FORMATION OF CLUSTERS IN SPUTTERING

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The results of our recent studies on the formation of clusters during sputtering of clean metal and semiconductor surfaces under bombardment with energetic ions are reviewed. The experimental method employed is based on time-of-flight mass spectrometry for mass and kinetic energy specific detection of sputtered particles that are emitted from the surface. As an important feature of the experiment, neutral species that leave the surface are detected by laser induced post-ionization using non resonant single photon ionization processes prior to mass analysis. In connection with the respective secondary ion signals, charge state as well as partial sputtering yield and kinetic energy distributions of sputtered clusters are determined. Using tunable laser radiation, the internal energy of sputtered clusters is investigated. Finally, the role of non-additive processes in cluster formation under bombardment with polyatomic projectiles is discussed.

INTRODUCTION

If a solid is bombarded with keV-ions, particles are released from the surface due to mostly elastic collisions, a process which is generally termed "sputtering". It is well known that the flux of particles ejected from the surface this way may contain agglomerates of several atoms (besides atomic species) with sizes ranging up to hundreds of atoms. The basic mechanisms leading to the formation and emission of such large clusters in sputtering represent one of the fundamental open questions, which has drawn much attention in the literature. The relatively large body of both experimental and theoretical work devoted to this subject has been comprehensively reviewed about ten years ago [1, 2]. The present paper is intended to focus on some newer developments that have been pursued in our laboratory since the time of these reviews.

A relatively straightforward method to investigate sputtered clusters is given by mass spectrometry of secondary ions, i.e. those species, which leave the surface in an electrically charged state. Using this technique, Katake et al. have been able to detect sputtered ionized metal clusters containing up to more than 200 atoms [3]. The physical mechanisms leading to the ionization of a sputtered cluster in the course of the very fast collision cascade leading to its ejection from the surface, however, are practically not understood. It is therefore highly questionable as to which extent the flux of secondary ions is actually representative of the total sputtered flux of the respective species. In fact, it has been demonstrated that the ionization probability of sputtered clusters may significantly depend on the cluster size [4]. In order to arrive at quantitative conclusions regarding the contribution of clusters to the total flux of sputtered particles, it is therefore mandatory to complement the data obtained for secondary ions by investigating those species which leave the surface in a neutral charge state. The basic problem here is that neutral particles have to be post-ionized after their emission from the surface in order to render them accessible to mass spectral analysis. Moreover, the post-ionization technique employed (mostly electron impact or photoionization) may lead to a significant fragmentation of the sputtered particle and therefore preclude the proper identification of molecules and clusters formed during the sputtering event.

While earlier postionization methods involving electron impact ionization restricted the size of detectable neutral clusters to about four atoms [5], laser based photoionization methods have recently evolved, which allow the detection of much larger clusters. A very promising technique in that respect is "Single Photon Ionization" (SPI), where ionization is achieved by non resonant absorption of only one photon from an intense pulsed laser beam. The major advantage of this technique is that ultrafast fragmentation losses from excited intermediate states, which often accompany multiphoton ionization schemes of molecular species, are completely avoided. On the other hand, the use of SPI requires the employed photon energy to exceed the ionization potential of the sputtered neutral species to be detected.

In general, this requires the use of UV or even VUV radiation which must be produced with sufficient intensity to render the photoionization process efficient. Such photon fluxes can, for instance, be generated by an F2 laser emitting at a wavelength of 157 nm. It has been demonstrated that the available photon flux density produced by such a laser often even suffices to drive the post-ionization process into saturation, a possibility which eliminates the need of knowledge about photoionization cross sections in order to arrive at a truly quantitative characterization of the flux of sputtered neutral particles [6, 7]. In this paper, we will review some of the results, which have been obtained in our laboratory throughout the past decade using this technique. In particular, it will be shown that sputtered neutral clusters can now be identified up to fairly large sizes of about a hundred atoms and more.
multaneously collected secondary ion data, it is possible to determine the secondary ion formation (or "ionization") probability, i.e. the probability that a sputter ejected particle is ionized in the course of its emission process.

Combining these data, it is now possible to characterize the abundance distribution of sputtered clusters irrespective of their charge state, and the long standing question concerning the total fraction of sputtered atoms that are emitted in bound states can be settled. The experimental findings are compared to computer simulations of the sputtering process which are based on molecular dynamics. These calculations also provide insight into the emission and formation dynamics of sputtered clusters, which up to now are practically inaccessible by experiment. As a consequence, predictions can be made with respect to the internal excitation of clusters leaving the surface. In order to verify these predictions, we will briefly describe an experimental technique that has been developed most recently in order to determine the internal energy distribution of sputtered clusters.

Last, but not least, we will report on our recent efforts devoted to study of the emission of clusters from surfaces under bombardment with polyatomic projectiles. These experiments allow to study the role of non linear sputtering effects which may be induced by the spatial and temporal overlap of individual collision cascades initiated by the different constituent atoms of a projectile, a subject which has drawn much interest recently [8]. Experimental results that have been published by a number of groups suggest that particularly the sputter ejection of large and complex molecules may be significantly enhanced by such effects [9]. Unfortunately, practically all of these experiments were performed on secondary ions and may therefore in principle be influenced by variations of the secondary ion formation probability rather than represent variations of the composition of the sputtered flux. The existing data need therefore to be complemented by the study of sputtered neutral cluster emission under bombardment with polyatomic projectiles. In the present work, we describe our first results in that direction.

1. EXPERIMENTAL METHODS

The experimental setup used for mass spectrometric detection of sputtered neutral and ionized atoms and clusters is sketched in Fig. 1. The setup as well as the procedures to obtain mass and kinetic energy spectra of sputtered neutral and charged particles have been described in much detail elsewhere [7, 10] and will therefore only be touched upon briefly here. The investigated sample surface is bombarded with projectile ions generated either by a commercial plasma gas ion source or by a special ion source developed in our lab. The operation of the latter is based on the irradiation of a second target surface with an intense UV laser pulse (193 nm, 1 mJ, 4 \cdot 10^7 W \cdot cm^{-2}), thereby creating gas phase atomic and cluster ions by laser ablation. These species are then accelerated to the desired kinetic energy, mass selected by their flight time along a linear drift path and directed onto the investigated surface, where they impinge under 45° with respect to the surface normal.

In both cases, the projectile ion source was operated in a pulsed mode with pulse lengths ranging from 100 ns to 10 μs. Neutral particles sputtered from the surface are postionized by single photon absorption from an intense, pulsed VUV laser beam operated at a wavelength of 157 nm, pulse energies up to 5 mJ and a pulse duration of about 20 ns. In connection with the applied focal conditions (cross sectional area of about 1 mm²), this results in peak power densities up to about 10^7 W \cdot cm^{-2}, which could be varied over several orders of magnitude by a set of two dielectric attenuators. The ions produced by the photoabsorption process are swept into a reflectron type time-of-flight (ToF) mass spectrometer by means of a pulsed electric field that is switched on about 20 ns after the ionizing laser pulse. Secondary ions leaving the bombarded surface are detected by simply switching off the ionization laser and leaving the remainder of the experiment unchanged.

As explained in detail elsewhere, this operation mode ensures that secondary ions and neutrals are detected under exactly the same experimental conditions with respect to the sampled solid angle, the sampled emission velocity interval and the mass spectrometer detection efficiency [10]. This unique feature permits the determination of secondary ion formation probabilities by simply comparing the respective signals of ions and neutrals, provided the postionization efficiency for the neutral species is known. As will be illustrated below, the available laser intensity is high enough to drive the photoionization process into saturation, thereby eliminating the a priori unknown photoionization cross section.

During the measurements determining the total yield of sputtered atoms and clusters, a relatively long projectile ion pulse duration of several μs was chosen. More specifically, it was ensured that the measured signals did not increase with increasing pulse length any more, thus indicating that particles of all emission velocities interact with the ionizing laser. In order to de-

Fig. 1. Schematic sketch of the setup used for time-of-flight mass spectrometric detection of sputtered neutral and ionized atoms and clusters.
termine the emission velocity distributions of sputtered neutral particles, on the other hand, the laser was tightly focused to a beam waist of about 50 μm FWHM, the primary ion pulse width was reduced to 100 ns and the time delay between the projectile ion and the ionizing laser pulse was varied. This operation mode selects the emission velocity of the detected particles via their flight time between the surface and the ionization volume. The velocity spectrum of sputtered neutral atoms and clusters is then determined by following the respective photoion signal as a function of the delay time.

In the experiments devoted to the determination of the internal energy of sputtered neutral clusters, the ionizing laser was replaced by a frequency doubled tunable dye laser delivering pulses of wavelengths between 200 and 280 nm. The photoionization efficiency (PIE) curve of a neutral species was then measured by following the respective signal as a function of the photon energy in a region ranging from closely below to closely above the ionization potential. Care was taken that these experiments were performed at sufficiently low laser intensity, where all measured signals depend linearly on the laser intensity as expected for a single photon absorption process. The laser intensity was monitored as a function of wavelength and the measured signals were corrected accordingly.

2. RESULTS AND DISCUSSION

One of the most interesting questions in sputtering physics is related to the total fraction of sputtered atoms that are emitted from the surface in a bound state, i.e., as part of a cluster. The first subsection of this chapter therefore deals with the overall mass distribution of particles that are ejected from a clean metallic surface under ion bombardment. In order to unravel the basic mechanism leading to the formation of such large bound entities during the collisional sputtering process, it is of interest to look at the distribution of the emission velocity of the sputtered clusters, since this distribution is predicted by theoretical cluster formation models and can therefore serve as a tool to judge their validity. In the second subsection, we will therefore present experimental data on the kinetic energy distribution of clusters and its dependence on the cluster size. One of the major predictions of computer simulations is that clusters generated in sputtering must be internally excited. In an attempt to verify this prediction, the third subsection is therefore devoted to the experimental determination of internal energies of the sputtered clusters. In the last subsection of this chapter, we report on first results of an attempt to investigate the role of non linear cluster formation processes that might occur under bombardment with polyatomic projectiles.

2.1. Mass Distribution

It has been long known that the distribution of secondary cluster ions sputtered from clean metallic sur-

faces may extend up to fairly large cluster sizes of more than hundred atoms. The single photon post-ionization technique for the first time allows the detection of sputtered neutral clusters in this size range as well. As an example, Fig. 2 shows the mass spectrum of neutral clusters that are released from a polycrystalline silver surface under bombardment with 15-keV Xe⁺ ions. Post-ionization was in this case performed with a wavelength of 157 nm, the corresponding photon energy of 7.9 eV is large enough to allow single photon ionization of Ag atoms and all Agₙ clusters. It is seen that sputtered neutral clusters containing up to more than 60 atoms are detectable. In fact, when we repeat the experiment with an indium target the observable size range extends up to 150 atoms.

To our knowledge, these are the largest neutral clusters ever detected in a sputtering experiment to date. Regarding the fairly low kinetic impact energy the cluster ions possess upon impact onto the MCP particle detector (about 5 keV), it seems likely that the detectable size range is limited by the detector sensitivity rather than by the sputtering process itself. For a quantitative interpretation of the measured signals it is important to study their dependence on the intensity of the ionizing laser.

Figure 3 shows the integrated ToF signals of a number of arbitrarily selected clusters as a function of the laser power density \( P_L \). The observed behavior is typical for all investigated clusters: in the regime of low \( P_L \) the signals increase linearly with increasing laser intensity, as is expected for a single photon absorption process. At some intermediate values of \( P_L \), the signals level off due to saturation of the photoionization process, until at higher \( P_L \), a decrease is observed which is due to the increasing importance of multiphoton induced fragmentation. In the regime below the observed maxi-
Fig. 3. Integrated signal of selected sputtered neutral silver clusters vs. power density of the ionizing laser. Solid line: fit of theoretically expected laser intensity dependence. (Data taken from ref. [47].)

Fig. 4. Ionization probability \( \alpha^* \) of clusters sputtered from different clean metal and semiconductor surfaces under bombardment with 5-keV \( \text{Ar}^+ \) ions vs. cluster size. (Data taken from ref. [4].)

\[ S(P_L) = \frac{S_{sat}}{1 - \exp\left(-\frac{P_L}{h \nu \Delta t}\right)} \]  

(1)

can be nicely fitted to the measured data. In Eq. (1), \( \sigma_L \) and \( \Delta t \) denote the photoabsorption cross section and the effective laser pulse duration, respectively. The resulting values of the saturated signal \( S_{sat} \) can then be used to determine the relative yields of sputtered clusters, i.e., their partial sputtering yields normalized to that of emitted monomers. In this context it is important to note that the measured signals represent the number density of the sputtered particles within the ionization volume rather than their flux emerging from the sample surface. The signal must therefore be further corrected by the mean inverse velocity of the sputtered neutral particles, a quantity which in turn can be determined from a measurement of the emission velocity distribution (see Section 2.2). By comparison with the corresponding secondary ion signals, the ionization probability of sputtered clusters can be determined as a function of the cluster size.

As an example of such data, Fig. 4 displays the results obtained for silver, tantalum, niobium and germanium clusters sputtered from the respective clean metal surfaces. As a general trend, it is always found that the ionization probability increases with increasing cluster size and reaches a saturation value at sizes between 5 to 10 atoms. While in some cases the maximum ionization probability is small, thus indicating that the majority of clusters is emitted in a neutral charge state, it may in other cases reach values close to unity (see, e.g., the Ta data in Fig. 4).

About the reason for this different behaviour we can only speculate. One of the possible ionization mechanisms that are imaginable for a sputtered cluster involves thermionic emission of an electron, i.e., the conversion of internal vibrational excitation originating from the sputtering process into electronic energy, after the cluster has left the surface. Moreover, it is not difficult to imagine that the average internal energy contained in a sputtered cluster will depend on the bond strength between cluster atoms. Ionization, on the other hand, will be governed largely by the ionization potential of the cluster. While for most metals the ionization potential of small clusters is significantly larger than their typical bond strength or dissociation threshold, refractory metals like Ta and Nb exhibit binding energies that are comparable to the ionization potential. Internally excited clusters of these metals could therefore exhibit a significantly enhanced probability to release excess excitation energy by emission of an electron instead of fragmentation.

The secondary ion and neutral data can now be combined to determine the partial sputtering yields of clusters regardless of their charge state. Figure 5 shows the
relative yields, i.e., the yields normalized to that of the sputtered monomers, as a function of cluster size for the case of different metal clusters sputtered from the respective clean polycrystalline surfaces under bombardment with 5-keV Ar⁺ ions. First, it is seen that the yields coarsely follow a power law decay with increasing cluster size. This behaviour has been found for all systems investigated so far and must therefore be regarded as a general trend. The decay exponent is generally found to depend on the sputtering conditions in such a way that, whenever the experimental conditions are changed such that a higher total sputtering yield results, the decay becomes less steep and the relative abundance of larger clusters is enhanced.

In order to illustrate the generality of this observation, Fig. 6 displays a plot of measured power law decay exponents vs. the total sputtering yield. The displayed data have been compiled from a number of different experiments on sputtering of various metal surfaces under bombardment with different primary ions and kinetic projectile energies. The physical origin of the simple scaling rule observed in Fig. 6 has not yet been fully established. Although for the specific case of a silver surface, the yield distribution of clusters as well as its variation under different sputtering conditions has been successfully reproduced in MD simulations [11] (cf. the open symbols in Fig. 6), no simple theoretical cluster formation model has been proposed that explains the power law distribution and the variation of its decay exponent in a satisfying manner.

The only published models, which predict a power law cluster yield distribution are either of thermodynamical character [12] or treat the cluster emission as a shock wave initiated process [13]. Both descriptions, however, result in exponents δ which are fixed to values around 2 by the physics behind the model and are therefore not expected to vary as a function of the bombarding conditions. Among the statistical molecule formation models, on the other hand, the so-called atomic combination or multiple collision model [14, 15] seems to be best suited to describe the formation of sputtered homonuclear clusters. This model, which has been successfully applied to sputtered metal dimers and trimers [16–18], describes the probability for the formation of a sputtered cluster as a product of statistically independent emission probabilities of the constituent atoms. If the emission time and velocities are correlated in an appropriate way, the internal energy within the center-of-mass system of an ensemble of n sputtered atoms may remain below the bond strength of the n-atom cluster. Although some recent variations of that model are claimed to result in a partial agreement with measured cluster yield distributions over a limited size range [19], it can be shown [6] that such a model must predict an exponential yield decay with increasing cluster size rather than the power law dependence observed here. We therefore conclude that the formation of larger clusters containing more than 5 atoms cannot be described by this model either.

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Fig. 5. Relative yields of clusters sputtered from different clean metal surfaces under bombardment with 5-keV Ar⁺ ions. (Data taken from ref. [48].)

Fig. 6. Decay exponent of power law cluster yield distribution vs. total sputtering yield (taken from the literature [49]). The data have been compiled from many different experiments on sputtering of various metal surfaces with different primary ions and energies. Open symbols: results of MD simulations for silver clusters.
2.2. Kinetic Energy Distribution

As described in section 1, the emission velocity distribution of sputtered neutral particles is measured by following the mass spectrometric signal as a function of the delay time between projectile and laser pulse. The resulting distribution \( f(t) \) of flight times \( t \) is converted into the corresponding distribution of kinetic emission energies \( E \) by

\[
f(E) \propto f(t)^2,
\]

a relation which is applicable here since the data was taken under conditions where the photoionization process is not saturated [20].

The resulting kinetic emission energy distributions of \( \text{Ag} \) atoms and \( \text{Ag}_n \) clusters sputtered from a polycrystalline silver sample are depicted in Fig. 7. The data collection procedure applied allowed the detection of particles sputtered into a small solid angle interval around the direction along the surface normal. For atomic species, the measured distribution can be compared to the prediction of linear cascade theory [21]

\[
f(E) \propto \frac{E}{(E + U_0)^3}.
\]

The corresponding curve with the surface binding energy \( U_0 \) taken equal to the sublimation energy of silver (3.0 eV) has been included in the figure. It is seen that the measured energy distribution of monomers is reasonably well described by Eq. (3). The energy distributions of clusters, on the other hand, deviate from the monomer distribution in such a way that the decay towards higher energy becomes steeper with increasing cluster size, while the position of the maximum remains roughly constant. This behaviour is in principle expected from theoretical statistical model descriptions of the cluster formation process in sputtering. On the basis of the multiple collision model, an expression describing the asymptotic slope towards high emission energies according to

\[
f(E) \rightarrow E^{-2.5n + 0.5}
\]

has been derived [6, 22]. As a characteristic signature of a statistical nature of the cluster formation process, the model therefore predicts high energy decay exponents which increase rather steeply with increasing cluster size. From the data presented in Fig. 7, asymptotic decay exponents of 1.7, 2.9, and 4.4 are deduced from least square fits to the high energy portion of the distributions of \( \text{Ag}, \text{Ag}_2, \) and \( \text{Ag}_n \), respectively. For all investigated larger clusters, the decay exponent remains roughly constant around the value 4. These findings are in pronounced contrast to the prediction of Eq. (4), which would already for the trimer yield the decay exponent of 7. In addition to the yield distributions presented in the previous section, the experimental data on kinetic emission energy distributions therefore provide further evidence against a purely statistical formation process of sputtered clusters containing more than just a few atoms.

If the data of the type presented in Fig. 7 are converted into emission velocity distributions, the average inverse velocity of the sputtered neutral particles can be evaluated as

\[
\bar{v}^{-1} = \int_0^\infty v^{-1} f(v)dv.
\]

Knowledge of this value is important since it allows to correct the measured yield distribution data by converting the number density ratios detected in a laser post-ionization experiment into sputtered flux ratios. From the data measured for different metal clusters sputtered from the respective clean metal surfaces, one usually obtains a cluster size dependence according to

\[
\bar{v}^{-1}(n) \propto n^\kappa
\]

with exponents \( \kappa \) between 0.5 and 1. For the silver data presented in Fig. 7, for instance, a value of \( \kappa = 0.8 \) is obtained.

2.3. Internal Energy Distribution

As mentioned in section 2, information about the internal energy contained in a sputtered cluster can be obtained from single photon ionization experiments in the...
pre-threshold region, where the photon energy is not sufficient to overcome the ionization potential of a ground state cluster. As an example for such an investigation, Fig. 8 shows the signal of photoionized sputtered neutral In$_{28}$ clusters as a function of the photon energy ("photoionization efficiency (PIE) curve"). For comparison, the same experiment has been repeated on In$_{28}$ clusters produced in a supersonic cluster beam [23]; the resulting PIE-curve is also displayed in Fig. 8. Since the ionization and detection methods used in both experiments are practically identical, the difference between both curves must be induced by the different cluster production processes. It is clearly seen that the clusters produced in a supersonic expansion are colder than those produced in sputtering. In particular, the "tail" towards low photon energies observed in the PIE-curve of sputtered clusters reflects the distribution of the internally excited cluster states, the effective ionization potential of which is reduced by the amount of excitation energy contained in the cluster.

In principle, this finding is well in accordance with MD simulations which predict a high internal energy of sputtered molecules. The magnitude of the effect, however, is rather different. While the average internal energy found in the experiment amounts to only a few tenths of eV, the simulations reveal average internal energies of the order of 1 eV/atom [11]. One possible cause of this discrepancy may be due to the measurement procedure itself, since the Franck-Condon factor distribution may not favor transitions from high lying vibrational neutral states into low lying vibrational ionic states of the cluster (cf. the discussion in ref. [23]).

The second possible cause is given by the different time scales involved in the experiment and the MD simulation. While the simulation identifies a sputtered cluster in the immediate vicinity of the surface (at times of the order of picoseconds after the projectile impact), the experiment detects a sputtered cluster at times of typically several microseconds after its emission from the surface. In cases where the internal excitation energy $E^*$ is higher than the (cluster size dependent) dissociation threshold $D(n)$, these clusters will undergo unimolecular fragmentation reactions and thereby loose internal energy after leaving the surface, a phenomenon which can be studied in the MD simulations [11, 24] as well as in experiments on secondary cluster ions [24-27]. The residual internal energy that may be left after this evaporative cooling process depends on the dissociation energy and the dwell time the clusters spend between their generation and ionization. Ultimately, at very large times the cluster must reach a stable state where the internal excitation energy is comparable to or even below the dissociation threshold, which for Indium clusters is of the order of 1 eV.

At the other end of the investigated cluster size range, Fig. 9 shows a semi logarithmic plot of the PIE curve measured for sputtered In$_2$. The vertical arrow indicates the ionization potential $E_{ip} = 5.8 \pm 0.25$ eV measured for sputtered In$_2$. The solid line is a linear fit corresponding to an excitation temperature of $T = 3850 \pm 100$ K (see text). The vertical arrow marks the ionization potential measured in ref. [28]. (Data taken from ref. [50].)
sured by electron impact ionization [28]. In this case of a diatomic molecule, where unimolecular fragmentation is not possible, the internal energy contained in the sputtered cluster is quite large. From the Boltzmann tail observed in Fig. 9, the internal temperature associated with the ro-vibrational excitation of the sputtered dimers can be estimated to be around 3850 K, a value that is well comparable with the MD predictions [11]). Similar data have been obtained for other sputtered metal dimers as well [29–31]). These results clearly manifest that sputtered clusters are hot, a finding that appears perfectly reasonable in view of the relatively violent collisional processes leading to their formation.

2.4. Polyatomic Projectiles

Although a number of experiments have been published investigating the influence of polyatomic projectile species on the yields of secondary cluster ions [32–42], practically no such data exist for sputtered neutral clusters. Due to the a priori unknown ionization probabilities leading to the formation of a secondary cluster ion, definite conclusions regarding the role of projectile nuclearity on relative cluster yield distributions are therefore difficult to draw. In a first attempt to determine the yield distributions of sputtered neutral clusters formed under bombardment with polyatomic projectiles, we have investigated the sputtering of a polycrystalline silver surface under bombardment with different polyatomic projectile ions. First, 11-keV SF$_3^+$ ion bombardment was used and the resulting cluster size distributions were compared to those obtained under bombardment with 15-keV atomic Ar$^+$ ions.

Figure 10 shows the resulting signal distribution which has been obtained by integrating the different peaks in the measured ToF mass spectra and normalizing them to the respective projectile ion current [43]. Note that these distributions do not directly reflect the yield distributions as displayed in Fig. 5, since differences between the velocity distributions of different clusters have not been accounted for. It is seen, however, that although the absolute yields increase by more than the factor 10 under SF$_3^+$ bombardment (in spite of the reduced impact energy), the relative size distribution of different clusters remains practically unchanged. The same observation holds for the positive secondary ion spectra as well.

In the second attempt, we decided to work under self sputtering conditions in order to eliminate the addition-
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al complication of surface chemistry induced by the projectile species [44, 45]. For that purpose, a sputter cleaned polycrystalline silver surface was bombarded with mass selected Ag\textsuperscript{+} projectile ions in the range \( m = 1, 2, 3 \) impinging onto the sputtering target with kinetic energies up to 25 keV.

Examples of the resulting mass spectra of neutral silver clusters sputtered from the target surface are shown in Fig. 11. It is seen that although the intensity of the projectile beam decreases by almost two orders of magnitude between Ag\textsuperscript{+} and Ag\textsubscript{3}\textsuperscript{+}, clusters containing up to nine silver atoms can be identified for all three projectiles. Again, due to possible differences in their emission velocity distributions, the intensities observed in the mass spectra do not directly reflect the relative abundance of clusters among the flux of sputtered particles. Since the velocity correction is presumably independent of the projectile, however, its influence will be roughly the same for all three spectra presented in Fig. 11. A visual inspection of the data therefore reveals that switching the projectile nuclearity \( m \) from 1 to 3 – while keeping the total projectile energy constant – does not significantly enhance the relative contribution of larger clusters among the flux of sputtered neutral particles.

These results are particularly interesting in view of the correlation with sputtering yields depicted in Fig. 6. Since the sputtering yield is significantly enhanced for all polyatomic projectiles, one would have expected a drastic decrease of the decay exponent for these cases. In fact, comparison with the strong non linear yield increase of silver under bombardment with Sb\textsubscript{3}\textsuperscript{+} [46] as well as Au\textsubscript{3}\textsuperscript{+} [8] projectiles suggests that the total sputtering yield of silver under 21-keV Au\textsubscript{3}\textsuperscript{+} bombardment should be significantly larger than 100 atoms per ion. The data presented in Fig. 11 therefore suggest that the correlation between total sputtering yield and relative cluster abundances must saturate in the limit of high yields. It is, however, evident that much more data of the kind presented in Fig. 11 are needed in order to clarify this point.

REFERENCES