding electron density depends strongly on instrument parameters like rf generator power, magnetic field current, tuning of the matching rf network, etc., and will not be discussed here.

In SNMS the ionization process is decoupled from the sputtering process. Since the plasma properties are not affected by the low concentration of sputtered particles, a matrix independent neutral-to-ion conversion factor $\alpha_X^0$ (NICIF) can be defined for a sputtered species $X$. The SNMS intensity of $X$ is then given by\textsuperscript{1-6}

$$I_X^0 = I_p \cdot Y_X^0 \cdot \eta_X^0 \cdot \alpha_X^0 \cdot D_X^0$$

$I_p$ is the primary ion current and $Y_X^0$ the partial sputter yield of $X$. $\eta_X^0$ is a geometry and transmission factor which contains the sampled fraction of sputtered particles as well as the in general mass-dependent transmission of the mass spectrometer. Hence, $\eta_X^0$ depends strongly on instrument parameters of the particular system and therefore cannot be discussed here.

As a first-order approximation assuming a uniform $\eta^0$ independent of $X$, $\alpha_X^0$ directly represents the elemental sensitivity factor $D_X^0$. It is therefore the objective of this study to calculate $\alpha_X^0$ for a given plasma condition from the known electron energy distribution, semiempirical ionization cross-section functions and heavy particle scattering cross sections and the theoretical energy distribution of sputtered particles. (The latter term corrects for the velocity-dependent residence time in the postionizing region.) It has been shown that $D_X^0$ values experimentally determined from standards of known composition fluctuate within a factor of 3 for most metallic constituents, whereas much larger deviations are observed for nonmetallic elements.\textsuperscript{10} The experimentalist may either use the calculated values to gain a better understanding of the experimentally determined sensitivity factors or can apply the calculated values to estimate the concentration of a constituent for which no standards are available.

II. CALCULATION

An exact mathematical treatment of the interaction of a neutral particle beam with an SNMS plasma has been given in Ref. 11. It follows from this reference that the NICIF including scattering losses is given by

$$\alpha_X^0 = \frac{i}{(i + i^0) + s^+} \cdot \frac{\exp[-(i + i^0 - s^+) \cdot l]}{\exp[s^+ \cdot l]} - 1$$

with

$$i = (n_s \cdot \bar{v}_X)$$

and $i^0 + s^+ = n_g \cdot q_X^0$. $\alpha_X^0$ is the rate constant describing the electron impact ionization; $q_X^0$ are heavy particle scattering cross sections for atoms or ions, respectively; $n_g$ is the gas density in the discharge; $l$ is the flight path length through the plasma; and $\bar{v}_X$ is the mean velocity of sputtered species $X$. For a Maxwellian velocity distribution of the plasma electrons $\alpha_X^0$ is given by

$$\alpha_X^0 = \int_{v_i} \sigma(v_e) \cdot v_e \cdot f(v_e) dv_e,$$

where $v_i$ is the velocity corresponding to the ionization potential $U_X^0$ and $f(v_e) dv_e$ is the Maxwell–Boltzmann distribution. Since for most elements no experimental values of the ionization cross-section function $\sigma(v_e)$ are available, we use the semiempirical formula developed by Lotz:\textsuperscript{12}

$$\sigma(E) = \sum_{i=1}^{N} q_i \cdot \ln\left(\frac{E}{E_i^0}\right) \cdot E / E_i^0 \times \left[1 - b_i \cdot \exp\left(-c_i \cdot (E/E_i^0 - 1)\right)\right],$$

$$\text{(4)}$$
with tabulated constants $a_i$, $b_i$, $c_i$, and binding energies $E^b$ ($E$ denotes the electron energy corresponding to $v_e$). A detailed discussion of the accuracy of this formula and comparison with available experimental data have been given in Refs. 8 and 12.

In order to include the influence of plasma gas particle (Ar) scattering, we have to distinguish in principle between the scattering cross sections $q_X^\pm$ for neutral and $q_X^\pm$ for already postionized particles $X$. Due to the low ionization fraction in the plasma ($\approx 10^{-3}$) we consider only the interaction with neutral gas atoms. The scattering cross sections are calculated in hard-sphere approximation using the distance $r_0$ of closest approach determined by

$$V(r_0) = \left[ M_{Ar}/(M_X + M_{Ar}) \right] \cdot E_X,$$

(5)

where $E_X$ is the energy of a sputtered particle $X$, and $M_{Ar,X}$ the atomic masses. For the repulsive term of the screened Coulomb interaction potential $V(r)$ we take the Kr–C potential published by Wilson et al.: 13:

$$V(r) = \frac{Z_1 Z_2 e^2}{r} \cdot \sum_{i=1}^3 C_i \cdot \exp[-b_i \cdot r/a]$$

(6)

with the Firsov screening radius

$$a = 0.8853 \cdot \left[ a_0 / (z_1^2 + z_2^2)^{2/3} \right].$$

(7)

Since (i) $r_0 > 10a$ for all energies of interest here and (ii) the additional attractive polarization term in $V$ which appears if an ion $X^+$ is scattered by an Ar atom can be estimated (using experimental values of the dielectric constant of Ar) to influence $r_0$ only very slightly, we conclude that the approximation

$$q_X^\pm \approx q_X$$

is justified in the present case. A particle is considered to be lost for detection if the scattering angle $\theta$ exceeds $\theta_{\text{min}}$ determined by the distance $z$ of the particle from the detection system and the opening diameter $d$ of the detection system

$$\frac{1}{v_X} \cdot \exp[-n_g \cdot q_X \cdot l] = \sqrt{\frac{M_X}{2}} \cdot \int_0^{E_0} \frac{N(E_X) \cdot E_X^{-1/2} \cdot \exp[-n_g \cdot q_X \cdot E_X \cdot l]}{N(E_X)} dE_X$$

(14)
been computed as a function of electron temperature \( T_e \). The results were normalized to a standard plasma density of \( n_e = 1 \times 10^{10} \text{cm}^{-3} \). As shown in Ref. 9, the only way to vary \( T_e \) experimentally is by variation of the discharge gas pressure \( p \). Since \( p \) enters the scattering correction term in Eq. (13), the relation between \( T_e \) and \( p \) is needed for the computation. For the present study we used the \( T_e(p) \) function which was determined experimentally on the INA3 system and is to be published in Ref. 9. For the standard Ar pressure of \( 1.6 \times 10^{-3} \text{mbar} \) used in our experimental work, the calculated particle loss due to Ar scattering ranges from 15% for light (Be) to 30% for heavy (Pb) elements. The \( \alpha_{\text{Ar}}^X \) values computed for 600-eV Ar\(^+\) bombardment are shown in Figs. 3–13. Variation of \( E_0 \) entering the computation via Eq. (15) between 500 eV and 2 keV yielded changes of \( \alpha_{\text{Ar}}^X \) of the order of 1% and may therefore be neglected. Since Lotz estimates a probable error of \( +40\%/-30\% \) for the ionization cross-section functions, the overall error of the computed \( \alpha_{\text{Ar}}^X \) will be of the same order.

The \( \alpha_{\text{Ar}}^X \) values shown in Figs. 3–13 have been computed for atoms \( X \) being in the electronic ground state. Hence, an important criterion for the applicability of the calculated \( \alpha_{\text{Ar}}^X \)
FIG. 7. See Fig. 3.

FIG. 10. See Fig. 3.

FIG. 8. See Fig. 3.

FIG. 11. See Fig. 3.

FIG. 9. See Fig. 3.

FIG. 12. See Fig. 3.

in SNMS is given by the fraction of particles sputtered in excited states. Since short-lived excited states of sputtered particles have been found to decay almost completely within a distance of a few mm from the sample surface, only metastable states may alter the value of \( \alpha_X^0 \). An estimate of this effect can be made using the measured metastable state populations of sputtered Fe\(^{10}\) and assuming the binding energy of the outermost electron to be lowered by the excitation energy while all other electron binding energies remain constant. The resulting \( \alpha^0 \) for Fe atoms in excited metastable states are shown in Table I to increase significantly with increasing excitation energy. The overall \( \alpha_{Fe}^0 \), however, is found to be only 1.1% higher than the ground-state value. Hence, we conclude that the influence of excited states on ionization probabilities is negligible.

### IV. COMPARISON WITH EXPERIMENTAL DATA

As mentioned in Sec. I, the calculated ratio \( \alpha_{Fe}^0 / \alpha_X^0 \) can be compared with experimentally determined SNMS relative sensitivity factors (RSF's) \( D_{Fe}^0 / D_X^0 \) only if a uniform value of \( \eta^0 \) is assumed. Figure 14 shows the ratio

\[
R_X = \frac{D_{Fe}^0 / \alpha_{Fe}^0}{D_X^0 / \alpha_X^0}
\]

as a function of the atomic mass of 30 elements X. The experimental RSF's were determined from the SNMS analysis of 19 standards of known composition using a standard plasma pressure of \( 1.6 \times 10^{-3} \) mbar and a bombarding energy of the primary Ar\(^+\) ions of 2 keV. Details of the experimental setup are given in Ref. 10. For each element X the value of \( D_{Fe}^0 / D_X^0 \) was averaged over all standards containing Fe and X. As seen from Fig. 14 the theoretical relative NICF and experimental RSF agree within a factor of 3 for all elements but Mg, Zn, and Mo. For 23 elements agreement within a factor of 2 and for 17 elements agreement within 30% is found. The observed differences between measured RSF and calculated relative NICF do not necessarily indicate an inaccuracy of the calculation. They may arise from different geometry and transmission factors \( \eta_X^0 \) [see Eq. (1)] which are introduced either via different angular and energy distributions of the sputtered particles X or via mass discrimination effects in the mass spectrometer. In addition, the relatively large \( R_X \) found for Be, Nb, and Mo may also result from the influence of alternative ionization mechanisms such as Penning ionization, nonresonant charge transfer, etc. Experimental indication for the introduction of competing ionization processes at high discharge pressures (> \( 2 \times 10^{-3} \) mbar) was found by Halden.\(^8\)

From the above, it is concluded that the present calculation of the NICF appears to be fairly accurate for most of the elements investigated experimentally. Further experiments are needed, however, in order to clarify the cause of the significant deviations between theory and experiment observed for some elements.

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**TABLE I.** Calculated NICF \( \alpha^0 \) for Fe atoms in excited metastable states and overall value \( \alpha_{Fe}^0 \) averaged according to given excited state populations.

<table>
<thead>
<tr>
<th>Excited state</th>
<th>Excitation energy (eV)</th>
<th>Population (%)</th>
<th>( \alpha^0 ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha^0 D_a )</td>
<td>0</td>
<td>55.7</td>
<td>0.433</td>
</tr>
<tr>
<td>( \alpha^0 D_1 )</td>
<td>0.052</td>
<td>24.2</td>
<td>0.438</td>
</tr>
<tr>
<td>( \alpha^0 D_2 )</td>
<td>0.087</td>
<td>11.7</td>
<td>0.442</td>
</tr>
<tr>
<td>( \alpha^0 D_3 )</td>
<td>0.11</td>
<td>5.4</td>
<td>0.445</td>
</tr>
<tr>
<td>( \alpha^0 D_4 )</td>
<td>0.12</td>
<td>1.6</td>
<td>0.446</td>
</tr>
<tr>
<td>( \alpha^0 F_a )</td>
<td>0.86</td>
<td>0.6</td>
<td>0.542</td>
</tr>
<tr>
<td>( \alpha^0 F_1 )</td>
<td>0.91</td>
<td>0.37</td>
<td>0.550</td>
</tr>
<tr>
<td>( \alpha^0 F_2 )</td>
<td>0.95</td>
<td>0.23</td>
<td>0.556</td>
</tr>
<tr>
<td>( \alpha^0 F_3 )</td>
<td>0.99</td>
<td>0.13</td>
<td>0.563</td>
</tr>
<tr>
<td>( \alpha^0 F_4 )</td>
<td>1.01</td>
<td>&lt;0.001</td>
<td>0.566</td>
</tr>
<tr>
<td>( \alpha^0 F )</td>
<td>1.4</td>
<td></td>
<td>0.635</td>
</tr>
</tbody>
</table>

\( \alpha_{Fe}^0 = 0.438\% \).
A. Wucher: Calculation of positionization probabilities