Self sputtering yields of silver under bombardment with polyatomic projectiles

A. Duvenbeck, M. Lindenblatt, A. Wucher *

Department of Physics, Institute of Experimental Physics, University of Duisburg-Essen, D-45117 Essen, Germany

Abstract

Molecular dynamics (MD) have been employed to model self sputtering yields of an Ag(111) surface under bombardment with Ag\textsubscript{m} (m = 1, 2, 3, 4) projectiles. It is shown that the effect of projectile orientation on the sputter yield decreases strongly with increasing m and becomes practically negligible under Ag\textsubscript{4} impact. For polyatomic projectiles we observe a nonlinear yield enhancement which is discussed in terms of the collisional spike model of Sigmund and Claussen. It is shown that the MD simulation provides a unique method to determine the essential input parameters \(T_0\) and \(\langle \rho_0^2 \rangle\) entering that model.

© 2004 Elsevier B.V. All rights reserved.

PACS: 31.15.Q; 31.70.Ks; 79.20.Ap

Keywords: Molecular dynamics simulations; Sputtering; Nonlinear effects; Cluster bombardment; Collisional Spikes

1. Introduction

The bombardment of solids with keV-ions leads to the removal of particles from the surface due to the evolution of mostly elastic collision cascades. This process is usually called sputtering. An interesting question in this context relates to phenomena occurring in the case of spatial and temporal overlapping of collision cascades. Because of the extremely short lifetime of collision cascades (~1 ps) and their limited spatial extension (several nm), this scenario can only be experimentally realized by using polyatomic projectiles, i.e. clusters composed of several atoms. Andersen and Bay [1] as well as Thompson and Johar [2] and, more recently, Andersen et al. [3,4] have demonstrated that in the case of polyatomic bombardment the total sputtering yield \(Y\), i.e. the average number of atoms sputtered per impinging projectile, may significantly exceed the sum of the yields induced by the constituent atoms arriving separately with the same impact velocity. These large nonlinearities have also been found in recent molecular dynamics simulations. 

* Corresponding author. Tel.: +49 201 183 4141; fax: +49 201 183 93 4141.
E-mail address: wucher@uni-essen.de (A. Wucher).
computer (MD) simulations that have been carried out for various cluster projectiles and surfaces [5–10]. While most of these studies have been performed for a fixed size of the impinging clusters, the present work aims at a systematic investigation of the effect of projectile nuclearity on nonlinear yield enhancements. For that purpose, we expand our previous work on self sputtering of an Ag(111) surface under bombardment with Ag\(_m\) \((m = 1, 2, 3)\) projectiles [8] to Ag\(_4\) projectiles. The results are interpreted in the context of the Sigmund–Claussen [11] collisional spike model of nonlinear sputtering.

2. Description of the calculation

We use a standard molecular dynamics code described in detail earlier [8] to follow the elastic collision cascades initiated by the impinging projectiles. Briefly, the classical Newtonian equations of motion are integrated numerically for all atoms of the system, i.e. for the projectile constituents and all atoms of an Ag(111) model crystallite containing about 10,500 atoms distributed over 15 atomic layers. The interaction among all atoms is described by the MD/MC-CEM many-body potential originally designed by DePristo and co-workers [12] which was fitted to the properties of silver.

The simulations are performed for Ag\(_m\) projectiles with \(m = 1, 2, 3, 4\) normally incident onto the Ag(111) crystallite at energies from 0.5keV to 8keV. Each projectile is assumed to impinge in its equilibrium ground state configuration as determined by the MD/MC-CEM potential. Most of the calculations have been carried out for a set of 120 impact points uniformly distributed over the smallest irreducible surface cell, to which the center-of-mass of the projectile was aimed. For \(m > 1\), those 120 events were calculated for different impact orientation of the projectile in order to investigate its influence on the total average sputter yield.

For the case of di- and tri-atomic projectiles, the employed impact orientation parameters as well as the projectile configurations have been described in detail in [8] and will therefore not be repeated here. For the equilibrium geometry of the Ag\(_4\) projectile we assume a tetrahedral structure with a side length of 2.71 Å as calculated in [13]. For simplicity, we only take into account three “main” types of impact orientation. The corresponding geometries, depicted in Fig. 1, differ from each other in the number of atoms simultaneously hitting the surface plane first. For each of the three illustrated impact configurations we additionally consider a three-fold azimuthal variation. In the case of the “tip” and “ground” orientation it is sufficient to cover the azimuthal range between 0° and 120° which was sampled using the equidistant values \(\varphi = 30°, 60°\) and 90°. The “twin” orientation only features a two-fold symmetry, and hence the azimuth interval \((0°, 180°)\) was sampled using the equidistant values \(\varphi = 45°, 90°\) and 135°. Therefore, a total of 12 different Ag\(_4\) impact orientations are calculated, which are equivalent to a total number of 1440 trajectories for most primary energies. At high

![Fig. 1. Illustration of the three main orientations of the Ag\(_4\) projectile: (a) “tip” orientation, (b) “ground” orientation, (c) “twin” orientation; the small points in the x–z-plane are the projections of the constituent atoms.](image-url)
bombarding energies $E_b \geq 5\text{keV}$, when the influence of the impact orientation on the average sputter yield can be neglected – as will be shown in detail later – the calculations are performed on a larger crystallite with 24,000 atoms and – due to the very time consuming trajectory integration – restricted to one fixed angular impact orientation. Moreover, test calculations have been performed for selected trajectories with even larger crystallites containing up to 155,000 atoms, but no significant changes of the resulting average sputter yields have been found.

3. Results

In order to illuminate nonlinear enhancement effects induced by the polyatomic character of the projectiles, we will compare the results for average total sputter yields obtained for projectiles of different nuclearity impinging onto the surface with the same impact velocity, i.e. the same energy per constituent atom. Under the assumption of a linear nature of collision dynamics, a plain superposition of the collision cascades initiated by the different constituents of the projectile should result in sputter yields which simply represent the sum of those determined for the constituents impinging independently from each other at the same velocity. Every deviation from this sum must therefore be considered as a nonlinear effect. Due to the fact that substituting a monoatomic projectile by a polyatomic species leads to additional degrees of freedom for the choice of impact orientation we will first discuss the dependence of the average sputter yield on the impact orientation.

3.1. Angular orientation effect

The variation of the average sputter yield as a function of the angular orientation of the projectile is compared for Ag$_2$ and Ag$_4$ impinging with the same kinetic energy of 4keV in Fig. 2. For each angular configuration, the average yield is calculated as the arithmetic mean value of that produced in the 120 individual trajectories. For Ag$_4$, all orientations are then averaged with the same statistical weight. For Ag$_2$, a slightly different averaging procedure is used which has been described in detail in [8]. It is seen that while the orientation of Ag$_2$ projectiles quite strongly influences the sputter yield, much smaller variations are found for Ag$_4$. From these observations, combined with similar data obtained for Ag$_3$ projectiles [8], we

![Fig. 2. Average sputtering yield for (a) Ag$_4$ bombardment and (b) Ag$_2$ bombardment as a function of impact orientation. For each main orientation and polar angle, respectively, the results for azimuthal variations are depicted in ascending order of $\varphi$.](image)
conclude that the impact orientation becomes less and less important with increasing nuclearity and impact energy of the projectile. In the case of Ag\textsubscript{4} bombardment, it is seen that its influence on the average sputtering yield is already of the order of the statistical error \( \Delta \approx 1.1 \). This finding is in accordance with other MD-investigations that have shown a decreasing influence of the individual impact point on the sputter process towards higher bombarding energy and projectile cluster size [6].

3.2. Sputter yields

The influence of the total impact energy \( E_B \) on the average sputter yield induced by an Ag\textsubscript{4} projectile in the energy range from 0.5 to 8keV is displayed in Fig. 3. For \( E_B \lesssim 4 \)keV, the data clearly indicate a linear dependence, whereas for higher energies we observe strong deviations from this linearity. The double-log plot in Fig. 3(b) shows a transition from linear to quadratic yield dependence on the bombarding energy. This result may be regarded as an indication of nonlinear sputtering and interpreted in terms of the collisional spike theory of Sigmund and Claussen [11]. In doing so, we note that [11] refers to a cylindrical spike geometry (which should be accurate in the limit of high projectile energies), while for the impact energy range explored here a hemispherical spike geometry may be more appropriate. The main results of the model, however, do not differ significantly between both descriptions [14]. More specifically, the linear cascade yield contribution

\[
Y_{\text{lin}} = 0.0484 \frac{F_D}{N \lambda_0 a^2 U} \tag{1}
\]

is assumed to be superimposed by an additional (thermal) spike contribution

\[
Y_{\text{sp}} = 0.0360 \frac{\lambda_0 a^2 F_D^2}{U^2} g \left( \frac{U}{kT_0} \right), \tag{2}
\]

with a function \( g \) that is given by

\[
g(\xi) = (1 + \xi^2) \exp(-\xi) + \xi^3 \int_\xi^\infty \frac{dr e^{-r}}{t}. \tag{3}
\]

In (1) and (2), \( \lambda_0 \approx 24 \) and \( a \approx 0.219 \)Å are constants familiar from linear cascade theory of sputtering, \( U \) is the surface binding energy and \( F_D = F_D(z=0) \) denotes the energy deposited per unit track length at the surface. The key parameter \( T_0 \) is the core temperature in a cylindrical

---

**Fig. 3.** Average sputtering yield for Ag\textsubscript{4} \( \rightarrow \) Ag(111) bombardment as a function of total impact energy; (a) linear plot, (b) plot with double-log scale.
spike volume of initial width $\langle r_0^2 \rangle^{1/2}$, which is related to $F'_D$ by

$$kT_0 = \frac{F'_D}{2\pi N\langle r_0^2 \rangle^{1/2}}.$$  \hspace{1cm} (4)

Combining (1) and (2) and assuming a number density $N = 5.85 \times 10^{-2}$ $\text{Å}^{-3}$ of silver target atoms, the spike model predicts the ratio of the total yield $Y = Y_{\text{lin}} + Y_{\text{sp}}$ and the linear yield $Y_{\text{lin}}$ to be

$$\frac{Y}{Y_{\text{lin}}} \approx 1 + 0.082 \cdot Y_{\text{lin}} \cdot g(U/kT_0). \hspace{1cm} (5)$$

In the frame of this model, the deviation from linearity observed in the MD simulation can therefore be used to determine the spike core temperature $T_0$. For the specific case of silver we assume $U = 2.95$ $\text{eV}$ (the sublimation energy) and evaluate $g$ numerically. For the case of 4-keV Ag projectiles, we estimate $Y_{\text{lin}}$ as four times the average sputtering yield of an Ag projectile impinging with $E_B = 1$ $\text{keV}$ ($\bar{Y} = 4.9$), underlying the assumption that in the latter case all sputtering originates from linear collision cascades. The spike contribution is then determined by subtracting $Y_{\text{lin}}$ from the calculated total average sputter yield, resulting in $Y_{\text{sp}}/Y_{\text{lin}} = 0.19$. The resulting spike core temperature deduced by inverting (3) is $T_0 = 1.5 \times 10^4$ $\text{K}$.

The value of $F'_D$ can also be easily extracted from the MD data. First, we determine the total stopping power $dE/dx$ experienced by all constituent atoms of the 4-keV Ag projectile within the first atomic layer of the target as described in detail in [8]. Using $F'_D = a \cdot dE/dx$ with $a \approx 0.3$ for equal target and projectile masses [15] yields $F'_D \approx 150$ $\text{eV/Å}$, which can now be inserted into (4) in order to calculate the initial track radius as $\rho_0 = 18$ $\text{Å}$. This value is of the correct order as predicted by theory [11,16] and in agreement with those derived from experimental yield data on Au$_m$ projectiles impinging onto gold and silver targets [3,4]. In principle, we can estimate $\rho_0$ from the MD simulation using, for instance, the lateral emission probability distribution of surface atoms around the impact point. As shown previously for $m = 1, 2, 3$ [8] and confirmed here for $m = 4$ as well, this distribution exhibits a maximum at distances $r$ around 5 Å from the impact point and then decays to zero towards large $r$. Defining, somewhat arbitrarily, the cascade radius as the distance where the emission probability has decayed to a fixed value of 3%, we obtain a cascade radius of about 20 Å for 4-keV Ag impact, which is in almost perfect agreement with the value of $\rho_0$ determined above. These observations indicate that the collisional spike theory works rather well to describe the yield nonlinearity predicted by the MD simulations.

For a further investigation of the parameter $T_0$, Fig. 4 shows the average sputtering yield as a function of projectile nuclearity for a bombarding energy of $E_B = 2$ $\text{keV/atom}$. In the absence of spike effects one would expect a linear increase of $Y$ as a function of $m$ (dotted line). Under the assumption that for 2-keV Ag projectiles the sputtering yield solely originates from linear collision dynamics, we can estimate a lower limit for the relative spike contribution to the total yield by evaluating

$$\frac{Y_{\text{sp}}}{Y_{\text{lin}}} = \frac{\bar{Y}_{\text{Ag}}(2 \text{keV})}{\bar{Y}_{\text{Ag}}(2 \text{keV})} - m \cdot \bar{Y}_{\text{Ag}}(2 \text{keV})$$

for each projectile. The obtained values can again be converted into $T_0$, yielding the data presented in Table 1. The magnitude of about $10^4$ K agrees with

![Fig. 4. Average sputtering yield as a function of projectile size for equi-velocity impact with a total kinetic energy of $E_B/m = 2$ $\text{keV}$. Dotted line: predictions from linear cascade theory; dashed line: theoretical prediction of thermal spike theory.](image-url)
what can be determined directly from the average kinetic energies of particles extracted from the MD simulation [17]. At this point, it is important to note that no knowledge of the parameter $q_i^2$ is necessary in determining $T_0$, and the MD simulation therefore allows the evaluation of this parameter without any degree of freedom. It is seen that $T_0$ increases approximately linearly with increasing projectile nuclearity $m$. In connection with the notion that the stopping cross section and, hence, the deposited energy $F_D$ also scales linearly with $m$ [18], this finding suggests that – for the range of $m$ and impact velocity explored here – the parameter $q_i^2$ in the spike model must be largely independent of the projectile size.

### 4. Conclusion

Molecular dynamics simulations of self sputtering phenomena at a silver surface reveal pronounced nonlinear yield enhancements if polyatomic projectiles are used. The results are found to be in accordance with the Sigmund–Claussen collisional spike model. In particular, the MD simulations provide a means to determine the input parameters $T_0$ and $\langle \rho_0^2 \rangle$ entering the analytical model. It is shown that under conditions of constant impact velocity the spike core temperature $T_0$ scales approximately linearly with the projectile nuclearity, while the initial spike dimension appears to be largely independent of the projectile size.

### Acknowledgements

The authors are greatly indebted to B.J. Garrison for providing the basis of the molecular dynamics simulation code used in this work. We also gladly acknowledge financial support from the Deutsche Forschungsgemeinschaft within the SFB 616 “Energy dissipation at surfaces”.

### References