The mass distribution of sputtered metal clusters
I. Experiment

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The sputtering of silver clusters Agₙ⁺ under 5 keV Ar⁺ ion bombardment was studied by time-of-flight mass spectrometry of secondary cluster ions Agₙ⁺ and their neutral counterparts. The sputtered neutral clusters Agₙⁿ were ionized by a combination of electron impact for n = 1,...,4 and single photon absorption from an ArF excimer laser beam for n = 3,...,18. By comparing ion and neutral cluster signals, the ion fraction of sputtered silver clusters was determined for clusters up to n = 15. It is found that the preferred charge state changes as a function of cluster size from predominantly neutral at n < 6 to predominantly ionic at n > 10. From the ion fraction data, partial cluster yields were evaluated which are independent of the charge state of the detected particles. It is seen that the yield Y(n) of sputtered silver clusters follows a power law dependence according to Y(n) ~ n⁻^6.5. From the resulting mass distribution of sputtered particles, it is estimated that around 17% of the sputtered atoms leave the surface in a bound state.

1. Introduction

It is well known that the flux of particles sputtered from a metal surface under keV ion bombardment may contain clusters of up to several hundred atoms [1]. The physical mechanisms leading to the ejection and/or formation of these species during the sputtering process, however, are not yet fully understood. Probably the most direct quantity to be determined experimentally is the mass distribution of sputtered particles, i.e. the size dependent variation of the number of clusters sputtered per impinging primary ion [a quantity which is often called the partial cluster (sputtering) yield]. Once this distribution is known, one of the fundamental questions in sputtering physics, namely the total fraction of sputtered atoms which are ejected in a bound state, can be answered. Hence, numerous studies have been conducted to determine the mass distribution of sputtered clusters, a review of which is given in refs. [1,2]. Historically, most of the early studies of cluster emission were performed on silver. Since the first observation of molecule sputtering in 1958 [3], several groups measured abundance distributions of sputtered silver clusters [4–6]. The record in cluster size was recently broken by Katakuse et al. [7] who found Agₙ⁺ cluster ions up to n = 200 from polycrystalline silver bombarded with 10 keV Xe⁺ ions. It should be noted that in the large majority of all studies on cluster emission the sputtered cluster ions were investigated. This is predominantly due to an experimental difficulty encountered in the analysis of sputtered neutral particles, since these species have to be ionized subsequent to the sputtering process in order to render them accessible to mass or energy analysis and detection. In most cases, and in particular during sputtering of clean metal surfaces, however, it is known that the fraction of atomic species which is ejected in a charged state is negligibly small [8]. This implies the interesting question, in how far the ion fraction α of sputtered metal clusters, i.e. the probability that an ejected cluster leaves the surface in a charged state, varies with the cluster size and, hence, in how far the abundance distribution measured for cluster ions reflects the true mass distribution of sputtered particles. To address this point, several attempts have been made to study neutral species as well [9–11]. In particular in refs. [10,11], the abundance distribution of sputtered neutral clusters was compared to that of the corresponding cluster ions. Until this work, no data on ionization probabilities (= ion fractions) of sputtered clusters had existed in the literature and, hence, no truly quantitative information about the cluster sputtering yields were available. The results of ref. [11] comprise the first quantitative evaluation of the ion fraction and, hence, of the true mass distribution of sputtered clusters. As all studies before, however, they
were obtained using electron impact ionization to detect the neutral species. As a consequence of the low efficiency of this postionization method, the investigations were restricted to cluster sizes of at most four atoms. Only very recently, postionization by single photon absorption from a UV laser beam provided a suitable tool to detect sputtered neutral clusters containing five and more atoms [12,13]. In the present study, we employ this technique to determine the abundance distribution of sputtered neutral silver clusters. By comparing the yields of neutral species Ag$_n^0$ with those of their charged counterparts Ag$_n^{+}$, we evaluate the ion fraction of the sputtered clusters as a function of the cluster size. These data can then be used to determine partial cluster yields which are independent of the emission charge state of the detected clusters.

2. Experimental

Details of the experimental setup sketched in fig. 1 have been described elsewhere [13]. Briefly, a polycrystalline silver sample mounted in a UHV chamber is bombarded under 45° with a pulsed Ar$^+$ ion beam of 5 keV and 1 μA. Shortly (~ 200 ns) after the end of the sputter pulse, an excimer laser (λ = 193 nm) is fired, the beam of which (cross section 1 × 2 mm) is directed parallel to the sample surface and intersects the plume of sputtered particles at a distance of 1 mm. The post-ionized neutrals are extracted towards a reflectron-type time-of-flight mass spectrometer by an acceleration field which is switched on simultaneously with the firing of the laser (rise time ~ 25 ns). As shown in ref. [13], all sputtered neutral Ag$_n^0$ clusters except silver atoms and dimers can be ionized by absorption of a single photon at the photon energy used (6.4 eV) and the ionization process is saturated at laser power densities of several 10$^6$ W/cm$^2$. Assuming the ionization efficiency to be unity at these photon fluxes, we take the corresponding signals of post-ionized particles (i.e. the integrated mass peaks) to be representative for the number densities of sputtered neutral clusters at the position of the laser beam. In other words, we neglect the possible role of photo-fragmentation via multiphoton absorption processes (which, however, should be unlikely due to the relatively low laser power densities employed here) and, hence, the densities determined this way represent lower limits to the true values. To convert the number densities into sputtering yields, the average velocity of the sputtered particles is needed. Here, we assume

$$\nu^{-1} \alpha n$$

and, hence, divide the density values by the cluster size $n$ in order to obtain relative cluster yields. The validity of relation (1) has been discussed in detail in refs. [11,13]. Briefly, it is based on the assumption that the kinetic energy distribution of sputtered metal clusters becomes narrower and falls off more steeply towards high energies if the cluster size is increased. It is of note that recent experimental data suggest that the kinetic energy distributions of sputtered metal clusters may be essentially independent of the cluster size [12–14] and, hence, the division by $n$ would have to be replaced by a division by $n^{0.5}$. This, however, would not significantly alter the conclusions of the present paper.

Mass spectra of secondary cluster ions were measured with the same setup as those of post-ionized neutrals except that now the laser was switched off. In this mode of operation, the time resolution of the TOF mass spectrometer is given by the rise time of the acceleration field $E_{acc}$ extracting the secondary ions from the sample surface into the spectrometer. During the sputter pulse, $E_{acc}$ is zero and secondary ions emerge from the surface with low kinetic energy, thus filling the “extraction volume” between the surface and the first extraction electrode. At 200 ns after the end of the sputter pulse, $E_{acc}$ is switched on within approximately 25 ns and all ions present in the extraction volume at this time are swept out into the mass spectrometer. During the extraction, every ion is accelerated to a different kinetic energy depending on its exact location within the extraction volume at the switching time. Due to the excellent energy refocusing properties of the reflectron TOF spectrometer, however, most of the ions are detected in a sharp peak of about 30 ns width at the flight time appropriate for the particle’s mass.

3. Results and discussion

As already stated above, atoms and dimers cannot undergo single photon ionization at the laser wavelength used and must therefore be ionized by multi-
Fig. 2. Relative yields of neutral and positively charged clusters sputtered from polycrystalline silver. Closed symbols: this work; open symbols: data taken from ref. [11].

photon absorption processes. As a consequence, the respective photoion signals are predominantly due to photo-fragmentation of larger clusters and, hence, do not reflect the number density of neutral atoms and dimers within the sputtered flux. The cluster yields for \( n > 3 \) were therefore normalized to the yield of \( \text{Ag}_3 \) and then matched to previous data on relative yields of sputtered silver atoms, dimers, trimers and tetramers obtained by electron impact ionization [15]. For details of the normalization procedure see ref. [13]. The resulting relative yields of sputtered neutral silver clusters (i.e. the cluster yields normalized to the yield of sputtered atoms) are shown in fig. 2. For comparison, the corresponding signals (= integrated mass peaks) of secondary cluster ions \( \text{Ag}_n^{+} \) normalized to the monomer \( \text{Ag}^{+} \) value are also displayed in fig. 2. The first important observation made is the striking difference between the two plots. While the abundance of sputtered neutral clusters decreases i) relatively fast and ii) rather monotonically towards larger cluster sizes, the cluster ions exhibit a pronounced odd–even alternation in connection with a much slower decay. In order to quantitatively compare the yields of neutral and ion clusters, the nature of the ion signals measured here needs to be discussed. At this point, it is difficult to decide a priori whether the secondary ion spectra obtained as described in section 2 reflect the number density or the flux of sputtered ions. To address this point, we compare the present results to our previous data on the relative yields of sputtered \( \text{Ag}_n^{+} \) \( (n \leq 4) \) which were obtained with a quadrupole mass spectrometer under otherwise identical bombarding conditions [11]. The corresponding values have also been included in fig. 2. From the good agreement between the two sets of data, we conclude that the ion signals determined here directly represent the flux of sputtered ions. Hence, the signal measured for a secondary cluster ion \( \text{Ag}_n^{+} \) is proportional to the ion yield

\[
Y_{\text{Ag}_n^{+}} = Y_{\text{Ag}_n^{+}} \alpha_{\text{Ag}_n^{+}},
\]

where \( Y_{\text{Ag}_n^{+}} \) is the partial sputter yield of \( \text{Ag}_n \) clusters and \( \alpha_{\text{Ag}_n^{+}} \) denotes the probability that a sputtered \( \text{Ag}_n \) leaves the surface as a positive ion. The yield of sputtered neutral clusters, on the other hand, is given by

\[
Y_{\text{Ag}_n^{0}} = Y_{\text{Ag}_n^{+}} (1 - \alpha_{\text{Ag}_n^{+}}),
\]

where \( \alpha_{\text{Ag}_n^{+}} \) denotes the total ion fraction of \( \text{Ag}_n \) clusters. In order to evaluate \( \alpha_{\text{Ag}_n^{+}} \) we have to discuss possible contributions of charge states other than the singly positive state shown in fig. 2. First, we note that in practically all cases observed so far the secondary ion spectrum is by far dominated by singly charged ions with only negligible contributions of multiply charged atomic ions [16]. Hence, in a very good approximation we obtain

\[
\alpha_{\text{Ag}_n} = \alpha_{\text{Ag}_n^{+}} + \alpha_{\text{Ag}_n^{-}}.
\]

The size dependence of positive and negative cluster ion yields can be taken from corresponding experimental data of Katakuse et al. [6]. Their data do, however, not include the relative scaling of the positive and the negative ion spectrum. We have therefore measured the intensities of atomic \( \text{Ag}^{+} \) and \( \text{Ag}^{-} \) ions sputtered from polycrystalline silver under bombarding conditions identical with those otherwise employed in this work. These experiments were performed on a commercial Leybold INA3 system by simply switching all ion optical potentials to the opposite polarity, and, hence, the transmission of the instrument should be comparable for positive and negative ions. As a result, the yield of \( \text{Ag}^{-} \) is found to be at least by a factor of eight lower than that of \( \text{Ag}^{+} \). Employing this ratio, we scale the two curves of ref. [6] and obtain the results shown in fig. 3. It is seen that for all silver clusters the negative ion yield is at least one order of magnitude below the positive ion yield. As a consequence, we conclude that the positive ions measured here represent the only major contribution to the spectrum of secondary cluster ions and set \( \alpha_{\text{Ag}_n^{+}} = 1 \) equal to the total ion fraction \( \alpha_{\text{Ag}_n} \). Then, the yield of sputtered neutral clusters is given by

\[
Y_{\text{Ag}_n^{0}} = Y_{\text{Ag}_n^{+}} (1 - \alpha_{\text{Ag}_n^{+}}),
\]

and the ion fraction of the sputtered clusters can be determined from the relative yields \( Y_{\text{Ag}_n^{+}}' \) and \( Y_{\text{Ag}_n^{+}}' \) plotted in fig. 2 by

\[
\alpha_{\text{Ag}_n^{+}} = \frac{1}{1 + c Y_{\text{Ag}_n^{+}}' / Y_{\text{Ag}_n^{+}}'}.
\]
in eq. (6), the constant \( c \) corresponds to the a priori unknown monomer ratio \( Y_{Ag^0}/Y_{Ag^+} \). From our previous data on absolute ionization probabilities of sputtered silver clusters Ag\(_n\) (\( n \leq 5 \)) we determine \( c \) by matching \( \alpha_{Ag^+} \) to the corresponding value given in ref. [11]. The resulting ionization probabilities of sputtered silver clusters Ag\(_n\) are shown in fig. 4. For completeness, the data taken from ref. [11] have been included in the figure. It is clearly seen that the preferred charge state of sputtered silver clusters Ag\(_n\) changes as a function of the cluster size. While atoms and small clusters (\( n \leq 5 \)) are almost exclusively sputtered as neutrals, the ionic state dominates for clusters larger than Ag\(_{10}\). Qualitatively, this finding is expected from a number of secondary ion formation models which relate the ionization probability to the ionization potential \( I \) of the sputtered particle and the work function \( \Phi \) of the emitting surface by the well known exponential dependence [17]

\[
\alpha^+ = \exp \left[ -\frac{I - \Phi}{\epsilon} \right],
\]

where \( \epsilon \) is a constant depending on the particular model used. If this expression (which was originally derived for sputtered atoms) may be generalized towards sputtered clusters, then, as the cluster size increases, the ionization potential of the clusters gradually approaches the metal work function, and \( \alpha_{Ag^+} \) should attain values close to unity. At the same time, the pronounced odd–even alternation of \( \alpha_{Ag^+} \) observed in fig. 4 shows a one-to-one correspondence to an inverse alternation of the cluster ionization potential [18]. Note, however, that for a quantitative examination of eq. (7), the effective ionization potential \( I_{\text{eff}} \) of sputtered silver clusters is needed. Due to internal excitation of sputter generated clusters [19] \( I_{\text{eff}} \) may differ significantly from the ionization potential determined for cold silver clusters. Experimental data on \( I_{\text{eff}} \) are available only for Ag\(_{n<4}\), where the validity of eq. (7) has been demonstrated [11].

Using the \( \alpha^+ \) values displayed in fig. 4, relative partial yields of sputtered Ag\(_n\) clusters can be evaluated which for the first time are independent of the emission charge state of the detected particles. The results are shown in fig. 5. As proposed in ref. [14], the data have been plotted on a double logarithmic scale to illustrate a power law dependence of the cluster yields on the cluster size. The best fit line indicated in fig. 5 corresponds to

\[
Y_{Ag_n} \propto n^{-\delta}
\]

with \( \delta = 6.5 \). Similar dependences with, however, different exponents have been found for sputtered copper (\( \delta = 7.9 \)) [14] and aluminum (\( \delta = 9.3 \)) [20] clusters as well, although in these cases only the neutral clusters were detected. Hence, the observed exponent obviously depends on the sputtering conditions employed in the particular experiment. To further demonstrate this, in fig. 6 we plot the ion yield data of Katakuse et al. [6] divided by the cluster ionization probabilities obtained here. It is seen that the resulting cluster yield distribution can also be coarsely approximated by a power law dependence, but now the exponent is \( \delta = 4.6 \) since the nature and the energy of the primary ions used in ref. [6] (10 keV Xe\(^+\)) differs from our present bombarding conditions described in section 2.
Fig. 5. Relative partial yields of sputtered silver clusters independent of the charge state of the detected species. The polycrystalline silver sample was bombarded under 45° by Ar⁺ ions of 5 keV.

Fig. 6. Silver cluster ion distribution obtained under bombardment of polycrystalline silver with Xe⁺ ions of 10 keV. Closed symbols: data taken from ref. [6]; open symbols: corrected for ionization probability as described in the text.

To our knowledge, no theoretical model of sputtered cluster formation has been published so far which explains yield distributions like those shown in figs. 5 and 6. The only models predicting a power law cluster mass distribution are the thermodynamic equilibrium model of URBASSEK [21] and the shock wave model of BITENSKI and PARILIS [22] yielding, however, exponents of around δ = 2 without any free parameters. Hence, in part II of this work we have performed a simple model calculation of cluster sputtering yields based on a combination of molecular dynamics and Monte Carlo simulations which at least roughly explains the experimental results.

4. Conclusion

We show that the preferred charge state of sputtered silver clusters changes from predominantly neutral for small cluster sizes to mostly ionic for large clusters. We also report the first set of partial cluster sputtering yields which is independent from the charge state of the detected species. From the resulting mass distribution of sputtered silver clusters, which shows a power law dependence on the cluster size, we can estimate the total fraction of sputtered atoms which leave the surface in a bound state. Assuming, as a worst case, a constant relative cluster yield between \( n = 15 \) and \( n = 250 \) (about the largest \( \text{Ag}^+ \)-cluster ions observed to date [7]), we find that about 17% of all sputtered silver atoms are ejected as part of a cluster. A closer look reveals that this number is almost exclusively due to sputtered dimers with only negligible contributions of trimers and larger clusters.

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References