CLUSTER EMISSION IN SPUTTERING

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1. Introduction

The bombardment of a solid with energetic atoms or ions leads to the release of a variety of secondary particles from the surface. Provided that each emission event is caused by a single particle impact, this process is usually called sputtering. Besides atomic species, the flux of sputtered particles contains an abundant fraction of agglomerates of two or more atoms. These species, which will in the following be called "sputtered clusters", attract special interest in analytical mass spectrometric techniques like SIMS and SNMS for mainly two reasons. First, molecular signals can create mass interferences with atomic signals and may therefore disturb the interpretation of measured mass spectra. Second, on the other hand, the interpretation of molecular signals can be extremely useful to obtain information about the chemical state of the investigated surface, provided the mechanisms leading to the formation and/or ejection of clusters during the sputtering process are sufficiently well understood. Hence, numerous studies have been devoted to the investigation of cluster emission in sputtering, a review of which is found in [1,2]. Much of this work was conducted on metallic samples as model systems for purely collisional sputtering conditions, and most of the published data has been collected for charged clusters (secondary cluster ions) due to the experimental difficulties encountered in the analysis of sputtered neutral particles.

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 yield). If this distribution is known, one of the fundamental questions in sputtering physics regarding the total fraction of sputtered atoms which are ejected in a bound state can be addressed. As an example, Fig. 1 shows a fairly recent measurement of the size distribution of both negative and positive cluster ions sputtered from polycrystalline silver sample by bombardment with 10 keV Xe$^+$ ions. The data were taken from Katakuse et al. [3] and scaled to the ratio between positive and negative atomic ions as

![Fig. 1 Relative signals of positive and negative cluster ions (after [3])](image-url)
described in [4]. Although only data up to a cluster size of \( n = 20 \) are shown, it has been demonstrated that cluster ions consisting of up to 240 atoms are present in the sputtered flux [5].

Since the charge fraction, i.e. the fraction of sputtered clusters of a given size which leave the surface in a charged state, is an a priori unknown quantity which, in addition, may critically depend on the chemical state of the bombarded surface, it is difficult to obtain quantitative information on cluster sputtering yields without detecting the corresponding neutral species as well. Therefore several attempts have been made to study sputtered neutral clusters, which have to be postionized subsequent to the sputtering process in order to render them accessible to mass or energy analysis. The first successful investigation of this type was performed by Oechsner and Gerhard [6,7], who determined the abundance of neutral dimers and trimers sputtered from various metallic samples by sub-keV \( \text{Ar}^+ \) ions. Very much later, this work was continued by Gnaser and Hofer [8] and Franzreb et al. [9], who compared the abundance distribution of sputtered neutral clusters with that of the corresponding positive cluster ions. Due to the relatively low ionization efficiency of the electron impact postionization method used in these investigations, the size of sputtered neutral clusters which could be detected experimentally was for a long time limited to at most five atoms. Only fairly recently, Coon et al. as well as the present authors demonstrated that the detection of larger aggregates is possible by the use of UV [10,11,12,13] or VUV [14,15] lasers to postionize the sputtered neutral species. In these experiments, it turned out to be of great importance that photoionization of the clusters is achieved by absorption of a single photon, since this technique combines a non resonant, i.e. non state selective ionization scheme (which is needed due to the large internal excitation of sputter generated clusters [16]) with a high ionization efficiency and relatively low fragmentation rates. It has been demonstrated that under these conditions the ionization of metal clusters can be saturated at moderate laser power densities, and the total yields of sputtered clusters can therefore be determined from measured mass spectra without prior knowledge of the photoionization cross sections. Using this technique, it is now possible to detect sputtered neutral clusters consisting of up to 35 atoms [13].

In this work, we report on experimental studies of sputtered neutral metal clusters which are generated by ion bombardment of a metallic surface under different bombarding conditions. For most of the experiments, silver was chosen as a sample since it exhibits high cluster yields and a low sensitivity to surface contaminations. The detection of the clusters is achieved by a pulsed VUV excimer laser (photon energy 7.9 eV) in connection with time of flight mass spectrometry. The experimental results obtained for the mass and kinetic energy distributions of sputtered clusters are then discussed in terms of existing statistical models describing the formation of molecules during sputtering.

2. Experimental

The experiments were performed in a reflectron time-of-flight mass spectrometer (TOF-MS) which has been described in great detail elsewhere [4,14]. Briefly, a polycrystalline target mounted in a UHV chamber is bombarded under 45° with a pulsed rare gas ion beam (energy 1 - 5 keV, pulse duration \( \sim 2 \)\( \mu \)s). The sputtered neutral particles are ionized by a pulsed laser beam (cross section \( 1 \times 2 \) mm\(^2\)) directed closely above (1 mm) and parallel to the sample surface. In order to prevent positively charged ionic species from leaving the surface (secondary ion background reduction), the sample was kept at a negative potential with respect to ground during the primary ion pulse. The postionized neutrals are extracted towards the TOF-MS by an acceleration field which is switched on shortly (\( \sim 100 \) ns) after the laser pulse.
The ionizing VUV laser employed in the present experiments is a conventional excimer laser (Lambda Physik model LPX 120i) operated with an F\textsubscript{2}/He gas fill. Under optimized conditions, this laser produced pulses of about 2 mJ energy and about 20 ns duration at a wavelength of 157 nm (hv = 7.9 eV). As shown in [14], all Ag\textsubscript{n} clusters are ionized by absorption of a single photon, and the ionization process is saturated at laser power densities of several 10\textsuperscript{6} W/cm\textsuperscript{2}. We therefore take the corresponding signals of post-ionized particles (i.e. the integrated mass peaks) to be representative for the number density of sputtered neutral clusters at the position of the laser beam. To convert this into sputtering yields, the inverse average velocity of the sputtered particles is needed. Therefore, the kinetic energy distribution of the sputtered neutral silver atoms and clusters was determined in an additional set of experiments. For this purpose, the velocity of the detected neutral species was selected via their flight time between the sample surface and the ionization volume by a controlled variation of the time delay between the primary ion pulse (which was shortened to approximately 200 ns) and the ionizing laser pulse.

3. Results

3.1 Cluster yields

Fig. 2 shows a typical mass spectrum of neutral Ag\textsubscript{n} clusters sputtered from a polycrystalline silver sample. The displayed spectrum represents an average over 1000 data acquisition cycles (primary ion and laser shots) and shows clusters containing up to 19 atoms. It was recorded under 5 keV Ar\textsuperscript{+} bombardment with a laser power density of 3·10\textsuperscript{6} W/cm\textsuperscript{2} for postionization. In contrast to the data displayed in Fig. 1, the signals of small clusters (2 \leq n \leq 7) exhibit a monotonic decay with increasing cluster size. For larger cluster sizes a slight odd-even alternation is observed which is similar to but much less pronounced than that observed for the corresponding ionic species.

The mass distribution of sputtered clusters is generally characterized by relative yields, i.e. the cluster yields normalized to that of the monomers. To determine the distribution of relative yields from measured mass spectra, it is necessary to closely investigate the saturation behavior of the ionization process. By recording the photoion signals as a function of the laser intensity, it can be shown that all detected species (monomers as well as clusters) are postionized by a single photon absorption process which is saturated at laser power densities of several 10\textsuperscript{6} W/cm\textsuperscript{2}. A detailed description of these experiments as well as the data evaluation procedure leading to the respective cluster yields has
been given elsewhere [14, 15]. As an example, Fig. 3 shows the resulting relative yields of sputtered neutral Agₙ clusters under bombardment with 5 keV Ar⁺ ions. For comparison, the yield distribution of the corresponding secondary cluster ions Agₙ⁺ is also displayed. 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. From these data, one must conclude that the ion fraction of sputtered silver clusters i) strongly increases with increasing cluster size and ii) alternates between odd and even numbers of atoms in the cluster [4,14,17].

The main observation in Fig. 3 is that the cluster yield distribution closely follows a power law corresponding to $n$ as a function of the cluster size $n$. This behavior has also been found for a number of other clusters (Alₙ [12,15], Cuₙ [12,18], Inₙ [13], Nbₙ and Taₙ [15]) sputtered from the respective metallic surfaces and therefore seems to be a general feature of cluster emission in sputtering. Detailed investigations reveal that the exponent $\delta$ strongly depends on the bombarded material [12,15] as well as on the bombarding conditions (such as energy and species of the primary ions [4,14,18]), while it is apparently independent of the crystallographic structure of the target material [19]. More specifically, it is found that $\delta$ is correlated with the total sputter yield $Y_{tot}$ in a way which is depicted in Fig. 4. It is seen that large values of $\delta$, i.e. low relative contributions of large clusters, are connected to low values of $Y_{tot}$ and vice versa. The physical origin of this correlation will be discussed below.

3.2 Kinetic energy distribution

As explained above, the emission velocity or kinetic energy distribution of the sputtered neutral particles can be determined by a controlled variation of the time delay between the primary ion pulse and the firing time of the postionizing laser. For details regarding the conversion of flight time into kinetic energy as well as for a complete description of these experiments the reader is referred to [11,14]. Examples for the resulting kinetic energy distributions of sputtered Ag, Ag₂, Ag₃ and Ag₄ are shown in Fig. 5. For clarity, the distributions have been shifted according to the base lines indicated on the ordinate axis. It is seen that the cluster energy distributions tend to peak at lower energies and fall off more steeply towards higher energies than those of the emitted atomic
species. This behavior has been long known for sputtered ionic species and is in fact frequently utilized in order to reduce mass interferences arising from molecular secondary ions in SIMS. For small sputtered neutral clusters \((n \leq 3)\), the same observation has been reported together with the tendency that the asymptotic decay of the distribution towards high kinetic energies becomes significantly steeper with increasing cluster size \([20,21]\). Interestingly, newer results show that the energy distributions of larger silver clusters (containing 4 or more atoms) look very much like that of \(\text{Ag}_4\) \([14]\). A similar trend has been observed for sputtered \(\text{Al}_n\) \([22]\), \(\text{Cu}_n\) \([12]\) and \(\text{In}_n\) \([23]\) clusters. This indicates, that the tendency towards steeper asymptotic decay with increasing cluster size vanishes for larger clusters, a finding which has some bearing on the theoretical interpretation with respect to cluster formation (see below).

4. Discussion

About two decades ago, two simple statistical models have been proposed describing the formation of molecules or clusters in sputtering. In the so-called direct emission model \([24,25]\), a pre-formed molecule is assumed to be removed from the surface by one single collision from the cascade initiated by the impinging primary ion. Energetic considerations quickly reveal that this mechanism cannot be responsible for the formation of sputtered metal clusters, since in this case the surface binding energy of the cluster is of the same order as its dissociation energy, and it is therefore practically impossible to transfer enough momentum to one of the constituent atoms in a single collision to eject the cluster without fragmenting it. In the so-called atomic combination model (ACM), on the other hand, all constituent atoms of a sputtered cluster are assumed to be removed from the surface by independent collisions. An ensemble of \(n\) sputtered atoms is then emitted as a cluster if its total energy (i.e. the sum of relative kinetic and potential energy) is below zero. This model has been successfully applied by Gerhard and Oechsner \([7]\) to describe the yields of sputtered metal dimers and trimers. Independently, Kön nen et al. \([26]\) evaluated the kinetic energy distributions of sputtered clusters predicted by this model. For a comparison with the experimental results presented above, we extend the yield calculation given by Gerhard \([27]\) to larger clusters by writing the yield of a sputtered cluster \(X_n\) as

\[
Y(X_n) = \gamma_n \cdot w_n
\]  

(1)

where \(\gamma_n\) describes the probability that at least \(n\) atoms are sputtered in a single event and \(w_n\) denotes the probability that the emission angles and velocities of these atoms are sufficiently correlated to ensure the binding of the \(n\)-atom cluster. Following \([27]\), \(\gamma_n\) can be written as

\[
\gamma_n \propto \left( \frac{f}{F} \right)^{n-1} \cdot \frac{1}{n!} \cdot Y_{\text{bot}} n,
\]  

(2)

where \(f\) and \(F\) denote surface areas which are determined by the range of the attractive forces between the particles \((f)\) and the lateral extension of the collision cascade \((F)\), respectively. For a crude description of \(w_n\), we assume that all constituent atoms of a sputtered cluster must be ejected essentially into the same solid angle element with essentially the same kinetic energy\(^1\). Then, if \(w(E',\theta,\phi)\) is the probability distribution describing the ejection of a single atom with energy \(E'\) into the direction \((\theta,\phi)\) and the emission of the \(n\) atoms is statistically independent, the probability \(w_n\) of finding a cluster with kinetic energy \(E\) in the same direction is given by

\(^1\)This assumption is questionable for sputtered dimers but will be increasingly accurate with increasing cluster size.
\[ w_n(E, \theta, \phi) \propto \left\{ w_i \left( E' = \frac{E}{n}, \theta, \phi \right) \cdot E'^{-\frac{1}{2}} \right\}^n \cdot E^{\frac{1}{2}}. \] (3)

As discussed in detail in [26], the Jacobian terms \( E^{+\frac{1}{2}} \) and \( E^{+\frac{1}{2}} \) in eq. (3) must be inserted to account for the transformation between the three dimensional velocity space and energy space, respectively.

Using the standard expression from linear cascade theory [2]

\[ w_i(E', \theta, \phi) \propto \frac{E'}{(E' + U_0)^3} \cdot \cos(\theta), \] (4)

we obtain

\[ w_n(E, \theta, \phi) \propto \sqrt{E} \cdot \left( \frac{\text{const} \cdot \frac{E}{n} \cdot \cos \theta}{(E/n + U_0)^3} \right)^n \] (5)

This expression in principle describes the kinetic energy distribution expected for the sputtered clusters. In the limit of high energies, this yields an asymptotic decay according to \( E^{-3.5\pm0.5} \) which is in accordance with the results of ref. [26]. Hence, the model predicts an increasingly steeper asymptotic slope with increasing cluster size. While the data in Fig. 5 seem to confirm this expectation, a close inspection [14] reveals asymptotic exponents of -2.9, -4.4 and -4.4 for Ag$_2$, Ag$_3$ and Ag$_4$, respectively, which are much lower than those predicted by eq. (5). For larger clusters, the exponent remains practically constant around a value of -4, a finding which indicates a qualitative disagreement between experimental data and the ACM.

For the description of cluster yields detected into a solid angle element \( \Delta \Omega \) around the direction \((\theta, \phi)\), eq. (5) must be integrated over \( E \). By numerical integration, it can be shown that the resulting integral can be well approximated by \( e^{-n} \) with \( c \) being a constant which is smaller than unity. Inserting this into eq. (1), the yield of sputtered clusters \( X_n \) is obtained as

\[ Y(X_n) \propto \left( \frac{F}{n!} \cdot \frac{1}{F} \cdot Y_{\text{tot}} \cdot \frac{2U_0}{\pi} \cdot c \cdot \cos \theta \right)^n, \] (6)

which results in the prediction of the relative cluster yield

\[ Y(n) = \frac{Y(X_n)}{Y(X)} \propto \left( \frac{C}{F} \cdot w \cdot Y_{\text{tot}} \right)^{n-1}. \] (7)

Provided the term in curved brackets is smaller than unity, this predicts decreasing cluster yields with increasing cluster size as is observed in the experiment. An increase of \( Y_{\text{tot}} \) will in this case lead to a weaker decay, a result which is in qualitative agreement with the correlation presented in Fig. 4. However, in contrast to the experimental finding of a power law relation, eq. (7) predicts a size dependence of the cluster yields which is slightly stronger than exponential. From Fig. 3, it is apparent that only the formation of very small clusters can be described by such a dependence,

\[ ^2 \text{It has been suggested that the number density instead of the flux distribution of sputtered atoms should be inserted into eq. (4), which results in an asymptotic decay according to } E^{-3.5\pm1} \]
whereas the yields of larger aggregates are significantly underestimated. One must therefore conclude that at least for the case of large clusters the ACM does not provide an accurate description of the cluster formation mechanism. To further illustrate this point, Fig. 6 shows a double logarithmic plot of the measured cluster yields versus the total sputter yield (which was varied by changing the bombarding conditions). According to eq. (7), one would expect a straight line for each cluster size with a slope corresponding to the number \( n \) of atoms in the cluster. It is seen that this prediction is only fulfilled to a reasonable degree for sputtered dimers. For all larger clusters, strong deviations from the predicted behavior are observed for bombarding conditions leading to sputtering yields in excess of approximately 8 atoms/ion.

5. Conclusion

The cluster yield data collected recently provide clear evidence that the emission of larger clusters in sputtering cannot be described by simple statistical models. Considering the complexity of the cluster emission process, this finding is not surprising. For instance, neither the temporal or spatial correlation between the ejection of different atoms nor the time evolution of the interaction potential between the sputtered atoms during their path away from the surface can be described even qualitatively by such a model. Since it is particularly the attractive part of this potential which governs the survival or formation of bonds during the particle ejection process, we feel that its time dependent variation must play a dominant role in cluster sputtering. Moreover, cluster emission will be predominantly a low energy process where simultaneous collisions between many atoms become important. It is obvious that these events are hard to describe in a statistical approach. On the other hand, they are automatically included in the model if the particle ejection process is treated by Molecular Dynamics (MD) computer simulations. We therefore suggest that MD simulations probably provide the most promising approach to the theoretical modeling of cluster emission in sputtering, in particular if many-body interaction potentials are used which allow an accurate description of the solid as well as of small isolated gas phase clusters. Examples for such treatments which have been published recently [28,29,30] clearly demonstrate that the experimental findings with respect to yields and energy distributions of sputtered clusters can be at least qualitatively reproduced by such simulations. From these calculations, the following picture of cluster sputtering emerges. First, atoms are removed from the surface by elastic collisions in a very short time (typically several 100 fs) following the impact of a primary particle. Immediately above the surface, "nascent" clusters can be identified in the sputtered flux which are formed in a late stage of the collision cascade by atoms ejected in highly correlated events. A detailed analysis reveals that most of these nascent clusters exhibit an extremely high degree of internal (vibrational) excitation and will therefore rapidly decompose on their path away from the surface. Due to the short (picosecond) time scale of the corresponding fragmentation processes, the experimentally detected clusters basically represent the "final" (meta)stable end products of such unimolecular decomposition chains. A model description of cluster emission must therefore
necessarily include the unimolecular reactions sputtered clusters undergo after their formation at or emission from the surface. If this is done and sufficiently realistic interaction potentials are used, it can be shown [31] that MD simulations can even quantitatively reproduce the experimental data and, hence, are capable of considerably improving our understanding of the complex matter of cluster formation in sputtering.

References

[31] A. Wucher, B.J. Garrison, to be published