

Formation of secondary cluster ions during sputtering of silver and copper

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By simultaneous measurements of neutral and ionized clusters sputtered from polycrystalline silver and copper, the absolute ionization probabilities $\alpha_{X_n^+}$ for the formation of the corresponding secondary ions X_n^+ ($n = 1, \dots, 4$) are determined. The alternating abundance of Ag_n^+ and Cu_n^+ is discussed quantitatively in terms of microscopic models for surface ionization. At least for silver clusters this effect is ascribed to an alternation of the ionization probability induced by the different ionization potentials of the sputtered clusters, which were also measured.

I. INTRODUCTION

Secondary cluster ions of the type X_n^+ sputtered from noble metals have been shown to exhibit a characteristic abundance pattern.¹⁻⁴ In particular, the intensities measured with secondary-ion mass spectrometry (SIMS) are always high if the number of constituent atoms n is odd, and low if n is even. On the basis of *ab initio* calculations for both the neutral and charged clusters, Joyes⁵ attributed this alternation to the variation of the ionization potential E_i and the dissociation energy E_d of the different clusters. More recently, corresponding E_i and E_d values have been calculated by several authors.⁶⁻¹¹ In particular, a complete set of E_i and E_d for silver and copper clusters with $n = 1, \dots, 4$ is given in Ref. 12 which shows a pronounced alternation of both values with cluster size n . No attempt, however, has been made so far to understand the alternating abundance of X_n^+ cluster ions in a quantitative manner. The present paper is intended to remove this gap by interpreting the variation of the secondary cluster ion yields with n in terms of theoretical models describing the ionization probability of sputtered particles. For this purpose the formation and ionization processes have to be studied separately. Hence it is necessary to determine the yields of both secondary ion and neutral clusters. In addition, experimental values of the ionization potentials are needed since the scattering of the respective values calculated by the different authors is too large to allow a quantitative evaluation.¹³

II. EXPERIMENTAL

The experiments were carried out with an ultrahigh-vacuum SIMS-SNMS arrangement which is schematically shown in Fig. 1. The polycrystalline samples are bombarded with a 5-keV Ar^+ beam. The sputtered particles enter a quadrupole mass filter under an angle of 10° with respect to the spectrometer axis in order to reduce the signal background. While the secondary ions are directly accessible to mass analysis, the ejected neutral species are post-ionized by a crossing electron beam of 50 eV and 1.5

mA. In the SNMS mode a voltage of -120 V was applied between the target and the mass spectrometer entrance aperture in order to sufficiently suppress the secondary ions. By varying the electron energy in the vicinity of the ionization threshold, the ionization potentials of the sputtered clusters have been determined, too. Details of these experiments and a comparison with existing theoretical calculations are given elsewhere.¹³ In the present paper we utilize the corresponding results presented in Table I.

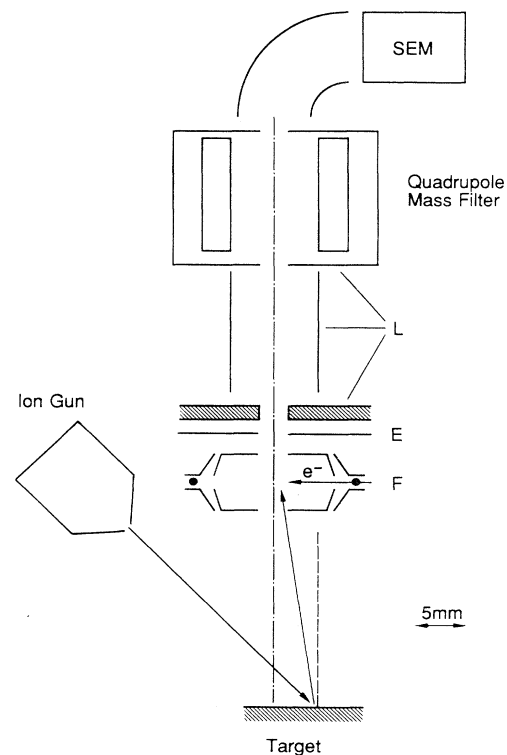


FIG. 1. Experimental setup for *in situ* SIMS and SNMS.

TABLE I. Ionization potentials E_i (in eV) of neutral Ag_n and Cu_n clusters measured by electron-impact ionization.

Ag_2	Ag_3	Ag_4	Cu_2	Cu_3	Cu_4
7.25 ± 0.1	6.2 ± 0.2	6.3 ± 0.3	7.45 ± 0.15	6.1 ± 1.0	7.0 ± 0.6

III. RESULTS AND DISCUSSION

The intensities measured for sputtered clusters Ag_n^0 , Cu_n^0 , Ag_n^+ , and Cu_n^+ are plotted in Fig. 2. While the secondary ion signals $I(X^+)$ can be assumed to be directly proportional to the respective ion yields $Y(X^+)$, the intensities of post-ionized neutral particles $I(X^0)$ have to be corrected for two effects.

(a) For stationary experimental conditions the electron impact ionizer is sensitive to the neutral beam density $n = j \langle v^{-1} \rangle$ rather than the flux j . Hence, the velocity distribution $N(v)$ of sputtered particles is needed in order to evaluate their average inverse velocity

$$\langle v^{-1} \rangle = \int_0^\infty v^{-1} N(v) dv / \int_0^\infty N(v) dv .$$

Experimental data on the respective energy distribution are available for Ag and Ag_2 ,¹⁴ and Cu, Cu_2 , and Cu_3 .^{15,16} It can be shown that for the energy region important here the distribution for a neutral cluster consisting of n atoms can be fitted by

$$N_n(E) \propto \frac{anE}{(anE + U_0)^3} \quad (1)$$

(U_0 is the surface binding energy) with $a \approx 1$ for Ag_2 and $a \approx 0.75$ for Cu_2 and Cu_3 .^{16,17} When assuming a similar behavior for larger clusters, one obtains

$$\langle v^{-1} \rangle (X_n) = an \langle v^{-1} \rangle (X) .$$

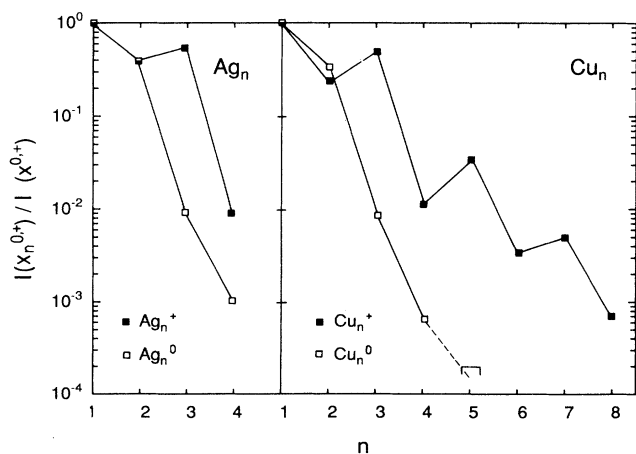


FIG. 2. Secondary ion and post-ionized neutral particle intensities measured for metal clusters sputtered from polycrystalline Ag and Cu by 5-keV Ar^+ ions.

Hence, the intensities measured for a post-ionized neutral cluster X_n must be divided by (an) to make the results for the different species X_n comparable.

(b) The electron impact ionization cross section σ_I will in general also depend on the cluster size. This effect can be taken into account^{18,19} by the approximation

$$\sigma_I(X_n) \approx n^{2/3} \sigma_I(X) . \quad (2)$$

For completeness we note that an additivity rule with $\sigma_I(X_n) = n \sigma_I(X)$ has been employed alternatively to Eq. (2).²⁰⁻²² As seen below, however, the difference between both approximations does not affect the conclusions drawn from the present measurements.

In principle, the detection sensitivity for a sputtered cluster may be also influenced by electron-induced fragmentation. Due to the moderate electron beam density employed, the influence of dissociation processes independent from the ionizing collision can be readily estimated to be negligible as long as the respective cross sections σ_D do not exceed the ionization cross section σ_I by at least 3 orders of magnitude. Hence, only dissociative ionization processes can play a significant role, but again, when considering the rapid decrease of sputter generated clusters X_n with increasing n (Refs. 23 and 24) the corresponding cross sections σ_{DI} would have to exceed σ_I by several orders of magnitude. Experimental data, however, taken, for instance, from Refs. 25 and 22 for gaseous molecules and homonuclear clusters, respectively, clearly show that this is not the case.

To obtain the yields $Y(X_n^0)$ of the sputtered neutral clusters the respective measured intensities must as a consequence of (a) and (b) finally be corrected by $an^{5/3}$ with $a=1$ for silver and $a=0.75$ for copper clusters.

The formation of secondary ions is usually described by the ionization probability α_X^+ defined by

$$Y(X^+) = Y_X \alpha_X^+ ,$$

where Y_X denotes the partial sputter yield of particle X . For the yield of sputtered neutrals we obtain²⁶

$$Y(X^0) = Y_X (1 - \alpha_X^+ - \alpha_X^-) .$$

Since for clean metal surfaces $\alpha_X^+, \alpha_X^- \ll 1$ (Refs. 27 and 28) the value of α_X^+ is determined from the signals in Fig. 2 as

$$\alpha_X^+ = \frac{Y(X_n^+)}{Y(X_n^0)} \propto \frac{I(X_n^+)}{I(X_n^0)} an^{5/3} . \quad (3)$$

Note that although the intensities $I(X_n^{0+})$ might be strongly influenced by mass discrimination in the mass

TABLE II. Experimental ionization probabilities for sputtered Ag_n and Cu_n clusters. Owing to the uncertainty of the atom post-ionization probability, the absolute values for $\alpha_{X_n}^+$ may contain an error by a factor of 2 which is removed in the relative values.

	Ag	Ag_2	Ag_3	Ag_4	Cu	Cu_2	Cu_3	Cu_4
$\alpha_{X_n}^+ / 10^{-4}$	0.3	1.0	115	26	1.3	2.2	352	177
$\alpha_{X_n}^+ / \alpha_X^+$	1	3.3	382	86	1	1.7	271	136

spectrometer, these effects cancel in the calculation of the ionization probabilities. Note also that the yields determined here represent only that fraction of sputtered particles which is ejected into the solid angle element $\Delta\Omega$ accepted by the detection system. Although this fraction may vary considerably with cluster size n , the evaluation of $\alpha_{X_n}^+$ is not affected since both sputtered neutrals X_n and secondary ions X_n^+ are detected with the same $\Delta\Omega$.

The proportionality constant in Eq. (3) is given by the *a priori* unknown post-ionization probability β_X^0 of neutral atoms X in the electron impact ionizer. By comparison with the absolute ionization probability $\alpha_{\text{Cu}}^+ = 1.3 \times 10^{-4}$ measured in Ref. 29 for secondary ion emission from a sputter cleaned copper surface and the measured absolute atomic SIMS and SNMS signals for Cu, a value of $\beta_{\text{Cu}}^0 \approx 5 \times 10^{-5}$ is obtained. In order to roughly estimate β_{Ag}^0 as well, we use the Lotz formula³⁰ to predict $\sigma_1(\text{Ag})/\sigma_1(\text{Cu}) \approx 1.4$ for an electron energy of 50 eV. With the velocity correction accounting for the different masses of Cu and Ag, this yields $\beta_{\text{Ag}}^0/\beta_{\text{Cu}}^0 \approx 1.8$. Then with the value for β_{Cu}^0 , the absolute ionization probabilities for sputtered Ag_n and Cu_n clusters are obtained from Eq. (3), and are displayed in Table II.

These values can now be compared with theoretical predictions of $\alpha_{X_n}^+$. The present state of the microscopic models describing the formation of secondary ions is reviewed in Refs. 31 and 32. It is seen that most of the models proposed so far yield an expression given by

$$\alpha_{X_n}^+ = C \exp \left[-\frac{E_i - \phi}{\epsilon_0} \right], \quad (4)$$

where C is always close to unity, E_i is the ionization potential of the sputtered particle, and ϕ is the work function of the surface. In general, the physical meaning of the parameter ϵ_0 in Eq. (4) depends on the particular model employed. In the excitation model, ϵ_0 is set equal to kT_e with T_e being the electron temperature induced by a collective excitation of surface conduction electrons.³² The electron tunneling model, on the other hand, predicts ϵ_0 to be proportional to the component v_{\perp} of the sputtered particle's velocity along the surface normal. While an exponential velocity dependence of α^+ was demonstrated at high velocities ($v_{\perp} \gtrsim 10^6$ cm/s) for a number of systems, a much weaker dependence was shown to occur in the low-velocity regime. For details, the reader is referred to the review articles cited above. In particular, measurements of Yu³³ show ϵ_0 to be nearly

independent of v_{\perp} for $v_{\perp} \lesssim 10^6$ cm/s. Since the average velocity of sputtered atoms is clearly below this value and the average velocity of sputtered clusters is even lower, we therefore assume ϵ_0 to be constant. The relative ionization probabilities in Table II can then be readily compared with the prediction of Eq. (4), i.e., with

$$\ln \left(\frac{\alpha_{X_n}^+}{\alpha_X^+} \right) = \frac{E_i(X) - E_i(X_n)}{\epsilon_0}. \quad (5)$$

Figure 3 shows the corresponding plot for sputtered Ag_n particles with $n = 1, \dots, 4$ using the respective ionization potentials from Table I. Within the experimental error, arising mainly from the uncertainties of the ionization potentials, the behavior expected from Eq. (5) is surprisingly well confirmed. It should be stressed that due to the large variation of $\alpha_{X_n}^+$ with increasing cluster size (several orders of magnitude, Table II) this result is not affected even if modified forms of Eq. (2) are employed for the conversion of measured SNMS intensities into cluster partial sputter yields. The slope taken from Fig. 3 yields $\epsilon_0 = 0.25$ eV for silver. This agrees well with $\epsilon_0 = 0.25 - 0.5$ eV determined by Yu for atoms ejected from various target systems,³³ and with $T_e = 3000 - 5000$

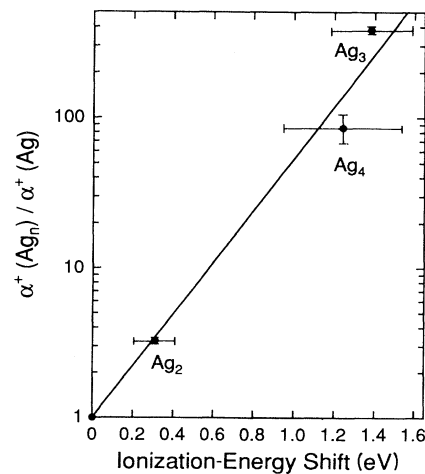


FIG. 3. Logarithm of relative ionization probabilities of sputtered metal clusters and atoms vs ionization potential difference between metal atom and cluster.

K given by Sroubek and Hulek for various secondary cluster ions sputtered from III-V compounds.³⁴ Hence, we conclude that the emission of secondary silver cluster ions can be understood quantitatively in terms of Eq. (4). For copper clusters, the experimental error of the ionization potentials in Table I is obviously too large for a definitive conclusion of the same kind, though the present results are not contradictory to an exponential E_i dependence as described in Eq. (4). The predictions of Eq. (5) would, however, not hold, if other E_i values for Cu_n measured recently³⁵ are correct.

IV. CONCLUSION

It is shown that the alternating abundance of sputtered silver cluster ions can be understood quantitatively by means of the odd-even alternation of the ionization potentials for the neutral clusters. According to the existing models we assume a homonuclear cluster X_n to be formed by simultaneous emission of the constituent atoms, if their relative energy does not exceed the cluster dissociation energy.²³ At this stage, most of the clusters are assumed to be neutral and, hence, the stability of the *neutral* clusters rather than that of the cluster ions is important. The charge state of the sputtered particle is assumed to be determined at a distance of several

angstroms above the surface.³⁶ As shown above, at least for Ag_n^+ the ionization probability can be described either by the electron tunneling model (if ϵ_0 is assumed to be independent of the cluster size) or by the electronic excitation model. For Cu_n^+ , more reliable data on the ionization potentials of neutral Cu_n molecules are still needed for clarification.

In addition to the cluster ion formation mechanism outlined above, several authors observed the abundance pattern measured for secondary ions X_n^+ to be strongly influenced by unimolecular decomposition of larger metastable clusters X_m^+ (with $m > n$).^{4,37,38} While the important role of such processes was clearly demonstrated for larger silver⁴ and copper³⁷ cluster ions ($n > 6$), the data show that for the small clusters investigated here the contribution of unimolecular fragmentation to the measured cluster ion intensities remains negligibly small (see, for instance, Fig. 5 in Ref. 4). Hence, we conclude that although fragmentation may dominate the intensity distribution measured for larger cluster ions, it presumably plays only a minor role in the present study.

ACKNOWLEDGMENT

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