Time-of-Flight Measurements of Nonlinear Effects in Sputtering by Dimer Ions

D. J. Oostra, R. P. van Ingen, A. Haring, A. E. de Vries, and F. W. Saris
FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands
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Time-of-flight distributions of sputtered Au atoms have been measured under 4 keV I^+ and 8 keV $I_2{}^+$ impact. The results show that a developing thermal spike contributes to the sputtering yield. It is higher under $I_2{}^+$ bombardment but the measured temperature obtained from Maxwell-Boltzmann fits is lower, suggesting a lower effective surface binding energy U_0 for $I_2{}^+$ bombardment. A correlation between spike temperatures and U_0 is discussed.

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Bombardment of solids by energetic ion beams generally leads to erosion, or so called sputtering. Sputtering has become an important field of research, among others, because of technological applications.[1] The theory of sputtering is based predominantly on the work of Sigmund[2] in which sputtering is visualized as follows: An energetic ion hitting a solid loses its energy via elastic and inelastic collisions with target atoms. Recoiling target atoms can cause new collisions with target atoms at rest. This leads to the development of a collision cascade (CC). When target atoms obtain sufficient energy to overcome the surface barrier, they can be ejected from the solid, which leads to sputtering. The time scale of this mechanism is 10^{-13} s. The linear CC theory predicts sputtering yields[2] and predicts kinetic energy distributions[3] of the form $dS/dE = CE/(E+U_0)^3$. S is the flux of sputtered species, E their kinetic energy, and U_0 the surface binding energy. C is a constant.

Experiments show that in specific cases the theory does not hold. Heavy metals have been bombarded by dimer ions and by atomic ions with the same velocity.[4-6] The dimer ions dissociate at the first collision, and both atoms lose their kinetic energy to the target atoms independently. The linear CC theory predicts that the sputtering yield per atom is the same in case of dimer ions and atomic ions, when the atomic ions have half the energy of the dimer ions. However, it is observed that for dimer ions the sputtering yield per atom can be higher.

It has been suggested that in these cases the CC has become so dense that moving particles collide with each other.[7-11] The CC ends up in a hot spot or thermal spike, from which target atoms can evaporate. When an equilibrium is reached, the kinetic energy distribution becomes Maxwell-Boltzmann-type (MB): $dS/dE = CE \times \exp(-E/kT)$. T is the temperature in the spike and k is the Boltzmann factor. The time scale of this sputtering mechanism is 10^{-11} s.

The enhancement of the sputtering yield, in the case of dimer-ion bombardment, can be explained by assuming that the two cascades overlap. This leads to a higher mean kinetic energy in the volume encompassed by the two cascades, and thus to a higher temperature in the spike. The sputtering yield will be higher because at a higher temperature the evaporation flux will be higher.

However, the sputtering mechanism in the nonlinear regime has not been firmly established. A general point of doubt is whether a thermal spike in equilibrium can exist.[11] As an alternative, shock-wave models are also used to explain results.[12,13]

Computer simulations of CC's indicate that sputtering takes place predominantly by multiple collisions[14] within 10^{-13} s after ion impact. After $\sim 10^{-12}$ s, local melting of the solid takes place leading to a thermal spike.[15] However, the spike does not contribute significantly to sputtering. This observation led to the conclusion that also in the case of nonlinear sputtering spikes do not contribute significantly to sputtering.[16]

Experimental results do not allow us to draw definite conclusions about the question of whether a spike in equilibrium can exist. Kinetic energy distributions of sputtered atoms have been obtained in the case of heavy-ion bombardment of heavy target materials. The observed MB-type distributions suggest that the CC's are so dense that spikes are formed.[17-20]

Other results are in contradiction with the spike model. Ahmad, Farmery, and Thompson[19,20] measured the kinetic energy distributions of Au atoms sputtered from Au by Ar^+, Kr^+, and Xe^+ ions. With increasing ion mass, the cascade becomes more and more dense. Then the mean kinetic energy per atom in the volume in which the cascade develops, is increasing. Thus the spike model predicts an increase in the spike temperature. However, the kinetic energy distributions of sputtered atoms show the opposite behavior.

Energy spectra of sputtered atoms under molecular-ion bombardment are needed to obtain more information on the nonlinear sputtering mechanism, as Sigmund has pointed out several times.[8,11] In this Letter such measurements are presented for the first time.

The experimental setup has been discussed previously[21] and therefore only briefly outlined here. I^+ and $I_2{}^+$ ions generated from I_2 gas in a unoplasmatron ion source are extracted and mass selected by a Wien filter. The beam of I^+ or of $I_2{}^+$ ions bombards a polycrystalline Au substrate with a flux of $\sim 10^{13}$ ions/cm^2 s under an angle of 55° with the substrate normal. Sputtered Au atoms are ionized after a flight path of 37 cm, mass selected by a quadrupole mass spectrometer, and detected by an electron multiplier. The incident ion beam is chopped electrostatically with a pseudorandom code. After deconvoluting the measured spectra, time-of-flight distributions are obtained. The total count rate of sputtered Au atoms indicates that nonlinear effects are observed in the sputtering of Au by I_2^+ ions. At the same current density, the Au count rate under 8-keV I_2^+ ion bombardment is ~ 3 times higher than under 4-keV I^+ bombardment. Thus the count rate per I atom is ~ 1.5 times higher under I_2^+ ion bombardment. The time-of-flight distributions of Au atoms sputtered by 4-keV I^+ and 8-keV I_2^+ are displayed in Fig. 1. When linear sputtering theory is applicable, the distributions should be the same. However, the distribution obtained for I_2^+ shows an enhanced count rate of particles with long flight times (corresponding to low kinetic energies).

After correction for the ionizer efficiency, kinetic energy distributions can be obtained from the distributions in Fig. 1.[22] These are displayed in Fig. 2. Clearly visible is the higher flux of species with low kinetic energies in the case of I_2^+ as compared to I^+ bombardment. Both spectra show an E^{-2} behavior at the high-energy side, which is characteristic for a CC mechanism. However, a fit with a CC distribution cannot reproduce the experimental distributions completely. It can explain only 62% of the intensity in the spectrum obtained under I^+ bombardment and only 38% of that obtained under I_2^+ bombardment.

In both cases the spectrum at energies below 10 eV can be fitted with a MB distribution at a high temperature. This suggests that a spike mechanism also contributes to the sputtering. The best fits are obtained with a temperature of 3.3×10^4 and 2.3×10^4 K for the spectra obtained under I^+ and I_2^+ bombardment, respectively.

In Fig. 1 extra peaks near 0.04 ms are present in the time-of-flight spectra, which correspond to the humps near 50–100 eV on top of the E^{-2} slope in the energy distributions in Fig. 2. These peaks might be ascribed to sputtering by direct knockoff collisions. The spectra suggest that for I_2^+ bombardment this contribution of knockoffs per I atom is higher, than for I^+ bombardment. Unfortunately, the resolution in this energy range is poor.

The results are very surprising. First, Kelly indicates that evaporation from a thermal spike can be expected when the temperature in the spike is so high that the (equilibrium) vapor pressure is $\sim 10^2$ atm.[9] For Au this means that the spike temperature should be ~ 5000 K. The temperatures obtained from the fits are extremely high in comparison with this value from Kelly's criterion.

Second, the temperature obtained from the fits in the case of I_2^+ bombardment is lower than in case of I^+ bombardment. In case of I_2^+ the cascades overlap and thus the mean kinetic energy per atom in a spike should be higher than in case of I^+ bombardment. This suggests that temperatures obtained from fits of kinetic en-

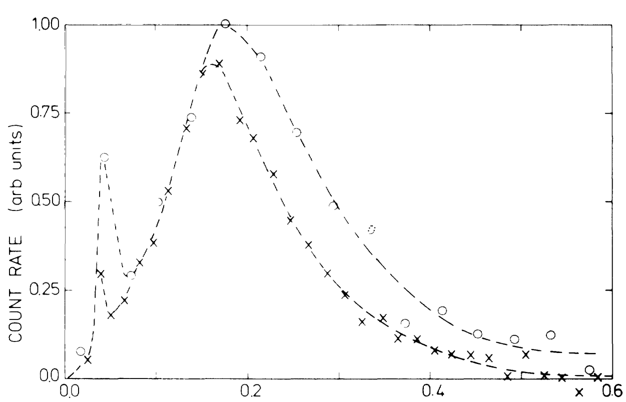

FIG. 1. Time-of-flight distributions of Au obtained under (×) 4-keV I^+ bombardment and (○) under 8-keV I_2^+ bombardment. The distributions are normalized such that the area under (○) is 1.5 times larger than the area under (×). This ratio reflects the ratio in the total count rates. The lines are a guide to the eye. The spectra have not been corrected for the detector efficiency. Thus count-rate distributions are shown and not flux distributions. The reason for this is the fact that in the count-rate presentation, effects on the count rate of particles with long times of flight are more pronounced.

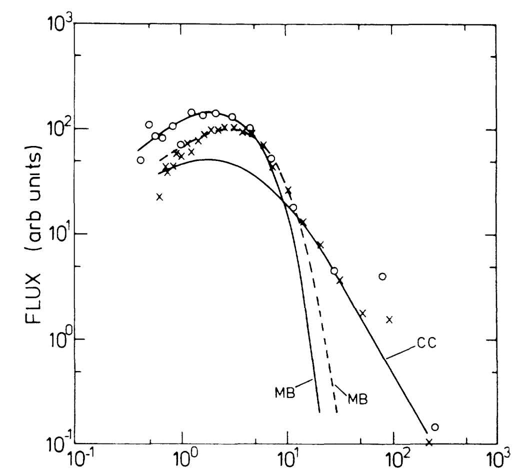

FIG. 2. Kinetic energy distributions of Au obtained (×) under 4-keV I^+ bombardment and (○) under 8-keV I_2^+ bombardment. The distributions are conversions of the distributions in Fig. 1 and are normalized in the same way as in Fig. 1. Line CC indicates a fit with a CC distribution with a surface binding energy U_0 of 3.8 eV. The fit reproduces 62% of the spectrum (×) and 38% of the spectrum (○). Lines MB indicate fits with MB distributions. The dashed line indicates a fit with a temperature of 3.3×10^4 K. The solid line indicates a fit with a temperature of 2.3×10^4 K from an interpolation between the other data points. The solid line represents the line $kT=\frac{1}{6}U_0$.

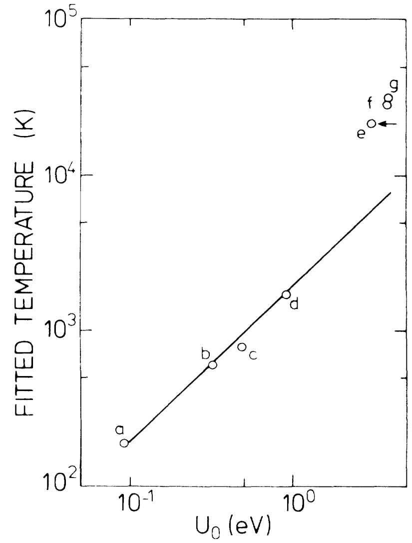

FIG. 3. Fitted spike temperature T obtained from kinetic energy distributions of sputtered species as a function of their surface binding energy U_0. Data points are referenced in Table I. The arrow indicates the position of the data point for the system 8 keV $I_2^+ \rightarrow$ Au, as obtained from an interpolation between the other data points. The solid line represents the line $kT = \frac{1}{6} U_0$.

TABLE I. Data points shown in Fig. 3.

Data point in the figure	System	Investigated sputtered species	Ref.
a	6 keV $Ar^+ \rightarrow CH_4$	CH_4	23
b	6 keV $Ar^+ \rightarrow NH_3$	NH_3	24[a]
c	6 keV $Ar^+ \rightarrow H_2O$	H_2O	24[a]
d	6 keV $Xe^+ \rightarrow$ NaI	I	25
e	6 keV $Xe^+ \rightarrow$ Ag	Ag	17,18
f	6 keV $Xe^+ \rightarrow$ Au	Au	17,18
g	4 keV $I^+ \rightarrow$ Au	Au	This work

[a]In this reference the high-energy side of the spectrum of the sputtered species is investigated. It was shown that sputtering by a collision-cascade mechanism takes place. However, a collision-cascade mechanism can explain only a minor part of the spectrum. In a reanalysis (unpublished) the whole kinetic energy distribution has been investigated. The low-energy side can be fitted excellently with a MB distribution indicating that a spike mechanism also contributes to the total sputtering yield.

ergy distributions of sputtered species are not related to temperatures which are reached in thermal spikes.

We propose that the sputtering which leads to MB-type energy distributions takes place during a transient state in which a thermal spike starts to develop. The effective temperature, as obtained from the MB fit is then determined predominantly by the surface binding energy. In our laboratory sputter experiments have been performed on materials with very different values for the surface binding energy. Kinetic energy distributions of the sputtered species have been measured. In many cases MB-type energy distributions have been observed under keV heavy-ion bombardment (see Fig. 3 and Table I). From these it was concluded that spike phenomena contribute significantly to the total sputtering yield. In Fig. 3 the temperatures, as obtained from fits, are shown as functions of the surface binding energy of the sputtered species for various target materials. Striking is the general trend in which an increase in surface binding energy is correlated with an increase in the temperature obtained from the fits.

Such a relation can be explained using the calculations of Szymonski and Poradsisz[26]: After the first stages of the CC the spike begins to develop. Initially, a few atoms are very hot, but the speed of cooling is very high. A lack of hot atoms and a lack of time prohibit a high flux of particles escaping the surface binding energy. As a function of time the developing spike extends over more atoms and the speed of cooling decreases. Then during a relatively long time a large number of atoms is able to escape the surface binding energy. When the spike develops further, too many atoms share the energy which becomes less than the surface binding energy and the atoms cannot escape anymore. Therefore the maximum in the flux of escaping species is determined by the surface binding energy. The distribution of sputtered species is determined predominantly by this maximum flux. Thus the temperature obtained from fitting this distribution, is also determined by the surface binding energy.

Figure 3 suggests that for insulators (data points a–d) the fitted temperature increases linearly with the surface binding energy. An extrapolation of the results obtained for insulators yields for Au a temperature of approximately 7000 K. This value is close to the minimum temperature for which spike effects can be observed in Au according to Kelly's criterion. However, for metals (data points e–g) the fitted temperatures are much higher than expected on basis of the extrapolation.

The observation of a lower temperature for I_2^+ bombardment indicates that in this case the effective surface binding energy is lower than for I^+ bombardment. From the fitted temperature the effective surface binding energy of Au under I_2^+ bombardment can be obtained. An interpolation between the results displayed in Fig. 3 shows that a reduction of the surface binding energy by 15% is enough to obtain the observed decrease in temperature. Ahmad, Farmery, and Thompson[19,20] also suggest a lowering of the surface binding energy to explain their results. Two mechanisms might contribute to such a decrease in the effective surface binding energy.

First, the sputtering yield is very high. Under I^+ bombardment the sputtering yields is ~ 14.[17,18] Then under I_2^+ bombardment the sputtering yield per dimer becomes so high that neighboring atoms simultaneously leave the surface. This reduces the effective surface binding energy which has to be overcome to be ejected.[27]

Second, the solid is in an extremely excited state. Pramanik and Seidman[28] demonstrate that the damage production in the solid is enhanced in the case of dimer bombardment. They observe that the number of vacancies produced per incoming atom of the dimer is higher than the number of vacancies per monomer. In our case, (55° incoming ions) this production of voids will take place in the very first atomic layers. Then Au atoms at the surface will be bound less strongly, in case of dimer bombardment.

A decrease in the surface binding energy under I_2^+ bombardment can explain a nonlinear enhancement in the sputtering yield in comparison with I^+ bombardment. A lower surface binding energy yields a higher evaporation rate from the developing spike induced by I_2^+ bombardment. Furthermore, evaporation can go on until the kinetic energy has been shared among more atoms. Thus atoms can escape for a longer time.

In conclusion, nonlinear effects in the sputtering of Au under I_2^+ and I^+ bombardment have been observed. Time-of-flight distributions of the sputtered atoms show that per dimer atom more low-energy particles are ejected from the solid than per monomer. MB-type energy distributions suggest that sputtering proceeds by a spike mechanism. The spike temperature obtained from the fits is lower in the case of I_2^+ bombardment, than in the case of I^+ bombardment. This indicates that the sputtering takes place during a transient state in which a thermal spike is developing. *The very short time scale for this process may be the reason that the fitted spike temperature is larger than the critical temperature.*[29] A general trend is found which shows that the fitted spike temperature is correlated with the effective surface binding energy over orders of magnitude. From this we conclude that under I_2^+ bombardment the effective surface binding energy of Au is lower than under I^+ bombardment. The lowering of the surface binding energy can also explain the nonlinear enhancement of the Au sputtering yield under I_2^+ bombardment.

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