Internal energy of sputtered clusters: The influence of bombarding conditions

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Abstract

We have investigated the internal (vibrational) excitation of nascent clusters formed during sputtering of metal surfaces. On one hand, theoretical model calculations were performed by Molecular Dynamics computer simulation using the MD/MC-CEM many body interaction potential. On the other hand, experimental data were collected by studying the fragmentation lifetimes of sputtered cluster ions on time scales of $10^{-9} - 10^{-6}$ s after their ejection and conversion of the resulting lifetime distributions into the distributions of internal energies. It is found that sputtered clusters possess average internal energies of about 1 eV per constituent atom, corresponding to vibrational temperatures of several thousand K. Special emphasis was put on the influence of the bombarding conditions on these results. Surprisingly, neither the nature or kinetic energy of the primary ions nor the bond strength of the ejected clusters seem to significantly influence the average internal energy. © 1998 Published by Elsevier Science B.V.

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1. Introduction

The interaction of keV ions with solid surfaces leads to the ejection of particles into the gas phase (sputtering). It is well known that the flux of sputtered material contains atoms and, in general, molecules or clusters. The formation of these latter species, which may contain up to several 100 atoms [1], represents an intriguing phenomenon in sputtering physics. In general, Molecular Dynamics computer simulations provide an efficient tool to model the complex collisions and interaction processes which may lead to the sputter ejection of polyatomic species. From such simulations, a picture has emerged in which the formation of sputtered clusters is divided into two steps [2–8].

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First, nascent clusters are ejected from the surface due to correlated atomic collisions from the volume beneath the surface which is energized by the impinging primary ion. Due to the collisional nature of their formation, these clusters contain a relatively high amount of internal energy and are mostly unstable with respect to dissociation. In a second step, nascent clusters will therefore undergo unimolecular fragmentation processes during their flight away from the surface, until at very large distances only stable fragments remain. Since most experimental methods detect sputtered particles on time scales of microseconds after their ejection, it is these (meta)stable final species which are readily accessible by experiment. As a consequence, size distributions as well as kinetic energy distributions have been measured for final clusters sputtered from a number of metallic and semiconductor surfaces (for a fairly recent review see [9,10]). While most of the earlier data were accumulated on sputtered ionic species (secondary cluster ions), a number of recent investigations was devoted to the detection of neutral clusters which were post-ionized by laser-photoionization. However, the information obtained from these data is always convoluted with the unimolecular decay processes occurring above the surface. With regard to the collisional processes governing the cluster formation mechanism in sputtering, it is therefore highly desirable to directly investigate the properties of sputtered nascent clusters. While this is relatively straightforward in computer simulations, it represents an extremely difficult experimental task due to the very short fragmentation times involved. For sputtered ionic clusters, fragmentation processes with lifetimes of microseconds and above can be detected by a method which is based on the measurement of the energy loss experienced by a cluster upon fragmentation in the ion accelerating field [11,12]. Only recently, it has become possible to extend this method to time scales ranging down to nanoseconds [13,14]. By extrapolation to even shorter times, this method then allows to extract information about the internal energy distribution of nascent clusters. In the present work, we compare the average internal energy of sputtered Fe$_n^+$ and Nb$_n^+$ cluster ions determined by this method to the prediction of theoretical MD simulations. Particular emphasis will be put on the influence of the bombarding conditions such as the nature or kinetic energy of the primary ion. Moreover, the role of the cluster bond strength will be discussed.

2. Experimental

The experimental procedure to determine the internal energy distribution of sputtered nascent clusters has been described in great detail elsewhere [15,14]. In short, a double focusing mass spectrometer consisting of a magnetic sector and an electrostatic prism is used to detect ionic clusters which are sputtered from clean metallic samples by 9 keV rare gas ions generated by a duoplasmatron ion gun. The secondary ions are accelerated from the sample surface by an extraction field of about $10^6$ V/m. The nominal kinetic energy of a singly charged particle leaving the surface with zero initial kinetic energy is then determined by the applied extraction voltage $U_{ac}$ which has been varied between 2500 and 5000 V. Keeping the pass energy of the electrostatic energy analyzer fixed at this value, the kinetic energy distribution of the sputtered particles can be measured by variation of the sample potential.

![Fig. 1. Kinetic energy distributions of Cu$_3^{+}$ and Cu$_5^{+}$ cluster ions sputtered from a polycrystalline copper surface by bombardment with 9-keV Ar$^+$ and Xe$^+$ ions, respectively.](image-url)
Typical spectra of this type which were accumulated for Cu\textsuperscript{+} cluster ions sputtered from a polycrystalline Cu target are displayed in Fig. 1. At energies higher than \( eU_{ac} \), particles are detected which leave the surface with initial kinetic energies above zero, and the spectrum measured in this energy range therefore simply represents the kinetic energy distribution of sputtered (stable) particles. At kinetic energies lower than \( eU_{ac} \), on the other hand, a long tail is detected which is more pronounced for larger clusters and practically absent for atoms. This tail towards “negative” kinetic energies is attributed to the occurrence of unimolecular fragmentation reactions of the type

\[ X_n^+ \rightarrow X_{n-m}^+ + X_m \]  

(1)

during the acceleration of sputtered nascent \( X_n^+ \) ions. If fragmentation occurs at a distance \( d \) from the surface, the kinetic energy of the fragment ion is lowered due to the mass loss, and the fragment ion will leave the acceleration region with a kinetic energy deficit of

\[ E_d = eU(d) \frac{m}{n}, \]  

(2)

where \( U(d) \) denotes the electrostatic potential at the fragmentation point. If the initial kinetic energy of the cluster is neglected and only one fragmentation channel corresponding to a particular value of \( m \) is active, the distribution of \( E_d \) will therefore reflect the fragmentation time distribution by

\[ \frac{dN}{dt}(t) \propto I_i(E_d[t]) \frac{dE_d}{dt} \]  

(3)

with \( I_i \) being the measured intensity at energy \( E = eU_{ac} - E_d \), \( E_d(d) \) given by Eq. (2) and the relation \( d(t) \) determined by the equation of ion motion within accelerating electric field. A detailed description of the conversion procedure as well as a thorough discussion of the underlying assumptions can be found in refs. [13,14]. The distribution of fragmentation times which is calculated using Eq. (3) is found to follow a power law dependence and is therefore approximated by a function

\[ F(t) = b(t + c)^{-a} \]  

(4)

with parameters \( a, b \) and \( c \) which are determined by a non-linear least squares fitting procedure. With the assumption that \( F(t) \) represents a superposition of exponential decay functions

\[ F(t) = \int_0^\infty k \varphi(k) \exp(-kt) \, dk, \]  

(5)

this function can be converted into the distribution \( \varphi(k) \) of fragmentation rate constants \( k \), which is then converted into the distribution of internal energies by

\[ \Psi(E_{int}) = \varphi(E_{int}) \frac{dk}{dE_{int}} \]  

(6)

using the quantum mechanical version of conventional RRK theory [16]

\[ k = k_0 \frac{i!}{(i-j)!(i+s-1)!} \frac{j!}{(i-j)!(i+s-1)!} \]  

(7)

to connect the fragmentation rate \( k \) with the internal energy \( E_{int} = \frac{\ih \omega}{2} \) and the dissociation threshold \( E_{diss} = \frac{\ih \omega}{2} \). In Eq. (7), \( k_0 \) represents a typical vibration frequency of the cluster, the value of which is arbitrarily set to 10\textsuperscript{15} s\textsuperscript{-1}. The necessary values of the dissociation energies \( E_{diss} \) of the cluster ions were either taken from literature data [17] or from measurements of the kinetic energy release upon fragmentation as described in much detail in [14].

3. MD simulation

The molecular dynamics simulation as well as its extension towards the formation and fragmentation of clusters in sputtering has been described in great detail earlier [2,8]. In short, the classical equations of motion are solved numerically for all atoms of a crystallite which in the present case has a surface area of 40 \( \times \) 40\AA\textsuperscript{2}, a thickness of nine atomic layers and contains approximately 2300 metal atoms. While the interaction between the impinging ion and the metal atoms was described by a conventional pair potential of the Molière type, a many-body potential originally designed by DePristo and coworkers [18,19] was used to describe the interaction between target atoms. The func-
tional form of this potential, which has been termed “Molecular Dynamics and Monte Carlo – Corrected Effective Medium” (MD/MC-CEM), as well as details about its construction can be found in Refs. [19,20]. For the present purpose, it is worth noting that this potential, which is fit to spectroscopic data of dimers as well as to the cohesion energy and elastic constants of the bulk solid, provides a fairly accurate description of the bond energies of small clusters [8,19].

The identification and classification of sputtered clusters was done in the same way as described in detail in Ref. [2]. Briefly, the trajectory integration of the collision cascade initiated by the impinging primary particle was terminated at a time when the total energy of all atoms within the model crystal had fallen below zero. In general, this condition was reached at times of a few hundred femtoseconds (fs) after the primary ion impact. Only at the highest primary ion energy of 5 keV, about 25% of the calculated trajectories did not reach this condition before being stopped at a maximum integration time limit of 1000 fs, for lower bombarding energies this value was much lower. Upon termination, the list of ejected atoms obtained for a given primary ion impact was examined for agglomerates of two or more atoms, the total (i.e. the sum of potential and relative kinetic) energy $E_{\text{tot}}$ of which was detected to be negative. These species, which we call “nascent clusters” consisting of $n$ atoms, were then subjected to a stability check by evaluating their total internal energy according to

$$E_{\text{int}} = E_{\text{tot}} + E_a(n)$$

and comparing it to the dissociation energy $E_{\text{diss}}$, i.e. the lowest energy threshold

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

for unimolecular decomposition reactions given by

$$M_n \rightarrow M_{n-m} + M_m \quad (m = 1, \ldots, n-1).$$

The cluster atomization energies $E_a$ as given by the MD/MC-CEM potential were determined by means of an additional MD simulation involving repetitive melting and freezing of the clusters, for details of this procedure the reader is referred to [8,19].

As described in Section 4, the experimental data on internal energies were accumulated for Fe and Nb$^+$ cluster ions sputtered from the respective metallic surfaces. Ideally, it would of course be desirable to perform MD calculations for ion bombardment of these metals. Unfortunately, both metals have bcc crystal structure, which is not predicted to be the most stable structure by spherically symmetric potentials like the MD/MC-CEM potential. Therefore, we have used a potential which was fit to the properties of solid silver and the Ag$_2$ dimer, respectively. The reason for choosing this particular potential is that we have worked with it before and know that it predicts reasonable yields and kinetic energy distributions of sputtered particles, and in particular allows a fairly accurate description of the experimental yield distribution of sputtered silver clusters. Nevertheless, we regard the simulation results as representative for a generic metal (in the following abbreviated as Me), the clusters of which (Me$_n^+$) are characterized by the dissociation threshold energies displayed in Table 1. It is worth noting that these energies are quite comparable to those of Fe$^+_n$ cluster ions (see Table 1). We are therefore confident that the

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<tr>
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<tr>
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<td>6.00</td>
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<td>6.53</td>
<td>5.93</td>
<td>5.78</td>
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* The Me$_n^+$ data were extracted from the MD/MC-CEM potential used in the MD simulations, the cluster ion values represent experimental data which were taken from Ref. [17]. Values are given in eV.
general trends predicted by the simulations are valid at least for Fe as well.

4. Results and discussion

From our previous MD simulations as well as from a number of experiments, it is known that the yield of sputtered nascent and final clusters strongly depends on the bombarding conditions. More specifically, larger cluster yields are generally found under conditions which correspond to larger total sputtering yield. Hence, it is of interest to investigate if there is also an influence of the bombarding conditions on the internal energy distribution of the sputtered clusters. Fig. 2 shows such distributions which are extracted from MD simulations of Ar$^+$ and Xe$^+$ ions normally incident onto a Me (1 1 1) surface with various kinetic energies. The resulting total sputtering yields vary from 3.9 atoms/ion (500 eV Ar$^+$) to 10.5 atoms/ion (5 keV Ar$^+$). It is seen that the internal energy distributions are practically independent of the bombarding conditions. This is also reflected in the cluster size dependence of the average internal energy which is plotted in Fig. 3. At a first glance, the negligible influence of the bombarding conditions might be surprising, since one would, for instance, expect the introduction of more energy into the collision cascade by higher bombarding energies to lead to higher internal energies. In order to qualitatively rationalize the result, one may argue that primary ions with higher kinetic energies penetrate deeper into the solid, therefore the spatial extension of the collision cascade becomes larger and the bombarding energy is distributed over this larger volume. The linear dependence observed in Fig. 3, which can be fit by

$$E_{\text{int}}^\text{av} = (1.40n - 1.86) \text{ eV},$$

has been noted before [2,8]. Using a cluster heat capacity of

$$C = (3n - \frac{9}{2}) k_B,$$

the slope of the straight line depicted in Fig. 3 converts into an internal cluster temperature of 5400 K.

In order to permit a quantitative comparison with the MD simulation results, it would be much desirable to perform the same type of experiment as described in Section 2 on Ag$_n^+$ cluster ions sputtered from silver. Unfortunately, for most of these cluster ions two competing fragmentation channels

Fig. 2. Internal energy distributions of nascent Me$_3$, Me$_4$ and Me$_5$ clusters which are sputtered from a Me(1 1 1) single crystal surface by normally incident Ar$^+$ and Xe$^+$ ions of various kinetic energies. The data were produced by MD computer simulation.

Fig. 3. Average internal energy of sputtered nascent Me$_n$ clusters as calculated by MD computer simulation versus cluster size $n$. 
according to Eq. (1) with \( m = 1 \) and \( m = 2 \) have been observed [21]. As a consequence, the conversion of kinetic energy deficits into fragmentation times by means of Eq. (3) is not unambiguous, and therefore the determination of fragmentation rate constant distributions and, hence, internal energy distributions, cannot be accomplished for Ag\( ^{\dagger} \) clusters in a straightforward manner. Previously published experimental data on sputtered Ta\( ^{\dagger} \) [14] and Nb\( ^{\dagger} \) [15] clusters, on the other hand, do not seem to be ideally suited for comparison with our simulations, since the binding energies of these species are much larger than those of silver clusters (see Table 1). In principle, it can be imagined that the average amount of internal energy stored in a sputtered cluster may be influenced by its stability with respect to fragmentation. We have therefore repeated the experiment on sputtered Fe\( ^{\dagger} \) cluster ions, the binding energies and, hence, dissociation thresholds of which are comparable to those of silver clusters as shown in Table 1. Fig. 4 shows the average internal energy of Fe\( ^{\dagger} \) cluster ions sputtered from a polycrystalline iron surface by 9-keV Xe\( ^{\dagger} \) ions impinging under 45\( ^\circ \). The data have been extracted from measurements of the kinetic energy distributions of the cluster ions as described in Section 2, details of the experiment and the data reduction procedure will be published elsewhere [22]. From the comparison of Figs. 3 and 4, is seen that the measured average internal energy is of the same order as that predicted by the simulation. Moreover, even the predicted linear dependence of \( E_{\text{int}} \) on the cluster size is reproduced very well by the experiment. The least squares fit indicated in the figure corresponds to

\[
E_{\text{int}} = (0.86n - 0.75) \text{ eV},
\]

the slope converts to an internal cluster temperature of about 3300 K. In order to examine the question regarding the influence of the cluster binding energy on these results, we plot in Fig. 5 similar data on sputtered Nb\( ^{\dagger} \) clusters which have been previously measured [15]. Also in this case, a linear cluster size dependence of the average internal energy is found. Interestingly, the slope of 0.81 eV corresponding to a cluster temperature of about 3100 K is about the same as that obtained for Fe\( ^{\dagger} \) clusters. In view of the large difference in cluster binding energy, this finding appears to be surprising, since at higher binding energies one would expect ensembles of sputtered atoms with higher relative energy to be kept together as nascent clusters during the ejection process. Obvious-

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Fig. 4. Average internal energy of nascent Fe\( ^{\dagger} \) cluster ions sputtered from a polycrystalline Fe surface by 9-keV Xe\( ^{\dagger} \) ions versus cluster size \( n \). The data were evaluated from experimental kinetic energy distributions like those shown in Fig. 1.

Fig. 5. Average internal energy of nascent Nb\( ^{\dagger} \) cluster ions sputtered from a polycrystalline Nb surface by 9-keV Xe\( ^{\dagger} \) ions versus cluster size \( n \). The data were evaluated from experimental kinetic energy distributions like those shown in Fig. 1.
ly, the internal energy distribution of sputtered clusters is determined by the energetics of the collision cascade initiating the sputtering event rather than by those of the formed clusters themselves, at least as long as the cluster binding energy exceeds the average internal energy. Inspection of the data presented in Fig. 2 seems to point in this direction: For Me$_3$, the peak of the internal energy distribution is very close to the atomization energy of $E_a = 3.3$ eV, and therefore the distribution seems to be more or less abruptly terminated at $E_a$. In this case, one could expect an increase of the average internal energy upon increasing the value of $E_a$. For Me$_4$ and Me$_5$, on the other hand, the distributions approach zero much more smoothly, and the relative contribution of the highest possible internal energies is smaller. As a consequence, an increase of the atomization energy would presumably not alter the average internal energy of these clusters very much. In any case, our experimental data indicate that the average internal energy of sputtered clusters is not strongly influenced by the cluster binding energy.

Another point of interest concerns the dependence of the experimentally determined internal energy distribution on the bombarding conditions. Here, we re-examine the data presented in Fig. 1 by plotting the logarithm of the measured signal versus the square root of the energy deficit $E_d$ as shown in Fig. 6. The reason for choosing this particular plot is that $\sqrt{E_d}$ should be proportional to the fragmentation time, and the slope of the curves displayed in Fig. 6 therefore represents the average fragmentation rate constant [23]. Two observations can be made from the figure. First, it is seen that the absolute number of fragmenting clusters is larger under bombardment with Xe$^+$ ions. This finding is reasonable, since for Xe$^+$ the total sputtering yield is higher than for Ar$^+$-bombardment (~9 atoms/ion versus ~6 atoms/ion [24]), and it is known that the relative yields of sputtered nascent clusters increase with increasing sputtering yield. Second, and probably more important, the slope of the distribution is seen to be identical in all cases. This means, that the distribution of fragmentation rate constants and, hence, the internal energy distribution of the sputtered clusters does not depend on the type of the primary ion. In agreement with the simulation data presented in Fig. 2, we therefore conclude that the internal energy distribution of sputtered nascent clusters is not significantly influenced by the bombarding conditions.

5. Conclusion

We have presented a combination of Molecular Dynamics computer simulations and experimental data to investigate the role of the bombarding conditions with respect to the internal energy of clusters generated by sputtering. Three major conclusions can be drawn from this work. First, the average internal energy of sputtered nascent clusters increases linearly with increasing cluster size, the slope corresponding to internal cluster temperatures of several thousand K. Second, the internal energy distribution of sputtered clusters appears to be independent of the nature and the kinetic energy of the primary projectiles initiating the sputtering event. This finding is in marked contrast to the relatively strong dependence observed for the cluster yields. Third, the average internal energy seems to be fairly independent of the cluster binding energies. This observation, which so far is based exclusively on experimental data, is surpris-
ing and should be examined in further MD simu-
lations using an interaction potential which can
treat the cluster binding energies as adjustable pa-
rameters.

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