The mass distribution of sputtered metal clusters II. Model calculation

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The mass distribution of clusters $M_n$ sputtered from an fcc metal surface is studied by a combination of molecular dynamics and Monte Carlo simulation. The cluster emission mechanism is subdivided into i) the formation of "nascent" clusters during the lifetime of the collision cascade developing in the solid and ii) the unimolecular decomposition of excited unstable nascent clusters yielding stable "final" fragments. It is shown that the size distribution of the cluster yields $Y(n)$ measured far away from the surface can be roughly described by a power law ($Y \propto n^{-\delta}$), the exponent $\delta$ being strongly dependent on the bombarding conditions.

1. Introduction

The bombardment of solid surfaces with energetic ions leads to the emission of particles ("sputtering"). It has long been known that the sputtered flux may contain atomic species as well as agglomerates of several atoms ("sputtered clusters"). Since the first detection of sputtered dimers in 1958 [1], many experimental and theoretical studies have been devoted to the determination of the mass distribution of sputtered clusters [2–5]. For technical reasons, most of the experimental work was performed on cluster ions leaving the surface already in a charged state. The interpretation of these results, however, is difficult due to the uncertainty of the ionization probability of the sputtered clusters which may depend strongly on the cluster size (cf. part I of this work [6]). For a long time, experimental data on neutral clusters, on the other hand, was restricted to small molecules containing less than five atoms [7,8]. Only very recently, the experimental detection of sputtered neutral clusters could be extended towards larger cluster sizes [9,10]. In part I [6] we describe how these data can be used to determine cluster sputtering yields which are independent from the emission charge state of the detected particles. The results show that the yield $Y(n)$ of sputtered silver clusters $Ag_n$ drops with increasing $n$ according to a power law

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

with $\delta = 6.5$. Similar power law dependences have been demonstrated for the yields of sputtered neutral copper [11] and aluminum [12] clusters with exponents $\delta$ of 7.9 ($Cu_n$) and 9.3 ($Al_n$). From the present theoretical understanding of the emission and/or formation of sputtered molecules, this experimental finding is rather unexpected. Of the various molecule sputtering mechanisms proposed in the literature, only the thermal equilibrium model of Urbassek [13] and the shock wave model of Bitsenski and Parilis [14] predict a power law dependence as given by eq. (1), but in both cases the exponent $\delta$ is fixed to values around 2. In addition, the experimental data were taken on metal clusters sputtered by impact of keV $Ar^+$ ions. Since these bombarding conditions are well within the linear cascade regime, the cluster emission should be clearly dominated by elastic collisions and the applicability of both models to the sputtering of metal clusters is at least questionable. In the present paper, we therefore try to explain the observed cluster yields by subdividing the cluster emission process into two separate steps. First, the formation of "nascent" clusters which are found immediately above the solid surface is studied by a molecular dynamics simulation. From our previous work [15] we know that these clusters, which are formed essentially within the lifetime of the collision cascade developing in the solid (in general several hundred femtoseconds), are almost exclusively unstable and will therefore decompose on their passage away from the surface. A body of experimental evidence has been collected which proves the occurrence of such fragmentation processes within the flux of sputtered cluster ions [16–21]. Due to the high average internal energy imparted to a cluster during the sputtering process, the corresponding unimolecular reactions were found to proceed mostly on a picosecond time scale.
As a consequence, nascent clusters are practically unaccessible to experimental detection, and the unimolecular dissociation of unstable species must under any circumstances be accounted for if theoretical predictions of cluster sputtering yields are to be compared to corresponding experimental data. Hence, in a second step we describe the decomposition of unstable nascent clusters into stable “final” products. In ref. [15], we followed the decomposition by molecular dynamics simulation. The resulting yields of final clusters were found to agree well with measured cluster sputtering yields, but the statistics of the calculation limited the available information to clusters containing at most four atoms. In the present paper, we attempt to extend the range of the prediction to larger clusters by employing a simple Monte Carlo simulation to model the unimolecular fragmentation of unstable nascent clusters.

2. Description of the calculation

The molecular dynamics simulations employed in the present work have been described in great detail elsewhere [15,22]. Briefly, the classical equations of motion are solved numerically for all atoms of a model fcc crystallite containing approximately 1000 atoms. The atom–atom interaction within the solid is described by a many-body potential constructed by the embedded-atom method (EAM). In order to establish some link to the experimental data presented in part I, a particular potential fit to known properties of solid silver [23] was chosen which was slightly modified for use in sputtering calculations [22]. It should be noted at this point, however, that this EAM potential was found to overbind small gas phase silver clusters by amounts ranging from 60% (dimers, tetramers) to 90% (trimers). Hence, it should be regarded as a model potential describing an arbitrary fcc metal rather than as an accurate description of silver. In order to document this, we will in the following use the symbol $M_n$ to denote a homonuclear metal cluster containing $n$ atoms, where $M$ stands for a generic metal.

The calculations reported here were performed for Ar$^+$ ions impinging onto an fcc metal (111) surface with energies between 100 eV and 5 keV. For a given ion energy, a total of 1000 primary ion impacts were calculated with impact points uniformly distributed over the smallest irreducible surface cell. For each impact event, the trajectory integration was stopped when all atoms which were detected to be sputtered did not interact with the remaining surface atoms any more. At this time, which was typically about several hundred femtoseconds after the actual impact, sputtered nascent clusters were identified by the condition

$$E_{\text{int}}(M_n) < 0,$$

with the total energy $E_{\text{tot}}$ being calculated from the positions and momenta of the constituent atoms by summing their relative kinetic and potential energies. While this condition ensures that the cluster cannot decompose into $n$ single atoms, it does of course not guarantee stability with respect to fragmentation. Hence, most of the nascent clusters identified this way will decompose at some time after the ejection, and inequality (2) must be regarded as a necessary but not sufficient condition for the formation of stable multimers during the passage away from the surface.

The unimolecular decomposition of nascent clusters into stable fragments was modeled by a simple Monte Carlo approach. Although several models describing evaporative cooling of hot clusters have appeared in the literature [24–26], we have for simplicity chosen to proceed as follows. First, the average internal energy $E_{\text{int}}^\text{a} (n)$ of nascent clusters of a given size $n$ was calculated from the MD results. For clusters containing more than 10 atoms, where the MD simulation reached its statistical limitation, the values of $E_{\text{int}}^\text{a} (n)$ were extrapolated as described in section 3.3. Then, each unstable $M_n$ cluster was assumed to possess a discrete internal energy corresponding to $E_{\text{int}}^\text{a} (n)$. Second, the rate constants $k_m^n$ for possible dissociation reactions

$$M_n \rightarrow M_m + M_{n-m},$$

were calculated as a function of the internal energy $E_{\text{int}}$ according to Rice–Ramsperger–Kassel (RRK) theory [27] by means of the classical Kassel equation

$$k_m^n(E_{\text{int}}) \propto \left( \frac{E_{\text{int}} - E_{\text{th}}^{n,m}}{E_{\text{int}}} \right)^{s-1}.$$

Here, $E_{\text{th}}^{n,m}$ denotes the threshold energy of reaction (3) and the parameter $s$ is taken to a first approximation as the number of vibrational modes present in the molecule, i.e. $s = 3n - 6$. The values of $E_{\text{th}}^{n,m}$ entering eq. (4) were determined from

$$E_{\text{th}}^{n,m} = E_a(n-m) + E_a(m) - E_a(n),$$

where $E_a(n)$ denotes the atomization energy of a cluster containing $n$ atoms. For small clusters ($n < 8$), the quantity $E_a(n)$ was determined by finding the minimum energy configuration of the atoms according to the EAM potential using a modified version of the MD code. Details of this procedure are given in ref. [15]. The resulting atomization energies are displayed in fig. 1. For clusters containing more than 8 atoms, the number of local minima of the potential hypersurface becomes rather large and the determination of $E_a(n)$ by molecular dynamics simulation becomes increasingly time consuming. Hence, we extrapolated the results obtained for small clusters by means of a modified liquid drop model yielding

$$E_a(n) = U_a(1 - cn^{-k}),$$

where $U_a$ denotes the atomization energy of a cluster containing $n$ atoms.
where $U_c$ denotes the sublimation energy of the solid metal (the EAM potential was fit to the respective value of silver) and the parameter $c$ is related to the surface tension of the cluster. Strictly speaking, the exponent should be fixed to $\kappa = 1/3$ if eq. (4) is justified in terms of a liquid drop model. In order to provide a better fit to the $E_a$ values obtained from the MD simulation, however, we chose to regard both $c$ and $\kappa$ as free parameters which were determined as $c = 0.78$ and $\kappa = 0.45$ from the least squares fit indicated in fig. 1.

Knowing the rate constants $k_{m}^{n}$, a particular dissociation reaction (3) was chosen by arbitrarily selecting a fragment size $m$ according to the probability distribution given by the relative values of $k_{m}^{n}$. In the next step, we need to estimate the average energy dissipated during a fragmentation process. First, we note that each dissociation according to reaction (3) will require an expenditure of at least $E_{\text{th}}^{(n,m)}$. Second, additional energy $\Delta E_{\text{trans}}$ will be carried away as translational energy of the fragments $M_{m}$ and $M_{n-m}$, and, hence, only the reduced excess energy

$$E'_\text{exc} = E_{\text{int}}(n) - E_{\text{th}}^{(n,m)} - \Delta E_{\text{trans}}$$

will be available for further fragmentation. In order to estimate $\Delta E_{\text{trans}}$, we assume a thermal distribution of the internal energy of a cluster. Since the average energy contained in a vibrational and rotational degree of freedom amounts to $kT$ and $\frac{3}{2}kT$, respectively, one obtains

$$E_{\text{int}}(n) = [ (3n - 6) + \frac{3}{2} ] kT_n$$

for a non-linear molecule of $n$ atoms. For the special case of $n = 2$ the term in square brackets of eq. (8) has to be replaced by 2. Following Klots [24], the assumption of a thermal energy distribution may be justified because the time scale on which thermal fluctuations damp out is short compared to typical rate constants of unimolecular decomposition reactions considered here. The value of $\Delta E_{\text{trans}}$ is estimated according to common theory of unimolecular reactions [28] by replacing one vibrational mode of the energized $M_n$ cluster by a free translational motion along the reaction coordinate. Hence, the average amount of energy contained in one vibrational degree of freedom will on the average be converted into translational energy upon dissociation, yielding $\Delta E_{\text{trans}} = kT_n$. The division of the reduced excess energy among the fragments is done by applying eq. (8) to both the $M_m$ and the $M_{n-m}$ subclusters and assuming $T_m = T_{n-m}$ for the fragment temperatures after dissociation. Hence, when the dissociation process is completed, the average internal energies of the fragments are given by

$$E_{\text{int}}(m) = \frac{m - 3/2}{n - 3} \cdot E'_\text{exc}$$

(9)

and

$$E_{\text{int}}(n-m) = \frac{(n-m) - 3/2}{n - 3} \cdot E'_\text{exc}$$

(10)

with

$$E'_\text{exc} = E_{\text{int}}(n) \frac{3n - 11/2}{2n - 9/2} - E_{\text{th}}^{(n,m)}.$$ 

Since eq. (8) has a different form for dimers and atoms [$E_{\text{int}}(1) = 0$], modified versions of eqs. (9) and (10) were used if either $m$ or $n - m$ were equal to 1 or 2. If the internal energy of a fragment was found to be below the minimum threshold energy for further dissociation, this subcluster was recorded to be stable. Otherwise, the fragments were added to the list of unstable subclusters and, in turn, subjected to the dissociation treatment again. This way, the decomposition cascade initiated by a single $M_n$ cluster containing an internal energy $E_{\text{int}}^0(n)$ was followed until only stable fragments remained. In order to obtain the statistical distribution of fragments, the whole procedure described above was repeated several thousand times.

3. Results and discussion

In the following, we discuss the formation of stable clusters during sputtering in terms of three steps. Accordingly, this section is organized into three subsections. First, as a necessary condition for the formation of $M_n$ clusters, at least $n$ atoms have to be sputtered by a single primary ion impact. Hence, in the first subsection we discuss the statistics of the sputtering process and evaluate the probability that a particular number of $n$ atoms is ejected in a sputtering event. Second, ensembles of $n$ atoms have to be found, the total energy of which is low enough that the con-
Table 1
Parameters $\mu$ and $\phi$ of negative binomial distribution vs bombarding energy $E_B$ for Ar$^+$ ions normally incident on a metal (111) surface

<table>
<thead>
<tr>
<th>$E_B$ (keV)</th>
<th>$\mu$</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>8.13</td>
<td>0.184</td>
</tr>
<tr>
<td>1</td>
<td>4.50</td>
<td>0.495</td>
</tr>
<tr>
<td>0.5</td>
<td>3.26</td>
<td>1.06</td>
</tr>
<tr>
<td>0.25</td>
<td>1.97</td>
<td>13</td>
</tr>
<tr>
<td>0.1</td>
<td>0.44</td>
<td>4292</td>
</tr>
</tbody>
</table>

Constituent atoms can at least temporarily be considered to be bound. This is done in the second subsection where the yields of nascent clusters are evaluated. The third subsection then describes the conversion of nascent clusters into stable final products by unimolecular decomposition.

3.1. Statistics of sputtering

From the MD simulation, the statistics of the sputtering process can be examined by plotting so-called atoms per single ion (ASI) distributions [29–31]. It is found that the probability of $n$ atoms being ejected by a single primary ion impact can be well fitted by a negative binomial distribution

$$ P(n) = \frac{\Gamma(n + \mu \phi)}{n! \Gamma(\mu \phi) (1 + \phi)^{n + \mu \phi}} $$

as proposed by Eckstein [30] with the parameters $\mu$ and $\phi$ given in table 1. Note that $\mu$ denotes the mean of the distribution and must therefore be set equal to the total sputtering yield. Note also that both $\mu$ and $\phi$ strongly depend on the primary ion impact energy $E_B$ in a way which is consistent with Eckstein’s results [30] obtained with the TRIM code.

In the present context, we need the probability $W(n)$ that at least $n$ atoms are ejected, which is obtained by summing $P(i)$ from $i=n$ to infinity. The resulting probability distribution is shown in fig. 2 for four different values of $E_B$. It is clearly seen that $W(n)$ strongly depends on the bombarding conditions employed. From the data depicted in fig. 2, it is already evident that the contribution of large clusters to the flux of sputtered particles must decrease with decreasing bombarding energy.

3.2. Nascent cluster yields

Fig. 3 depicts the average number of nascent clusters sputtered per ion impact as determined from the MD simulation. We note again that these clusters, which are identified immediately after the ejection process, are mostly unstable and will therefore not be detectable at large distances from the surface. Interestingly, the size distribution of nascent clusters can be almost perfectly fitted by a power law dependence

$$ Y_{nasc}(n) \propto n^{-\alpha} \quad (11) $$

Table 2
Calculated total sputtering yield $Y_{tot}$ as well as exponents $\alpha$ and $\delta$ determined for sputtered “nascent” and “final” clusters vs the bombarding energy $E_B$ of the impinging Ar$^+$ ions

<table>
<thead>
<tr>
<th>$E_B$ (keV)</th>
<th>$Y_{tot}$</th>
<th>$\alpha$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>8.1</td>
<td>2.9</td>
<td>3.9</td>
</tr>
<tr>
<td>1</td>
<td>4.5</td>
<td>4.7</td>
<td>6.2</td>
</tr>
<tr>
<td>0.5</td>
<td>3.3</td>
<td>5.5</td>
<td>7.3</td>
</tr>
<tr>
<td>0.25</td>
<td>2.0</td>
<td>7.1</td>
<td>9.6</td>
</tr>
</tbody>
</table>
with exponents α which are given in table 2. It is seen that α increases drastically with decreasing bombarding energy, a finding which is qualitatively expected from fig. 2. Unfortunately, already at relatively small cluster sizes the distributions obtained from the MD simulation disappear in the statistical noise. Increasing the statistics of the calculation by increasing the number of calculated trajectories – although in principle possible – seems too time consuming to largely extend the range of cluster sizes observable in a MD simulation. On the other hand, decomposition of large nascent clusters may significantly contribute to the yields of final fragments (cf. section 3.3). Hence, we chose to extrapolate the power law dependence observed for small clusters towards larger cluster sizes as well and assume the size distribution of sputtered nascent clusters to be given by eq. (11) in a range extending up to n = 100.

3.3. Unimolecular decomposition of nascent clusters

Fig. 4 shows the average internal energy of sputtered nascent clusters as determined from the MD simulation. First, considering that all dissociation thresholds E_{th}^{(n,m)} calculated from the EAM potential assume values between 2 and 3 eV, it is evident that many clusters contain internal energies in excess of E_{th} and are therefore unstable. For later use, we define the survival probability p_{surv}(n) of a nascent cluster by the fraction of stable molecules detected among the total number of nascent clusters of a given size n. Evidently, p_{surv}(2) = 1, since nascent dimers are absolutely stable. A detailed analysis of the calculated internal energy distributions yields p_{surv}(3) = 0.2, p_{surv}(4) = 0.01 and p_{surv}(n \geq 5) = 0 [15]. The second important observation made in fig. 4 is the apparent linear increase of E_{int}^{aw} with increasing n which indicates that the average internal energy per constituent atom of a nascent cluster is practically independent of the cluster size. In fig. 4, the linear behavior of E_{int}^{aw} is observed up to n = 13. For larger values of n, only a few clusters could be detected and, hence, the statistical meaning of E_{int}^{aw} is questionable. It should be noted, however, that also up to the largest nascent cluster found by the MD simulation (n = 31) the linear behavior of E_{int}^{aw} is roughly continued. Hence, we feel safe to extrapolate to even larger clusters by a least square fit yielding

\[ E_{int}^{aw}(n) = (1.54n - 1.65) \text{ eV}. \]  

As already mentioned, we model the unimolecular decomposition of nascent clusters by assigning a fixed internal energy value of E_{int}^{aw}(n) to a given cluster size n. Then, using the formalism described in section 2, we employ a Monte Carlo simulation to calculate the size distribution of stable fragments M_{m} which remain at the end of the decomposition cascade. Fig. 5 shows a typical result for three arbitrarily chosen nascent cluster sizes of n = 10, 20 and 40. It is seen that in all cases the dominating fragments are dimers and atoms. This is understandable from the dissociation threshold energies E_{th}^{(n,m)} calculated by eq. (5). For small nascent clusters (n < 10), E_{th}^{(n,m)} is always lowest for m = 2, and the evaporation of a dimer is therefore the most probable dissociation reaction. This is different if the original cluster is large. Here, evaporation of single atoms becomes more favoured and, hence, the ratio between the numbers of final atoms and dimers is increased. In addition, a second peak is observed in the fragment distribution of large clusters. Obviously, the original unstable M_{n} cluster cools down by repeatedly evaporating small particles and eventually reaches itsterminal size at about m \sim n/3.

From the size distributions of stable fragments M_{m}, we calculate fraction functions f_{m}(n) which denote the

![Fig. 4. Average internal energy of sputtered “nascent” clusters as determined from the MD simulation.](image-url)

![Fig. 5. Distribution of stable fragments M_{m} produced by unimolecular decomposition of unstable nascent clusters M_{n}.](image-url)
fraction of atoms contained in an original unstable nascent cluster \( M_n \) which eventually end up in final clusters \( M_m \). Fig. 6 shows plots of the resulting \( f_m(n) \) vs the size \( n \) of the parent cluster. For comparison, corresponding data extracted from the MD simulation have been included as horizontal bars. It is seen that the MD results, which due to statistical reasons were averaged over the range of nascent cluster sizes indicated by the length of the bar, agree almost perfectly with the Monte Carlo calculations. Two interesting features can be seen from the figure. First, final dimers are preferably formed by fragmentation of small clusters, but also represent the major contribution to the final fragment spectrum of nascent clusters containing up to 100 atoms. At the same time, the contribution of final atoms increases with increasing \( n \), as is expected from the dissociation threshold values as explained above. Second, it is seen that only a specific range of nascent cluster sizes centered around \( n \approx 3m \) contributes to the yield of a final fragment \( M_m \) containing three or more atoms. This finding is consistent with the terminal sizes of nascent clusters determined above.

Using the fraction functions displayed in fig. 6, the contribution of fragmentation to the yield of sputtered clusters of a given size \( m \) can be calculated from

\[
\Delta Y_{\text{frag}}(m) = \sum_{n > m} Y_{\text{nasc}}(n) \frac{n}{m} f_m(n). \quad (13)
\]

The term \( n/m \) on the right hand side must be included to convert \( f_m(n) \) into the number of final fragments \( M_m \) produced per nascent cluster \( M_n \). In order to calculate the total cluster yield \( Y(m) \) detectable far away from the surface, this contribution must be added to the number of stable nascent clusters given by \( Y_{\text{nasc}}(m) p_{\text{surv}}(m) \). Inserting eq. (11) for \( Y_{\text{nasc}}(m) \), we obtain

\[
Y(m) \propto m^{-\alpha} p_{\text{surv}}(m) + \frac{1}{m} \sum_{n > m} n^{-(\alpha - 1)} f_m(n). \quad (14)
\]

Fig. 7 shows the size distribution of sputtered clusters calculated by means of eq. (12) using a value of \( \alpha = 2.9 \). According to table 2, this corresponds to a primary ion energy \( E_B = 5 \) keV. For comparison, the distribution of nascent clusters [eq. (11)] has been included in the figure. It is seen that \( Y(n) \) decreases more rapidly with increasing cluster size than \( Y_{\text{nasc}}(n) \). This finding is easily understandable, since the unimolecular decomposition obviously shifts yield contributions from larger to smaller clusters. The major conclusion which can be drawn from fig. 7 is that the final cluster yields can also be roughly approximated by a power law dependence

\[
Y(n) \propto n^{-\delta}
\]

yielding an exponent of \( \delta = 3.9 \). Although not explicitly shown here, we state that similar power law dependences were also found for all other bombarding energies with, however, different exponents \( \delta \) which are listed in table 2. As seen from the table, the value of \( \delta \) increases strongly with decreasing \( E_B \), a finding which
is of course expected from the results presented in section 3.1. Interestingly, the ratio of $\delta$ and $\alpha$ in table 2 seems to be fairly constant, indicating

$$Y(n) \propto \left[ Y^{\text{nas}(n)} \right]^{1/3}$$

independent of the bombarding conditions.

4. Conclusion

Using a very simple model, we have studied the unimolecular decomposition of ejected unstable species produced during sputtering of a generic metal surface. In particular, the yields of sputtered "final" clusters which represent the stable end products of fragmentation chains taking place within the flux of sputtered particles were calculated. Only these values can be compared to corresponding experimental data on sputtered cluster yields, since the large majority of the decomposition processes involved occur on a time scale which is much faster than any experimental detection scheme. It is found that the calculated final cluster yields exhibit a power law dependence on the cluster size. Apparently, this is in good agreement with the experimental findings on sputtered silver clusters reported in part I of this work [6] and on copper and aluminum clusters measured by Coon et al. [11,12]. However, the exponent $\delta = 3.9$ calculated here for the same bombarding energy as used during the experiment described in part I (5 keV) is lower than the experimental value of $\delta = 6.5$. We attribute this to the fact that the EAM potential used here overbinds the silver clusters. As a consequence, predicted cluster yields will necessarily be too high, and the amount of overestimation will presumably increase with the number of bonds involved in the formation of a sputtered cluster. Hence, the size distribution of sputtered clusters calculated from the EAM potential cannot be expected to quantitatively reflect the mass distribution of sputtered particles measured for silver. The calculations can, however, predict trends in a semi-quantitative manner. For instance, the data presented in table 2 clearly indicate that the observed distribution must be strongly dependent on the bombarding conditions (i.e. the nature, impact angle and energy of the primary ions and the nature of the target material) employed in a particular sputtering experiment. This explains why experimental mass distributions determined for sputtered silver, copper and aluminum clusters show different exponents. In fact, a clear anti-correlation can be extracted from table 2 between the total sputtering yield on one hand and the calculated exponent on the other hand. Since under the specific conditions employed in the different experiments the sputtering yield decreases between silver ($Y_{\text{tot}} \approx 8$), copper ($Y_{\text{tot}} \approx 5$) and aluminum ($Y_{\text{tot}} \approx 2$) [32], the drastic increase of the measured exponents between $\delta = 6.5$ (Ag$_n$) [6], $\delta = 7.9$ (Cu$_n$) [11] and $\delta = 9.3$ (Al$_n$) [12] is almost quantitatively predicted by the present calculation.

Apart from predicting the cluster yields, the results presented in section 3 also offer a possibility to understand the preferred charge state of sputtered clusters. Experimentally, it is found that large silver clusters leave the surface predominantly as positively charged ions (cf. part I of this work [6]). In view of the high internal excitation of nascent clusters, this finding may be rationalized in terms of thermionic emission of an electron subsequent to the sputter ejection event. This process, which provides an additional cooling mechanism in concurrence with the unimolecular fragmentation reactions discussed above, has been observed experimentally as the so-called delayed ionization of photo-excited neutral metal [33] and other [34,35] clusters. It should be feasible if the average internal energy of a sputtered nascent cluster exceeds its ionization potential. Comparison of the respective values calculated from eq. (12) with ionization potential data taken from ref. [36] reveals that this condition is fulfilled for silver clusters containing more than five atoms. Since $E_{\text{lat}}^* \text{ increases}$ with increasing cluster size while at the same time the ionization potential decreases, thermionic electron emission will be a likely process for large nascent and, hence, also final clusters.

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References

[28] Ref. [27], p. 10.