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Sputtering of a Au surface covered with large spherical clusters

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Abstract

Using molecular-dynamics simulation, we study the effect of 100 keV Au atom bombardment of a Au (111) surface, which is covered with large spherical Au clusters (radius $R = 40$ Å). Only a limited number of atom impact locations could be studied, all of which were focused within 2 Å of the center of the cluster. Depending on the exact atom impact point on the cluster surface, strong fluctuations in the sputter yield are found; in the most dramatic cases, the cluster completely disintegrates. The $1/E^2$-energy distribution of sputtered atoms is in agreement with a collisional emission mechanism. Large fragment clusters are emitted during sputtering.

Further, in order to study the possibility of intact cluster desorption, we performed a model study, in which a hemispherical part of the substrate immediately below the cluster is heated up to high temperatures, corresponding to an initial energy E_0 per atom. Such a scenario may be relevant for fast heavy-ion bombardment, where the substrate is heated by strong electronic stopping. Intact desorption of the cluster is observed above a threshold of $E_0 \cong 3$ eV/atom. Then the kinetic translational energy of the desorbed cluster is more than around 20% of its internal energy. (Int J Mass Spectrom 208 (2001) 29–35) © 2001 Elsevier Science B.V.

Keywords: Sputtering; Cluster; Desorption; Surface roughness; Molecular dynamics simulation

1. Introduction

The sputtering of Au surfaces by Au atoms and clusters has been studied in the recent past intensely both experimentally and by computer simulation. Huge sputter yields [1,2] as well as pronounced crater formation [3] have been observed. Even more drastic phenomena can be expected for a roughened Au surface. Such a surface may be prepared by the deposition of large clusters on a flat surface. In fact, experimental studies of fast heavy-ion bombardment of Au-cluster-covered surfaces found dramatically high sputter yields; and even the desorption of entire clusters from the surface was observed [4–9]. These latter experiments were performed in the electronic-stopping regime using fission fragments as projectiles. Experiments in the nuclear-stopping regime are planned [10].

Here we present molecular-dynamics simulation results of the sputtering of a Au surface covered with large spherical Au clusters. Bombardment is performed with 100 keV Au atoms, i.e. in the nuclear-stopping regime. In view of the large number of parameters relevant for this system—besides the substrate material, orientation, and atomic location of the cluster on the surface, as well as the impact point of the projectile on the cluster—no systematic study could be performed. Rather, an overview of the

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phenomena occurring for atom impact centrally on the cluster is presented. In this case, no intact desorption of the cluster could be observed, since either energy is only deposited in the substrate, leaving the cluster intact, or so much energy is deposited within the cluster that it more or less disintegrates.

In order to obtain insight into the possibility of intact cluster desorption, we performed an additional model study, in which a hemispherical part of the substrate beneath the cluster is heated up. This scenario is meant to model a situation, in which a fast heavy ion deposits only little energy in the cluster itself, but produces a large amount of electronic excitation in the substrate below it. We then assume that this electronic excitation is swiftly converted to atomic motion; this sets the starting point for our simulation. Although the excited zone will be of cylindrical symmetry in reality, we chose a hemispherical zone for computational convenience. We note further that also in the nuclear-stopping regime such an energy deposition may be relevant, e.g. for noncentral atom impacts at the periphery of the cluster, where a subcascade deposits a high fraction of the projectile energy in the substrate immediately below the cluster. We shall show in Sec. 3.3 that from such a heat spike we indeed observe intact desorption of the cluster.

2. Method

As substrate we use a 240 000 atom Au crystal with a (111) surface. On top of it, a spherical Au cluster, containing 15 784 atoms (radius $R = 40$ Å) is laid, cf. Fig. 1. Damping boundary conditions are used on the lateral and bottom sides of the crystallite, the surface is of course left free. The cluster is oriented such that its top part forms again a (111) facet.

A 100 keV Au atom impinges centrally on the cluster. Fourteen different impacts have been simulated, where the exact impact point has been varied randomly within a small irreducible surface impact triangle [11,12], deviating at most 2 Å from the ideal central impact point. Although the statistical weight of this impact area is small, we nevertheless find here a variety of results which we think gives us a good

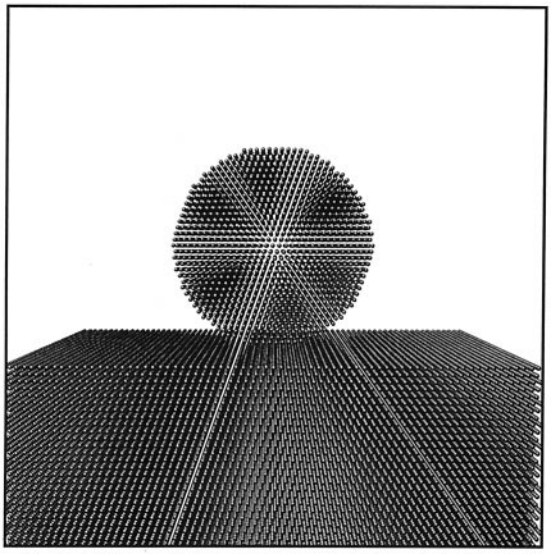

Fig. 1. Perspective view of the system studied before bombardment, $t = 0$. The Au (111) surface is covered by a 15 784 atom Au sphere.

overview of what may occur after such impact phenomena. The simulation was run until 20 ps after atom impact. An embedded-atom potential [13–15] was employed to model the many-body interaction among Au atoms. It is known [16] to reproduce well bulk (and also surface) properties of Au, such as the melting temperature, bulk modulus and cohesive energy, which may be of importance for the present study. We mention that it has not been optimized for describing small clusters; thus, e.g. the dimer binding energy is 4.8 eV in comparison to the experimental value of 2.3 eV. Toward high energies, the potential has been splined to the Ziegler-Biersack-Littmark potential [17]. Electronic stopping has been disregarded in this study.

3. Results

3.1. Scenarios

Three different scenarios could be observed. Fig. 2 displays these by giving both a perspective and a cross-sectional view at $t = 1$ ps and at $t = 20$ ps after ion impact:

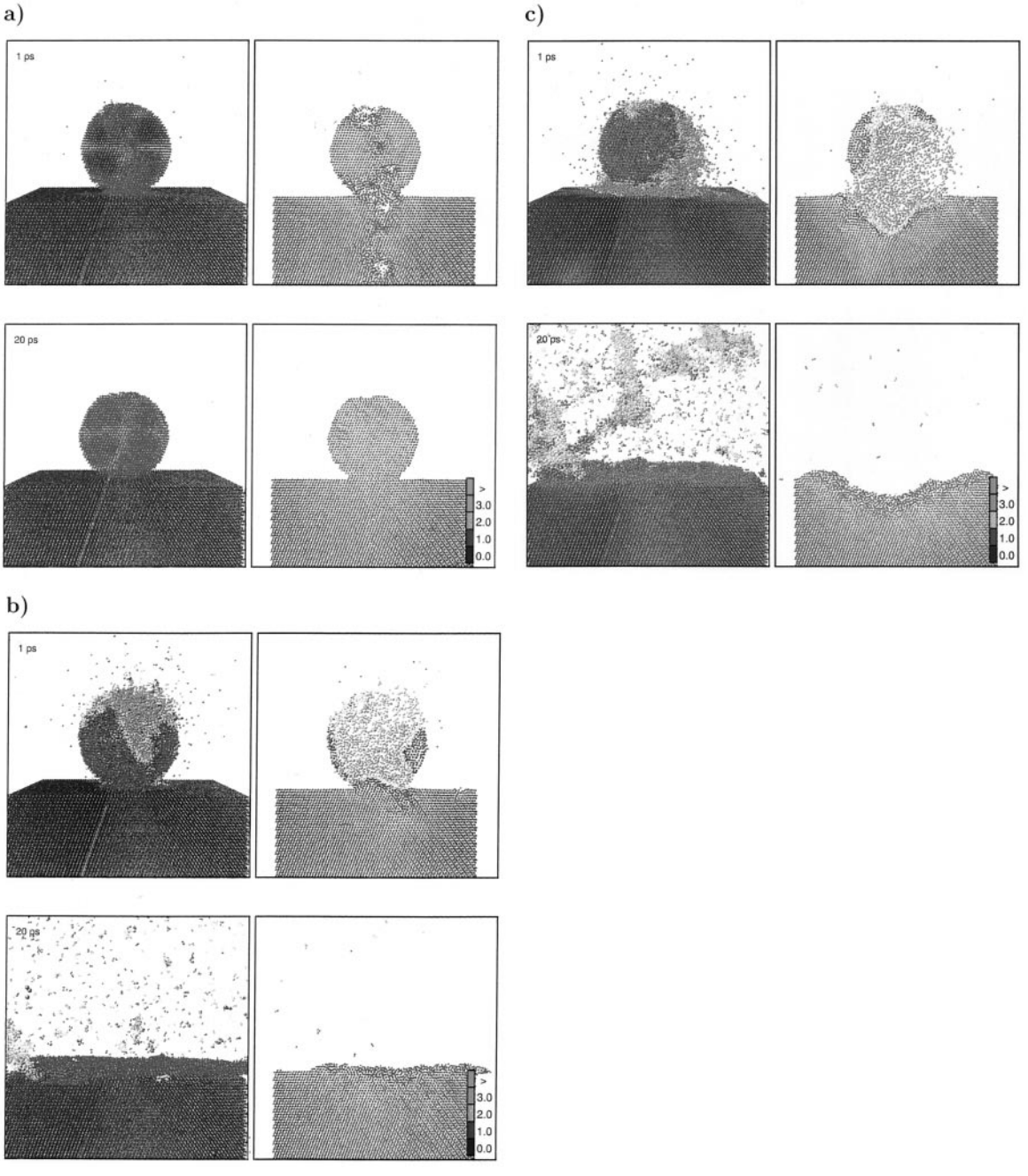

Fig. 2. Three different bombardment scenarios. (a) Energy deposition deep in the bulk. The cluster remains essentially intact. (b) Energy deposition within the cluster, which consequently disintegrates. The substrate is only little affected. (c) Intermediate case of energy deposition both in the cluster and in the substrate. Large clusters are sputtered off the sphere, a crater develops on the substrate. Each part shows perspective and cross-sectional views of the system at $t = 1$ ps after atom impingement, when the size and location of the collision cascade and hence the energy deposition zone are determined, and at $t = 20$ ps, which shows a late stage in the development of sputtering and surface features. Gray shade code: local temperature in units of the melting temperature of Au. Animation available at www.physik.uni-kl.de/urbassek/english.html

(1) As visualised in the event displayed in Fig. 2(a), the projectile can penetrate deeply into the substrate, delivering only little energy into the cluster or the surface part of the substrate. This leads to only little sputtering. Here and in the following we shall quantify the results of impact by the sputtering yield Y which denotes the total number of atoms emitted from the cluster or the gold surface. To this purpose, all atoms are counted, irrespective of whether they are sputtered as monatomics or bound in clusters. The sputtering yield for the event shown in Fig. 2(a) is only $Y = 12$. However, the albeit small amount of energy deposited at the cluster/surface interface leads to partial melting there and improves adhesion of the cluster to the surface in this case, comparable to sintering. Note that our substrate was not thick enough to fully contain the projectile trajectory.
(2) In some cases the projectile energy is deposited mainly within the cluster, see Fig. 2(b). This leads to the more or less complete disintegration (explosion) of the cluster on top of the substrate. The substrate becomes covered with some debris; in this case no crater was left on the surface. The sputter yield in this case was huge, $Y = 6409$, i.e. almost half the cluster was sputtered.
(3) Intermediate states, in which energy is deposited both within the cluster and in the substrate, exist in all variations between scenario (1) and (2). In the example shown in Fig. 2(c), we see that such a case may lead to sputtering of large clusters, which are formed of coherent parts of the original cluster sphere. Further, a crater remains on the surface. The sputter yield in this case amounted to $Y = 8810$.

We note that our statistics is not sufficient to quantify the probabilities with which scenarios (1) or (2) and the various intermediate stages pertaining to (3) occur.

3.2. Sputter characteristics

On the average, a number of $Y = 2454$ atoms are sputtered; as mentioned previously, the sputter distribution has a very large variance. A high percentage of atoms are sputtered bound in clusters. Fig. 3 shows the cluster distribution as a function of cluster size n at $t = 20$ ps after ion impact. The distribution roughly follows a polynomial decay

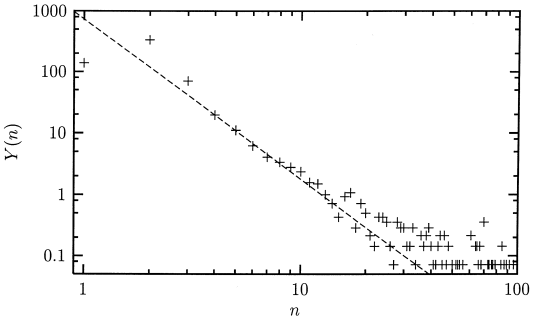

Fig. 3. Cluster mass distribution $Y(n)$ vs. cluster size n. Dashed line: fit to a polynomial decay, Eq. (1), with $\alpha = 2.6$.

$$Y(n) \propto n^{-\alpha} \tag{1}$$

with $\alpha = 2.6$. Large clusters with n exceeding 100 have been observed. The falloff is quite slow, certainly slower than that observed for kiloelectron volt ion bombardment of metals [18,19]. The exceptionally high yields of dimers and trimers (cf. Fig. 3) are an artifact of the potential which overbinds the small clusters. It is known from other studies that the abundance distribution of the clusters will evolve further in time due to unimolecular fragmentation of the large clusters possessing a high internal energy [20,21]. This will lead to a steepening of the distribution; further, the number of monomers, and possibly also of dimers, will increase beyond the present, rather low, value, due to atom evaporation.

In the following we study the characteristics of emitted monomers. Fig. 4 gives the energy distribution of monomers, $Y_1(E)$, and compares them with the sum of a Thompson distribution [22] and a thermal evaporation component,

$$Y_1(E) = aE \exp\left(-\frac{E}{kT}\right) + b\,\frac{E}{(E+U)^3}. \tag{2}$$

The fit value of the effective evaporation temperature is $T = 1500$ K, slightly above the melting tempera-

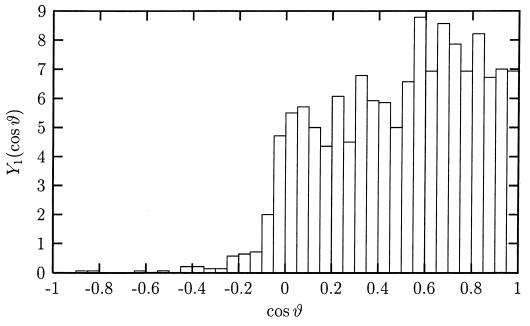

Fig. 4. Angular distribution $Y_1(\cos\vartheta)$ of emitted monomers. $\vartheta = 0°$ denotes the direction normal to the surface.

ture of Au. Only four atoms originate on average from this thermal contribution. The best-fit value of the effective surface binding energy U amount to 3.56 eV and is close to the cohesive energy of Au, 3.93 eV. This demonstrates that monomers are mainly emitted due to a collisional sputter mechanism.

The angular distribution, Fig. 5, shows a rather isotropic emission in the outward half-space. This is evidently due to the curved surface of the bombarded cluster, and has been observed also for sputtering of a spherical target [23]. The few "backwards" emission events are mainly due to monomers evaporated with slow velocities from larger clusters toward the surface, and will disappear at later times.

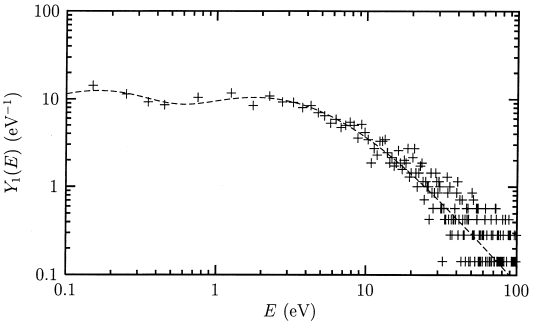

Fig. 5. Energy distribution $Y_1(E)$ of emitted monomers, including fit to a two-component distribution, Eq. (2), with best-fit surface binding energy $U = 3.56$ eV and effective evaporation temperature $T = 1500$ K.

3.3. Intact desorption

In this section, instead of bombarding the cluster/substrate system (Fig. 1) with an energetic atom, we want to study under which conditions the intact desorption of the spherical cluster is possible. To this end, we model at time $t = 0$ a heat spike in the substrate beneath the cluster by giving each atom in a hemisphere below the cluster (of radius equal to the cluster radius R) a kinetic energy E_0 with random velocity direction. The hemisphere contains 7892 atoms. We then let the system evolve in time for 20 ps and monitor whether the cluster sphere desorbs. We note that although our initial conditions at $t = 0$ certainly do not correspond to the exact conditions obtained after any ion bombardment situation, this simulation may be used to represent a situation of strong electronic energy deposition in the substrate below the cluster, or alternatively to model a subcascade, in which a sizable fraction of the projectile energy is deposited in the surface-near part of the substrate without damaging much of the cluster. The latter situation may occur for projectile impact at the cluster periphery, or for cluster/substrate orientation misfits, in which the projectile may channel deeply in the cluster but not in the substrate.

Fig. 6 shows the result of such a simulation at $t = 20$ ps after the initiation of the heat spike for an initial energy of $E_0 = 4$ eV/atom. The cluster has desorbed from the surface. This was the consequence of the ablation pressure of the atoms evaporating from the heat spike into the substrate below. The cluster grew in size by almost 9% in the process by condensation of substrate atoms on its bottom part. Its kinetic translational energy amounts to $E_{\text{trans}} = 324$ eV corresponding to a velocity of 1.36 Å/ps. This may be considered a low effectivity since it corresponds to only 1% of the initial heat content of the spike, 31.6 keV. The cluster was also heated up; it contains an internal energy of $E_{\text{int}} = 1894$ eV, corresponding to roughly 850 K.

We examined cluster desorption as a function of the energy E_0 given initially per atom to the heat spike. Fig. 7 summarizes the results by presenting the resulting translational energy of the cluster E_{trans} and

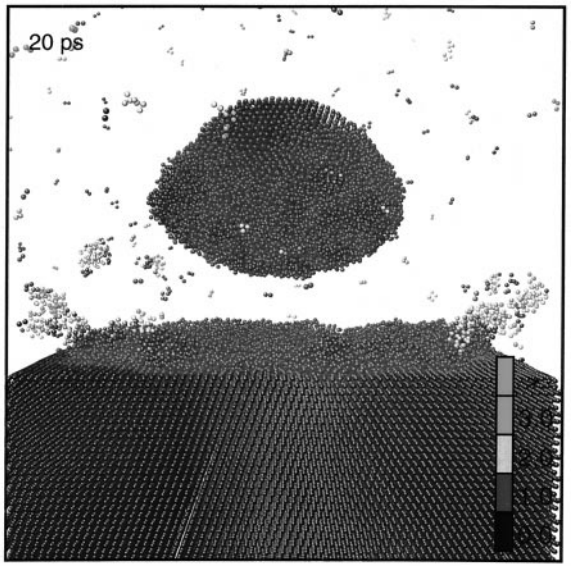

Fig. 6. Perspective view showing lift-off of the cluster from the surface at $t = 20$ ps due to a heat spike at $t = 0$ in the substrate below the cluster. The heat spike was modeled by giving each substrate atom in a hemispherical zone below the cluster an initial energy of $E_0 = 4$ eV.

its internal energy E_{int} for each simulation. We observe an almost linear increase of both quantities with E_0. We note, however, that the cluster did not desorb for the $E_0 = 2$ eV/atom and even 2.5 eV/atom heat spikes, even when we prolonged our simulations until $t = 50$ ps; after this time, the temperatures in the cluster and also in the bulk have settled to below the melting temperature so that no further emission processes can be expected. For the $E_0 = 3$ eV/atom heat spike, after $t = 23$ ps, the cluster has desorbed. Thus the threshold energy to cluster desorption lies between $E_0 = 2.5$ and 3 eV/atom, and hence slightly below the cohesive energy of Au. The linear dependence indicated as dashed lines in Fig. 7 does not hold down to threshold values.

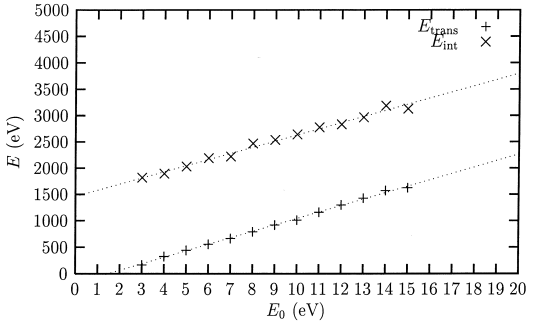

Fig. 7. Internal energy E_{int} and translational energy E_{trans} of the desorbed cluster as a function of the energy E_0 given initially per atom to the heat spike. Dashed lines are to guide the eye.

Fig. 7 shows that the desorption process becomes more and more efficient with increasing energy deposition E_0. Thus for $E_0 = 15$ eV/atom, the translational energy of the cluster is more than 50% of the internal energy of the cluster, and 1.4% of the heat-spike energy was used for desorption. The cluster still contained 95% of its initial number of atoms. Of course, this case must be considered as an extreme, since the spike contained initially 118 keV, and the final temperature of the desorbed cluster is 1600 K and hence further mass and energy loss by evaporation must be assumed.

4. Conclusions

Using 100 keV Au bombardment of a Au (111) surface covered with 15 874 atom spherical Au clusters, we could show the existence of different bombardment regimes. As a consequence of the fluctuations in the projectile slowing and energy deposition, in some events, the cluster was completely disintegrated, giving rise to huge sputter yields, whereas the surface remained more or less intact. In other events, the projectile penetrated deeply, leaving the surface and cluster virtually intact. Intermediate cases of all forms exist, where the cluster is heavily damaged, emitting large clusters and also craters remain on the surface. No intact desorption of a cluster could be observed; we think this is due to the fact that in this study we could sample only a small part of the relevant parameter space.

Intact desorption was observed, however, in a situation, where a heat spike developed in the substrate immediately below the cluster. This was modeled in a separate simulation, and the threshold to desorption could be determined.

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