Abstract

We have investigated the formation of neutral clusters during self-sputtering of a silver surface under bombardment with Ag\(^+\) projectile ions \((m = 1, 2, 3)\). Particular emphasis was put on the size distribution of the sputtered clusters and its dependence on the projectile nuclearity \(m\) under conditions of constant impact velocity. It is found that the relative abundance of larger clusters increases from mono- to diatomic but decreases again from di- to triatomic projectiles. At the same time, the total sputtering yield exhibits a strong non-linear increase in both cases. This finding breaks the unique correlation between cluster abundance pattern and sputtering yield that has been observed many times in the past. The results indicate that the nature of the cluster formation process in sputtering must change at large sputtering yields connected with polyatomic projectile impact.

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1. Introduction

If a solid is bombarded with keV-ions, particles are released from the surface due to a cascade of mostly elastic collisions (“sputtering”). It has been known for a long time that the flux of sputtered particles contains not only atomic species but also agglomerates of several atoms. For elemental surfaces, these molecular sputtered species manifest as homonuclear clusters containing varying numbers of target atoms. For the case where the target is bombarded with atomic projectile ions, the relative abundance of such clusters has been investigated many times. As a general result of these studies, it has been found that the size distribution of sputtered clusters closely follows an inverse power law decay with increasing number of atoms in the cluster, the decay exponent of which is found to be correlated with the total sputtering yield (i.e. the average number of target atoms released per impinging projectile ion). More specifically, it has been established as a general rule that whenever the conditions are changed such as to lead to a higher sputtering yield, the abundance of larger clusters in the spectrum of sputtered particles is increased, thus leading to a lower value of the apparent decay exponent. It is a most interesting and still open question in sputtering physics whether this trend continues into the regime of very large sputtering yields and, hence, conditions can be found where the vast majority of the sputtered material is emitted in form of clusters.
Unfortunately, the sputtering yield generally goes through a maximum as a function of the projectile energy and is therefore limited to values of several ten atoms per projectile ion if atomic projectiles are used. As a consequence, the above mentioned correlation has so far been explored only up to yield values of around 20 atoms/ion. An interesting possibility to increase the sputtering yield further arises if polyatomic projectiles are used instead of atomic ions to bombard the target surface. In this case, the temporal and spatial overlap of collision cascades initiated by the individual constituents of the projectile may lead to a pronounced non-linear yield enhancement, i.e. the total sputtering yield induced by a polyatomic projectile may be considerably larger than the sum of the sputtering yields induced by the constituent atoms impinging independently with the same velocity [1]. In addition, a number of mass spectrometric experiments have been published which indicate that the contribution of complex molecular species to the total flux of sputtered particles can be substantially enhanced if polyatomic instead of monatomic projectiles are used, the effect being the more pronounced the larger the sputtered molecule [2–6]. In practically all of these experiments, on the other hand, exclusively the charged fraction of the sputtered flux (“secondary ions”) has been analyzed. Since it is known that the majority of sputtered particles is generally neutral, it is not clear whether these results reveal an enhancement of the partial sputtering yields of complex species or rather relate to their ionization mechanism which may of course also be enhanced under polyatomic projectile bombardment. In the present work, we therefore investigate the size distribution of neutral clusters that are formed under bombardment of a clean metal surface with mono-, di- and triatomic projectile ions of the same element using a well established laser post-ionization technique [7]. Silver was chosen as a target and projectile material since for this element the largest database of cluster sputtering data under various sputtering conditions exists. In order to identify the possible role of non-linear enhancement effects, all projectiles are accelerated to different kinetic energies such that they impinge onto the surface with the same impact velocity. The use of self-sputtering conditions eliminates any influence of chemistry and therefore constitutes the purest way to study the collisional mechanisms underlying the cluster formation process in sputtering.

2. Experimental

The experiments were performed in an ultrahigh vacuum tandem time-of-flight mass spectrometer that is sketched in Fig. 1 and has been described in detail elsewhere [8]. The system comprises of an ion source generating atomic and cluster ions of a selectable element (here: silver) and a time-of-flight mass spectrometer with laser post-ionization used to detect the neutral species sputtered from a selectable target (here: also silver). The projectile ions are generated by a pulsed laser ablation process at a polycrystalline silver surface using an intense UV excimer laser pulse at a wavelength of 193 nm and a peak power density of about \(4 \times 10^7\) W/cm\(^2\). By keeping the ablated surface at high positive potential, the ions are accelerated to kinetic energies up to 25 keV and mass selected by a linear time-of-flight technique involving a deflection pulse applied to a pair of blanking plates located downstream in the projectile path. The projectile ion pulses impinging onto the investigated surface were monitored by means of a chevron microchannel plate (MCP) mounted adjacent to the sputter target. For use in the present work, the pulses corresponding to Ag\(^+\), Ag\(_2^+\) and Ag\(_3^+\) have been selected from the flight time spectra recorded at impact energies of 7, 14 and 21 keV, respectively, thus leading to a constant impact velocity of the different projectiles corresponding to a kinetic energy of 7 keV/atom. The resulting projectile pulses are shown in Fig. 2. Outside the depicted flight time range, the spectra are blank since all unwanted ions have been blanked out of the beam using the deflection plates. The apparent scatter being visible in the track obtained for Ag\(_2^+\) is due to high frequency noise induced by the fast high voltage switching device used to generate the deflection pulse. It is seen that the temporal width of the projectile pulses depends on the impact energy and decreases from 1.8 μs for Ag\(^+\) (at 7 keV) to 0.2 μs for Ag\(_3^+\) (at 21 keV). This
behavior is presumably due to the fact that the spatial potential distribution within the laser induced plasma above the ablated surface becomes less influential with increasing acceleration voltage. The projectiles impinge onto a high purity polycrystalline silver foil under an incidence angle of $45^\circ$ with respect to the surface normal. Prior to each experiment, the target surface was sputter cleaned by bombardment with a rastered 5-keV $\text{Ar}^+$ ion beam. The flux of neutral particles sputtered from the surface is investigated by means of a laser post-ionization reflectron time-of-flight spectrometer that has been described in detail earlier [9–12]. In short, neutral species leaving the surface are photoionized by means of an intense pulsed VUV laser emitting radiation at a wavelength of 157 nm. The corresponding photon energy of 7.9 eV is large enough to allow single photon ionization of silver atoms and all silver clusters, a condition which is necessary to minimize photofragmentation of clusters during the photoionization process and, in addition, ensures a constant effective ionization volume for all sputtered species. A relatively low peak power density of the ionizing laser of about $5 \times 10^5$ W/cm$^2$ was
deliberately employed in these experiments to ensure that the measured signal is strictly proportional to the laser intensity. This was done in order to eliminate possible laser intensity variations during the acquisition of subsequent spectra by monitoring the laser pulse for each spectrum using a photoelectron detector [13] and normalizing the measured spectra to the integrated laser signal. The laser beam is steered in a direction parallel to the target surface at a distance of about 0.5 mm. The time delay between the projectile ion pulse hitting the surface and the ionizing laser pulse is critical since it may act as an emission velocity selector for the sputtered neutrals. In order to integrate over the entire velocity distribution, several mass spectra were taken at different delay times between projectile and laser pulses – separated by the temporal half width of the projectile pulse – and added. This was done until the recorded spectrum did not contribute to the summed data any more, thus ensuring that sputtered particles of all relevant emission velocities could interact with the ionization laser.

The post-ionized particles are detected using a chevron MCP detector. For signal pulses containing more than one photoion per instrument cycle (projectile pulse and laser shot), a direct digitization of the output charge was employed, while smaller signals were recorded in a single ion counting mode. Since all ions impinge onto the detector with the same kinetic energy of about 3.7 keV, no correction for different detection efficiencies of atomic and cluster ions has been applied since under these conditions the variation of this quantity is assumed to be small in the limited range of cluster sizes investigated here [14]. For a more detailed description of the experimental set-up as well as of the procedures used to acquire mass spectra and yield distributions of sputtered neutral atoms and clusters with this system, the reader is referred to our previous publications [9–12].

3. Results and discussion

Fig. 3 shows mass spectra of post-ionized sputtered neutral atoms and clusters which have been ejected from the polycrystalline silver surface under bombardment with Ag⁺, Ag₂⁺ and Ag₃⁺ projectile ions of the same impact velocity corresponding to 7 keV/atom.

![Fig. 3. Mass spectra of neutral particles sputtered from a polycrystalline silver surface under bombardment with Ag⁺, Ag₂⁺ and Ag₃⁺ projectile ions of the same impact velocity corresponding to 7 keV/atom.](image-url)
post-ionization experiment detects the number density of sputtered particles rather than their flux. Since we are interested in the partial sputtering yield, i.e. the average number of a certain sputtered species per projectile impact, we must determine the flux of different sputtered species and therefore account for possible differences between the emission velocity distributions of the detected species. More specifically, the measured signal must be divided by the average inverse emission velocity $\langle v^{-1} \rangle$ which in principle needs to be evaluated from measured velocity spectra. Corresponding experiments performed with atomic rare gas projectiles yielded an increase of $\langle v^{-1} \rangle$ with increasing cluster size $n$ that could be roughly approximated by $\langle v^{-1} \rangle \propto n^{-0.82}$ [11]. Due to the relatively large temporal width of the projectile ion pulses, we cannot employ the same technique to measure the velocity distributions in the present experiments. We therefore adopt the same cluster size dependence in order to correct the data measured here, thus assuming that the velocity spectrum of sputtered silver clusters does not significantly depend on the projectile species. In the limit of high sputter yields, the nature of the sputtering process may change and this assumption may fail (see below). In order to estimate the possible role of this uncertainty, we assume as an extreme change a Boltzmann-like velocity spectrum with the same “temperature” for all sputtered species, which in turn would result in a correction according to $n^{0.5}$ instead of $n^{-0.82}$.

The resulting relative cluster yields, i.e. the partial sputtering yields of clusters normalized to that of the sputtered monomers, are depicted as a function of cluster size in Fig. 4. Probably the most important observation is that the relative abundance of clusters increases upon switching from mono- to diatomic projectiles but decreases again between di- and triatomic projectiles. This trend is clearly visible for all cluster sizes and therefore certainly beyond the statistical scatter of the data. In order to arrive at a more quantitative measure of this effect, we coarsely approximate the overall decay of the relative cluster yield with increasing cluster size by an inverse power law according to

$$Y(n) \propto n^{-\delta}.$$  

(1)

The same approximation was made to all of our previously acquired data that had been obtained for atomic projectile ions. Since the previous work was performed with a different ion source delivering much higher projectile current, the yield distribution could be followed to much larger clusters containing up to about 50 atoms. It was shown that the power law slope $\delta$ determined from a least square fit did not change significantly when the cluster size range included in the fit was restricted to $n \leq 9$. From a corresponding least squares fit to the data presented in Fig. 4 one finds decay exponents $\delta$ of 5.3, 4.3 and 5.1 for mono-, di- and triatomic projectiles, respectively. Due to possible systematic changes in the velocity spectrum of the emitted clusters, the values for triatomic and – to a lesser extent – also for diatomic projectiles may reduce by 0.3. The ordering of the values, which is already apparent from a visible inspection of Fig. 4 and therefore clearly outside these uncertainties, appears surprising. From the correlation between cluster abundance distributions and sputtering yields observed in previous experiments performed both in our group and by others [15,16], the decrease between mono- and diatomic projectiles is in principle expected since
the sputtering yield increases upon switching from Ag\(^+\) to Ag\(^{+2}\) impact. The increase of the exponent which is observed for Ag\(^{+3}\), however, is unexpected since the sputtering yield must certainly still increase much further upon switching from Ag\(^{+2}\) to Ag\(^{+3}\) impact.

For a more quantitative discussion, numeric values of the total sputtering yields are needed. Since the self-sputtering yield of silver under bombardment with polyatomic projectiles has never been measured, we extract such data from the mass spectra displayed in Fig. 3. For that purpose, the integrated and corrected signals \(S\) are summed and normalized to the relative primary ion pulse height \(I_p\) according to

\[
Y_{\text{tot}} / P_n n / C_1 S(\text{Ag}_n) I_p.
\]

(2)

It is of note that the integration procedure employed by summing the time-of-flight spectra of sputtered particles for different delay times between projectile and ionization laser pulses results in the same spectrum that would be recorded for an infinitely long projectile pulse. As described in detail elsewhere [17], this signal is then proportional to the height of the projectile pulse rather than its integral. The problem in evaluating Eq. (2) for different projectiles is the accurate determination of \(I_p\), since the projectile spectra depicted in Fig. 2 are recorded with an MCP detector which will exhibit a projectile dependent detection efficiency. In that respect, it is advantageous that all Ag\(^{+}\) projectiles used in this work impinge onto the target and MCP surface with the same velocity. As a consequence, use can be made of the fact that the ion induced electron yield at the front detector surface and, hence, the detector gain [18] for homonuclear metal cluster ions is proportional to the number of atoms in the cluster [19]. This way, the spectra depicted in Fig. 2 reveal a projectile pulse height ratio of 100:4:2:0.7 between mono-, di- and triatomic projectiles, respectively. Introducing these values into Eq. (2), the total sputtering yield is found to increase by factors of 4.9 and 10.1 upon switching from mono- to di- and from mono- to triatomic projectiles, respectively. These values compare well with recently measured sputtering yield data for polycrystalline gold and silver targets under bombardment with Au\(_m^+\) projectiles [20,21], where the yield was found to scale with projectile nuclearity as \(m^2\) thus leading to yield enhancement factors of 4 and 9 for \(m = 2\) and 3, respectively. More specifically, if the silver yield data of [21], which have been measured at higher impact energies than employed here, are extrapolated down to 7 keV/atom, one finds enhancement factors of 5 and 10.5 which are in very good agreement with those determined here. Moreover, somewhat older published yield data for polycrystalline silver under bombardment with Sb\(_m^+\) projectiles [22], again extrapolated down to 7 keV/atom, yield enhancement factors of 4.8 and 14.4, which again compare well with the self-sputtering data determined here.

In order to put the cluster size distributions depicted in Fig. 4 into context with previously published data, we plot in Fig. 5 the power law decay exponent \(\delta\) versus the total sputtering yield, the latter being determined from the yield ratio values described above using published data on the self-sputtering yield of silver under atomic ion bombardment [23]. For comparison, exponents determined for silver and other metal clusters sputtered under bombardment with atomic rare

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Decay exponent \(\delta\) power law fits to measured cluster size distributions versus total sputtering yield. Closed symbols: this work. Open symbols: data taken from [32,33]. The solid line is drawn just to guide the eye.}
\end{figure}
gas projectile ions have been included. In all cases, the sputtering yield data were taken from the compilation of Andersen and Bay [24], and, hence, refer to normal projectile incidence in contrast to our experimental impact angle of $\theta = 45^\circ$. As a consequence, the absolute calibration of the yield axis in Fig. 5 may be off by a factor of approximately $\cos(\theta) = 0.7$, but the relative scaling of the different yield values should not be altered by this ambiguity.

In order to allow a fair comparison with the data obtained here, the power law exponents taken from our previous work were re-fitted to the corresponding experimental data using a restricted cluster size range $n \leq 9$. It is seen that the monotonic decrease of $\delta$ with increasing sputtering yield that had been observed earlier is not continued in the regime of high sputter yields. Instead, the exponent is found to go through a minimum and increase again in the limit of large yields. The theoretical interpretation of this result is tedious. This is particularly caused by the fact that no model of cluster formation in sputtering has been published so far which explains power law cluster size distributions with varying exponents. We can therefore at this point only speculate about the reason for the observed behavior. It is apparent that the character of the sputtering process must change at yield values around 20 atoms/ion. Interestingly, it is exactly this yield range which has been suggested to form the boundary between the linear cascade and the collisional spike regimes of sputtering [1]. The former, being characterized by a low average density of moving atoms in the irradiated volume, must lead to a linear superposition of the collision cascades induced by the individual constituent atoms of a polyatomic projectile. The latter, on the other hand, involves a high density of moving atoms and has therefore been treated theoretically using thermodynamic concepts [25]. In fact, the pronounced non-linear enhancement of the total yield clearly indicates that the sputtering conditions for di- and triatomic projectile bombardment employed here fall into the spike regime. The results presented in Fig. 5 therefore suggest that the production of sputtered clusters under spike conditions must be different from that in the linear cascade regime. Interestingly, power law cluster size distributions with fixed decay exponents are predicted by thermodynamical [26] or hydrodynamical [27] models of cluster formation. In particular the assumption of local thermodynamical equilibrium in [26], though doubtful in the linear cascade regime, may well be valid under spike conditions. In view of the minimum $\delta$ observed in Fig. 5, it is particularly interesting to note that MD simulations have shown that cluster production under spike conditions is most efficient at an optimum energy density in the spike volume which corresponds to approximately the sublimation energy per atom [28]. The impact of a triatomic projectile must therefore already deposit sufficient energy in a region close to the surface to efficiently diminish the yield of large clusters. In order to examine this statement in a slightly more quantitative manner, we estimate the energy density by simply assuming the total projectile energy $E_p$ to be uniformly distributed within the cascade volume which, in turn, is crudely approximated by

$$V_{\text{cas}} \approx R_d \cdot \pi \cdot R_{\text{lat}}^2,$$

(3)

where $R_d$ and $R_{\text{lat}}$ denote the depth and lateral extension of the volume energized by the impinging projectile, respectively. Since all projectiles impinge with the same velocity, $V_{\text{cas}}$ will be essentially the same for mono-, di- and triatomic projectiles. In principle, $R_d$ and $R_{\text{lat}}$ can be determined from Molecular Dynamics computer simulations of the collision cascade by determining the lateral and in-depth width of the distribution of energized atoms. For the impact of 16-keV/atom gold clusters onto an Au (1 1 1) surface, Colla and Urbassek [29] have published such data which clearly show that under keV sputtering conditions compact collision cascades develop which extend over several nanometers in both directions. From their Figs. 1 and 2, one obtains values of $R_d = 4.6$ nm and $R_{\text{lat}} = 2.3$ nm, respectively, which do not vary between impact of Au atoms and Au$_4$ clusters. In connection with the atom density of $5.85 \times 10^{22}$ cm$^{-3}$ [30], this yields a total number of about 5000 atoms in the cascade volume. Assuming roughly the same cascade dimension for the bombardment conditions employed here, the resulting values of the average energy density are 1.4,
2.8 and 4.2 eV/atom for mono-, di- and triatomic projectile impact with \( E_B = 7, 14 \) and 21 keV, respectively. With the sublimation energy of silver being 3.0 eV \[30\], it is seen that one would expect the optimum energy density for cluster formation to be generated under bombardment with diatomic projectiles. This expectation nicely coincides with our experimental finding that under these conditions the observed relative cluster yields maximize and, hence, the power law exponent minimizes.

4. Conclusion

We find that the formation of silver clusters under bombardment with di- and triatomic silver projectiles is governed by spike conditions and therefore behaves differently from that observed in the linear cascade regime. This finding may also explain the apparent discrepancy between our data and that obtained in \[3,31\] where large non-additive enhancements of the relative yields of \( \text{Ta}^+ \) and \( \text{Nb}^+ \) secondary cluster ions sputtered from tantalum and niobium surfaces under bombardment with \( \text{Au}^- \), \( \text{Au}^+_2 \) and \( \text{Au}^+_3 \) projectiles were found. Due to the large sublimation energy of Ta and Nb, the sputtering yields of these elements are probably too low to reach the spike regime even under polyatomic projectile bombardment with the parameters employed. In contrast to the silver case, the cluster abundance distribution therefore exhibits the strong correlation with sputtering yield which appears to be typical for linear cascade sputtering. In fact, MD simulations of cluster formation in sputtering indicate that the emission of large clusters practically always occurs in impact events that lead to collision cascades which fall into the spike category, i.e. exhibit a large density of simultaneously moving atoms. Such events, which form the average under spike sputtering conditions, are rare under conditions where the average cascade is linear. In the linear cascade regime, the cluster yield must therefore be strongly determined by the probability of such large events which is – dependent on the cluster size – strongly coupled to the average sputtering yield. In the spike regime, on the other hand, the probability for large events is always high and therefore the correlation between cluster abundance distribution and average sputtering yield is lost. Instead, the deposited energy density seems to play a major role in determining the cluster abundance distribution in this regime.

References