Characterization of the Fluxes of Neutral and Positively Charged Clusters (Ag\textsubscript{n} and Ag\textsubscript{n}\textsuperscript{+}; n ≤ 4) Produced by Argon Ion Sputtering of Silver

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Abstract. The emission of neutral and positively charged silver clusters during sputtering of a polycrystalline silver target by 5 keV Ar\textsuperscript{+} ion bombardment has been studied and the sputter ejected silver flux has been characterized. As a result, the silver flux is found to be strongly dominated by neutral clusters rather than cluster ions. The contribution of neutral clusters in the overall silver flux decreases rapidly and monotonically with increasing cluster size n and decreases, in addition, with decreasing bombarding energy. The well known alternation of the secondary ion intensities of Ag\textsubscript{n} as a function of cluster size (higher intensities for odd n) is found to be correlated with the effective "ionization potentials" of the corresponding sputtered neutral clusters.

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1. Introduction

The bombardment of solid surfaces with energetic inert gas ions causes the emission of neutral as well as positively and negatively charged target atoms and clusters (sputtering) and has been extensively studied, both, with respect to a fundamental understanding of the ejection mechanisms and to surface analysis applications [1-3]. Most studies, however, had been devoted to the sputtering of monoatomic target particles. Only recently, due to the growing interest in sputtered molecules for quantitative surface analysis [3-5] and in using sputtering for cluster ion sources [6,7,18,19], more detailed information about sputtered neutral clusters [8-16] and secondary cluster ions [6,8-10,17-19,31] became available. But very little is known about the relative contributions of neutral and charged clusters in the sputtered particle flux. It is the purpose of this paper to close this gap in the case of silver and to characterize the cluster emission.

2. Experimental

The experimental setup for the simultaneous measurements of sputtered neutral and positively charged metal clusters has been described in detail elsewhere [8,23] and, hence, only a short description will be given here. The clusters Ag\textsubscript{n} and Ag\textsubscript{n}\textsuperscript{+} were sputter generated by bombarding a clean, polycrystalline silver target under 45° with an Ar\textsuperscript{+} ion beam of 5 keV. The positively charged secondary cluster ions were measured under an emission angle of 10° (with respect to the target normal) using secondary ion mass spectrometry (SIMS) (quadrupole mass spectrometer and single ion detection) [8]. For the analogous measurement of the sputtered neutral clusters (secondary neutral mass spectrometry (SNMS)), postionization of Ag\textsubscript{n} by a crossing electron beam of 50 eV was applied, while, at the same time, the simultaneously emitted secondary cluster ions Ag\textsubscript{n}\textsuperscript{+} were suppressed by a retarding electrostatic field [8,23]. In addition, varying the electron energy in the region of threshold electron impact ionization, the information about the effective "ionization potentials" \(E_i(Ag_n)\) of the sputtered neutral clusters were obtained [23].

3. Results

The intensities measured for neutral and positively charged silver clusters are shown in fig. 1 as a function of cluster size n. For convenience, the corresponding data for copper [8] are additionally included in fig. 1, since comparable literature data are available in the case of copper [9-11,31], but not for silver. To convert the measured intensities \(I(Ag_n)\) of the postionized neutral clusters Ag\textsubscript{n} into the corresponding sputter ejected cluster fluxes \(F(Ag_n)\), it has to be kept in mind, that the electron impact postionization is sensitive to the neutral beam density \(n(Ag_n)\) rather than the flux \(F(Ag_n)\). We adopt in the following the approximation [8,13]

\[
F(Ag_n)/F(Ag) = \frac{1}{n} \cdot n(Ag_n)/n(Ag)
\]
Table 1: Characterization of the sputter ejected silver cluster fluxes. Clusters have been studied under an emission angle of 10° for the bombardment of a clean, polycrystalline silver target with 5 keV Ar⁺ ions under 45°.

The values C(Agₙ) and C(Agₙ⁺) denote the contributions of the corresponding fluxes F(Agₙ) and F(Agₙ⁺) in the overall silver flux. The ionization probability α⁺(Agₙ) is defined as α⁺(Agₙ) = F(Agₙ⁺)F(Agₙ). Eᵢ(Agₙ) denotes the effective “ionization potential” of sputter ejected Agₙ⁺. Tᵥ(Agₙ) is the vibrational temperature of Agₙ⁺.

<table>
<thead>
<tr>
<th>n</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(Agₙ)/F(Ag) (a)</td>
<td>1</td>
<td>12.2·10⁻² (d)</td>
<td>1.4·10⁻³</td>
<td>1.1·10⁻⁴</td>
</tr>
<tr>
<td>C(Agₙ)</td>
<td>89.0·10⁻²</td>
<td>10.9·10⁻²</td>
<td>1.25·10⁻³</td>
<td>1.0·10⁻⁴</td>
</tr>
<tr>
<td>α⁺(Agₙ) (b)</td>
<td>0.3·10⁻⁴ (c)</td>
<td>1.0·10⁻⁴</td>
<td>1.15·10⁻⁴</td>
<td>2.6·10⁻⁴</td>
</tr>
<tr>
<td>C(Agₙ⁺)</td>
<td>0.27·10⁻⁴</td>
<td>1.09·10⁻⁵</td>
<td>1.44·10⁻⁵</td>
<td>2.6·10⁻⁷</td>
</tr>
</tbody>
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Eᵢ(Agₙ) [eV] [23] | 7.57 | 7.26 ± 0.1 (e) | 6.2 ± 0.2 | 6.3 ± 0.3 |

Tᵥ(Agₙ) [K] [16] | ca. 5000 |

a) The error is mainly due to the inaccuracies in the assumptions (equa. 1 and 2) leading to the conversion formula:

\[ F(Agₙ)/F(Ag) = \frac{I(Agₙ)}{I(Ag)} \cdot n^{-5/3} \]

b) Data are taken from ref. [8]. An error in the order of a factor 2 is estimated for the absolute values of α⁺(Agₙ). This error cancels, however, for the corresponding relative values α⁺(Agₙ)/α⁺(Ag) (see equ. 3).

c) α⁺(Ag) depends strongly on the chemical environment of the target surface. Comparable data of α⁺(Ag) have been given in ref. [31].

d) The flux ratio F(Agₙ⁺)/F(Ag) was found to be slightly influenced by the angular acceptance of the mass spectrometer, ranging from 13% to 10%.

e) Eᵢ(Agₙ) is found to be about 0.34 eV - 0.40 eV lower than the ionization energy of Ag₂ [28,29] in agreement with the calculated value Tᵥ(Ag) [16].

Fig. 1. Abundance distributions of clusters sputtered from clean, polycrystalline silver and copper by 5 keV Ar⁺ ion bombardment. Closed squares: Positively charged secondary cluster ions. Open squares: Neutral clusters, positionized by 50 eV electron impact.

Fig. 2. Dependence of the sputtered neutral silver cluster flux distribution on the Ar⁺ bombarding energy. Data are normalized to the corresponding values F(Agₙ)/F(Ag) at 5 keV, which are summarized in table 1.

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for the conversion of density ratios into flux ratios taking kinetic energy distributions of sputtered neutral clusters into account. In addition, we use the empirical formula \( \sigma(X)/\sigma(X) = n^{22} \), proposed in ref. [26] for the cluster size dependence of the electron impact ionization cross section [25,26], for the conversion:

\[
I(A_g) / I(A_g) = n(A_g) / n(A_g) \cdot n^{23}
\]

This approximation is supported by the experimental result [24] \( \sigma(A_g)/\sigma(A_g) = 1.53 \pm 10\% \) obtained for an electron energy of 50 eV. Independent of above assumption, the density ratio \( n(A_g) / n(A_g) = 20.2\% \) for 5 keV Ar⁺ sputtering has also been obtained directly [13,24] using saturation two-photon ionization at \( \lambda = 248 \) nm. Table 1 summarizes the contributions of sputtered neutral and positively charged silver clusters in the overall silver flux, which is generated by 5 keV Ar⁺ ion bombardment. Note that the flux \( F(A_g) \) of neutral silver atoms is far dominating and that the contributions \( C(A_g) \) of neutral silver clusters decrease rapidly and monotonically with increasing cluster size. The contributions of large clusters \( (A_g > n > 4) \) as well as doubly charged particles and negative clusters \( A_g^- \) are assumed to be very small [2,6,27,31]. Included in table 1 are data for the ionization probabilities \( \alpha^+(A_g) \) (taken from ref. [8]), which describe the formation of sputtered positively charged silver cluster ions and are defined as the flux ratio \( \alpha^+(A_g) = F(A_g^+)/F(A_g) \) in the case of a clean silver surface. Since \( \alpha^+(A_g) \) has been found to be in the order of 1% or less, secondary cluster ions \( A_g^+ \) play only a minor role and, consequently, the sputtered silver flux is dominated by neutral atoms and small neutral clusters \( A_g^- \). Comparing \( \alpha^+(A_g) \) with the effective “ionization potentials” \( E_1(A_g) \) of the corresponding sputtered neutral clusters \( A_g^- \) (taken from [23]), the characteristic alternating cluster size dependence of the secondary ions \( A_g^+ \) can be understood (at least in the case of \( n \leq 4 \)) in terms of the correlation: (see ref. [8] for details)

\[
\ln \left( \frac{\alpha^+(A_g)}{\alpha^+(A_g)} \right) = E_1(A_g) - E_1(A_g)
\]

The values \( E_1(A_g) \) do not necessarily represent the true (vertical) ionization energies \( IP(A_g) \) of the “cold” clusters \( A_g^- \) and might, moreover, be seriously affected by excitation mechanisms during sputter induced cluster formation [16].

The dependence of the contributions of neutral clusters \( A_g^- \) in the sputtered ejected silver flux on the bombarding energy \( E_b \) is shown in fig. 2. The contributions of all silver clusters are found to decrease systematically with decreasing \( E_b \leq 5 \) keV, the relative change being more dramatic with increasing cluster size. In other words: An increase of the bombarding energy in the low keV region produces an overproportional increase of the contributions of large neutral silver clusters. A discussion of this result in terms of a statistical model for the formation of sputtered neutral clusters [20-22] will be given elsewhere [30].

References


*Unimolecular fragmentation of metastable clusters [8,19] and electron induced neutral fragmentation are found to have a negligible disturbing influence on our silver data (\( n \leq 4 \)). Electron induced dissociative ionization plays only a minor role due to the drastic decrease of \( F(A_g) \) with increasing \( n \) (see refs. [8,23,24] for details).