Sputtering of freestanding metal nanocrystals

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Abstract

The sputtering mechanisms of nanocrystals are of interest both from a basic science and application development point of view. Since the surface-to-volume ratio of nanocrystals is huge compared to normal bulk matter, one could expect enhanced sputtering yields, and indeed both simulations and experiments show sputtering yields which are clearly larger than those for flat bulk targets. We present a simple analytical model for the sputtering from nanocrystals, and apply it to two different kinds of irradiation, 25 keV Ga and 200 keV Ar irradiation of 1 – 15 nm diameter Au nanocrystals. The model predicts sputtering yields from the nanocrystals in good agreement with molecular dynamics simulations and experiments.

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Nanoclusters, Metals, Sputtering

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1. Introduction

Nanoparticles are used widely in contemporary society, in a wide range of applications as different as suntan lotions, detection of pharmaceutical molecules and enhancing the strength of materials in sports equipment [1]. Most of these applications do of course not involve ion beams in any way. However, there is a growing range of situations where ion irradiation of nanoparticles is of practical interest [2]. Moreover, it is also of basic nanoscience interest to ask the question of how finite-size effects make radiation effects in nanoparticles differ from those in the bulk counterparts. Since nanosystems involve a very large surface-to-volume ratio, the question of how sputtering yields in them differ from the bulk yields is of particular interest.

One of the major application motivations for examining sputtering from nanoparticles is the recent observation of cluster-enhanced secondary ion mass spectrometry (SIMS). SIMS is a standard technique for analysis of depth profiles of hard condensed materials, but it is also useful for analyzing the composition of the top few monolayers of molecular solids. Previously molecular analysis was plagued by the problem of very low yields for sputtering of intact large molecules. However, in 2006 it was shown that the time-of-flight (TOF) SIMS analysis of molecular solids can be dramatically enhanced by first coating the sample with metal nanoparticles.[3] This study showed that the mass range of molecules that can be analyzed was extended to 5000 Daltons (atomic mass units) and that the sputtering yield was enhanced up to a factor of 400 compared to a surface not treated with nanoparticles. The effect was attributed to metal ions which have been sputtered from the nanoparticle forming metastable complexes with the polymer

molecules. The ionized polymers were then more stable during the SIMS experiments.

The approach was developed further by attaching Au nanoparticles to well-controlled surfaces such as self-assembled monolayers.[4] This approach was applied for analysis of peptides (protein segments) with masses in the 1000 Dalton range.

The SIMS-enhancing effect of metal nanoparticles gives a clear motivation to study the sputtering of nanoparticles, since regardless of the exact mechanism of the polymer sputtering, metal atoms are ejected by exposure to the incident ion beam.

Molecular dynamics (MD) simulations of the sputtering of Au nanoclusters have been carried out by several groups.[5, 6, 7, 8, 9] Sputtering of Au nanoclusters by 38 keV Au ion bombardment with MD simulations was examined,[5] and it was reported that the sputtering yield has no significant dependence on the impact point in the clusters (impact parameter). The average sputtering yield for an Au_{6051} cluster was reported to be about 1200 atoms. Similar computer simulations of the sputtering of Au nanoclusters by impinging 180 eV/atom Au_{400} nanoclusters [6] showed large sputtering yields of the order of several thousands of atoms. The bombardment of 8 nm diameter Au nanoclusters by even higher energy (100 keV) Au projectiles has also been examined [7]. This was shown to lead to most ions passing the nanoclusters with little or no effects on them, but a few collisions causing essentially the disintegration of the whole cluster. Simulations of 20 nm diameter Au nanoclusters by 16 and 64 keV Au projectiles were reported to lead to sputtering yields that could be more than a factor of two higher than

the yield for a bulk target [8].

In the current paper we first overview our systematic MD simulation results on sputtering of nanoclusters, and present an analytical model for the sputtering. We then present application of the model to two different kinds of irradiation, and show that consideration of how the ion energy is related to the damage distribution in a given-sized nanoclusters is crucial in applying the model.

2. Molecular dynamics simulations of sputtering

Radiation effects in freestanding nanoparticles can often be reasonably approximated by simulating irradiation of particles in vacuum, considerably reducing the computational power needed.[9, 10, 11, 12] An example is given by Ref. [9], where cascade producing irradiation of gold nanoparticles was examined. Particles were initially equilibrated and randomly rotated in vacuum prior to the impact simulation. The ion was then allowed to impact with a random impact parameter chosen inside a radius given by a cylinder wrapped around the cluster. No temperature control was used during the simulations, since in vacuum and on weakly coupling substrates, heat dissipation happens on a slower time scale than what is simulated. As an example, Fig. 1 shows snapshots of a simulation, where a 25 keV Ga-ion impacts on an 8 nm Au nanoparticle causing cascade formation and sputtering.

3. Analytical model for sputtering

In previous work [9], we have developed a model for cascade-producing irradiation based on physical considerations within the Sigmund model,[13]

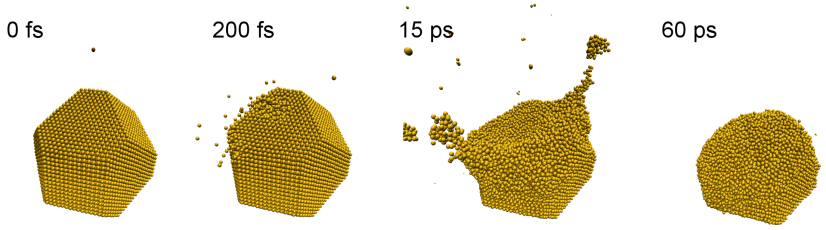

Figure 1: (Color online) Snapshots of a 25 keV Ga-ion impacting on an 8 nm Au nanoparticle.

and molecular dynamics simulations. The initial version is described in detail in Ref. [9], and here we summarize the central features of the model.

The sputtering yield of a single ion impacting the surface at r_0 is given by integrating the damage distribution (F) over the target surface ∂T,

$$Y_0(r_0) = \Lambda \int_{\partial T} \mathrm{d}^2 r \, F(r, r_0), \tag{1}$$

with Λ a proportionality constant. The total sputtering yield, averaged over the impact points on the target surface (the average is taken over the projection of the surface perpendicular to the ion direction), is then

$$Y = \int \mathrm{d}^2 r_0 \, Y_0(r_0) / \int \mathrm{d}^2 r_0. \tag{2}$$

In Ref. [9] we used a standard Gaussian damage distribution of the form

$$F(r, r_0) = \frac{E}{(2\pi)^{\frac{3}{2}} \alpha \beta^2} e^{-\frac{1}{2\alpha^2}[z - h(x_0, y_0) + a]^2} \times e^{-\frac{1}{2\beta^2}\left[(x-x_0)^2 + (y-y_0)^2\right]}, \tag{3}$$

where E is the deposited energy, $r = (x, y, z)$, and a gives the depth of the center of the distribution under the impact point r_0. $h(x_0, y_0)$ is the height of the target surface at the impact point.

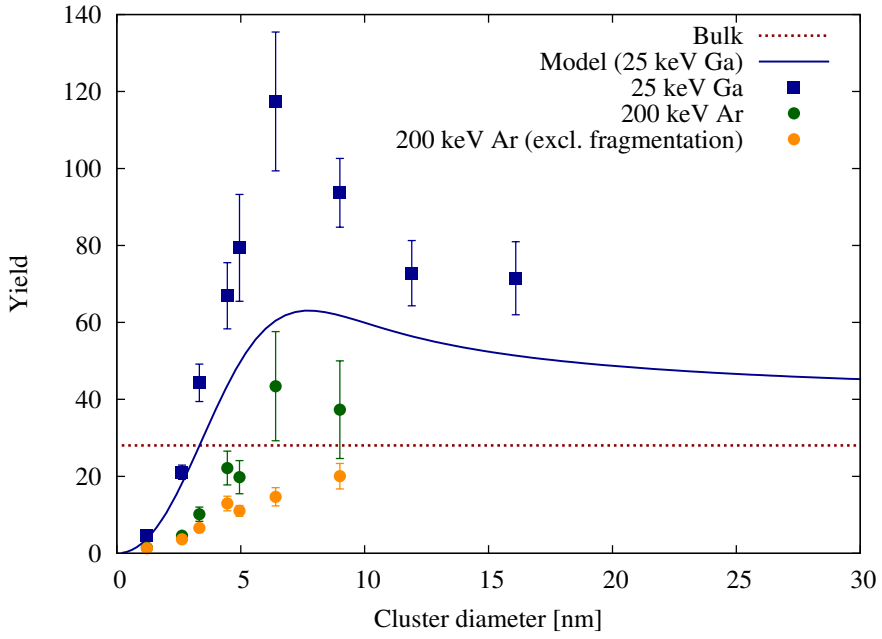

Figure 2: (Color online) Result from molecular dynamics simulations of the sputtering of Au nanoclusters by 25 keV Ga ions. (Adapted from Ref. [9]). The horizontal line gives for comparison the bulk sputtering yield. The curve gives the prediction of the analytical model described in the text, when applied for a damage distribution of 25 keV Ga ions. Also shown are results for 200 keV Ar ions, calculated for the current Article. The markers refer to simulation results.

3.1. Application for 25 keV Ga

In. Ref. [9], the above model was applied to irradiation of gold nanoparticles by 25 keV gallium ions. As displayed in Fig. 2, rather good reproduction of molecular dynamics simulation results could be obtained, although the simplicity of the model leads to some quantitative differences.

3.2. Application for 200 keV Ar

In a recent article,[14] experimental data is presented on the burrowing and sputtering of around 2–10 nm gold nanoparticles supported on various substrates. In analysis of the data, the model developed in Ref.[9] is used for the size-dependent sputtering yield of nanoparticles. However, the experimental sputtering yield and the model's prediction are shown to differ by around two orders of magnitude, the model underestimating the yield.

In Ref. [14], the authors used a similar Gaussian distribution as for 25 keV Ga ions. However, we shall show here that the damage distribution for 200 keV Ar ions is quite different, and hence the analytical model should be applied with a differently shaped distribution.

In Ref. [14] the Gaussian damage distribution was obtained using SRIM.[15] SRIM is well suited for describing the ballistic phase of the cascade in this energy range, as it has been shown that the binary collision approximation is quite accurate for kinetic energies $\gg$ 1 keV [16]. The exact parameters were not reported, so we repeat here the calculation with our own parameters for completeness. We calculated the full damage cascades for 200 keV Ar incident on a planar Au surface, and used the default lattice binding energy (3 eV). The threshold displacement energy (36 eV) and surface binding energy (3.8 eV) were taken from Ref. [17]. Around 25000 ions were used for statistics and the primary recoil atom coordinates and recoil energies were extracted.

The recoil data from SRIM can be fit to the Gaussian distribution. We took the recoil energies as weights when fitting the recoil coordinates so that the distribution would reflect the damage created in the target in terms

of energy instead of just the primary recoil coordinates. The parameters $a = 50\,\mathrm{nm}$, $\alpha = 32\,\mathrm{nm}$, and $\beta = 29\,\mathrm{nm}$ were obtained. These differ somewhat from the ones used in Ref. [14], but are similar in magnitude. Our result for the sputtering yield of a bulk surface (Y=6.5) agrees well with their one, as well as with experiment, although the experimental yield may be slightly larger.[18]

The proportionality constant in Eq. 1 can be fit from the bulk sputtering yield using Eq. (3) of Ref. [9],

$$Y_{\mathrm{bulk}} = \frac{2\pi\Lambda E}{(2\pi)^{\frac{3}{2}}\alpha} e^{-\frac{a^2}{2\alpha^2}}, \tag{4}$$

giving $\Lambda = 8.84\,\mathrm{nm/eV}$, where we approximated the deposited energy by the ion energy.

In Ref. [14] (see Fig. 9), a sputtering yield of 7.5 was obtained for particles with starting radii of 3.9 nm. With the above parameters, our model[9] gives a yield of $\sim$0.3, the discrepancy being similar to the one reported in Ref. [14]. However, the center of the damage distribution is far below the nanoparticles, inside the substrate. Note that the center of damage is at a depth of 50 nm while the particles on the surface are below 10 nm in size. Thus it is questionable whether the simple Gaussian fit can give a good description of the damage near the surface, very far from the center of the Gaussian. The problem is clearly seen in Fig. 3, where the deviation from Gaussian shape is particularly strong between the center of damage and the impact point.

There is no obvious way to determine the shape of the damage distribution. Close to the surface, the part relevant for the nanoparticle, the incoming ion has not lost much energy. Also the nanoparticle size is smaller than the

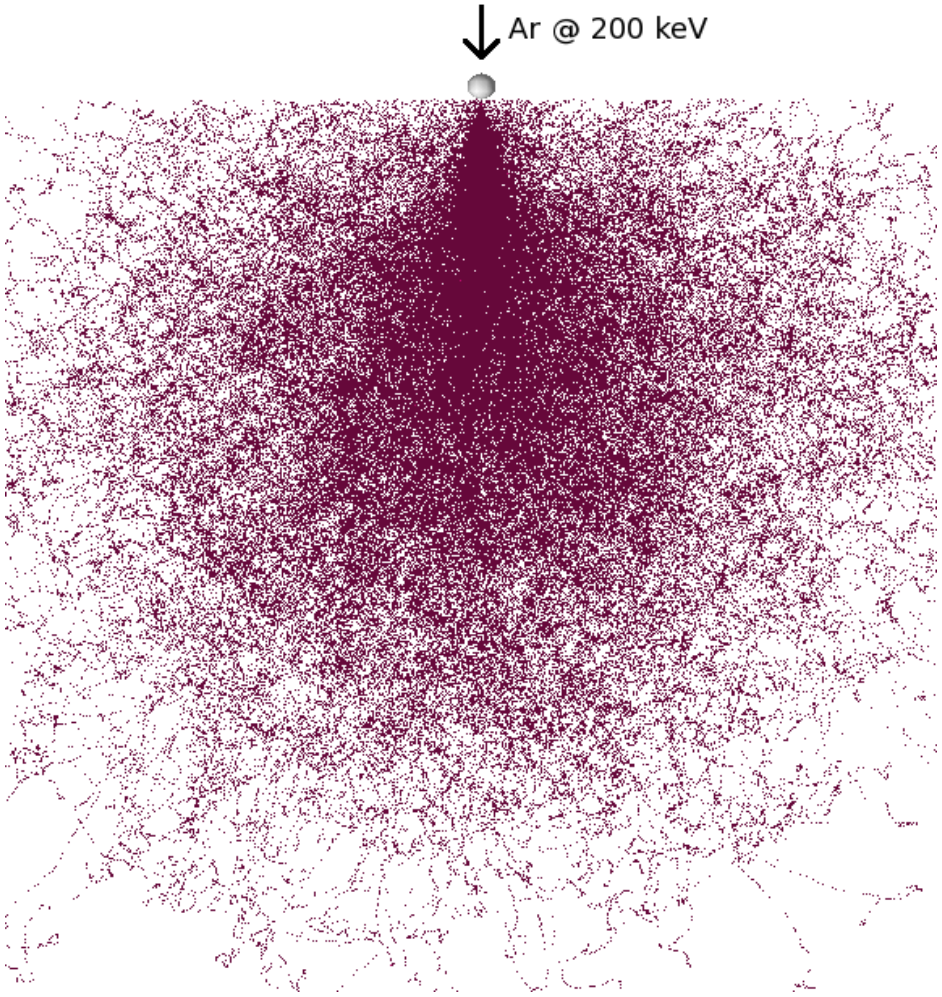

Figure 3: Positions of primary recoil atoms in Au under 200 keV Ar bombardment according to SRIM. The ions impact downwards showing the shape of the damage distribution, with a nanoparticle of 5 nm in diameter on the surface.

ion path's straggling. Thus a stopping-based constant distribution should be a reasonable approximation, simply giving $F = \frac{E}{V}$, where the damage is assumed to be evenly distributed in the particle volume V. SRIM gives a nuclear stopping value of $d_E = 84\,\mathrm{eV/\AA}$ for 200 keV Ar in Au. The deposited energy is then $E = d_E\,h$, where h is the distance which the ion travels inside the nanoparticle. We will assume here a hemispherical shape for the particle, so that h is given as a function of the particle radius R and radial coordinate r by $\sqrt{R^2 - r^2}$. The damage distribution is then $F = \frac{E}{\frac{2}{3}\pi R^3}$. Note that this approach differs somewhat from that used with the Gaussian distribution as both the deposited energy and the damage distribution are assumed to depend on particle size.

The sputtering yield for an ion impact at r_0 is thus

$$Y_0(r_0) = \Lambda \int_{\partial T} d^2r\, F = \frac{3\Lambda E}{R}. \tag{5}$$

In the integral over ∂T we only took the vacuum-facing part assuming that the interface towards the substrate would stronly hinder sputtering. Also gold sputtered on the sapphire surface can be expected to diffuse back to the clusters. From the above equation

$$Y = \frac{1}{\pi R^2} \int d^2r_0\, Y_0(r_0) = 2\,\Lambda\, d_E. \tag{6}$$

The sputtering yield thus surprisingly turns out to be constant with respect to particle size. This can roughly be understood by the fact that the deposited energy per volume scales as R^{-2} while the surface area of the particle scales as R^2.

Inserting the numerical values obtained above gives a nanoparticle sputtering yield of 15, which is $\sim$2 times larger than the value of 7.5, fit from

experiment.[14] Considering the extremely simplified nature of the model, this can be considered a good result. Note also, that a roughly constant sputtering yield is in agreement with the behaviour observed in Ref. [14] (Fig. 9), when no burrowing occurs, as a linear fit perfectly matches the data.

In using models like this one for predictive purposes, the careful examination of the approximations made, and especially the choice of an accurate damage distribution cannot be emphasized too much. The small size of the nanoparticles compared to the total damaged volume makes this case especially hard, and thus quantitative agreement with the experiment cannot be achieved with the usual simple damage distributions.

We also simulated the sputtering under these conditions with molecular dynamics simulations, for particles in vacuum as in Ref. [9]. The simulation results, shown in Fig. 2, do indicate size-dependence of the yield for small sizes, but for sizes above ca. 5 nm, the yield seems to saturate as predicted by the model. From a more detailed examination, it was found that the sputtering yield was dominated by a few high-yield events, which could be described as fragmentation of the cluster. Excluding these events (by excluding 1 % of events with the highest yields) resulted in lower yields, which also saturate approximately after ca. 4 nm particle size. In any case, the size dependence of 200 keV Ar-irradiation is found to be much weaker than that of 25 keV Ga-irradiation.

Modelling 200 keV Ar irradiation is thus made more difficult by the fact that argon is not a very heavy ion, and radiation damage therefore acquires some characteristics of light ion irradiation[12], increasing demands on sta-

tistical sampling in the simulations.

The simulated yield and the one predicted by the model seem to be somewhat larger than the experimental yield. However, note that the presence of a substrate will decrease the yield by a factor on the order of two. The presence of a substrate will also influence the fragmentation-like events strongly.

4. Conclusions

We presented a simple analytical model for the sputtering from nanocrystals, and applied it to two different kinds of irradiation, 25 keV Ga and 200 keV Ar irradiation of 1 – 15 nm diameter Au nanocrystals. Comparison with molecular dynamics simulations and experiments showed that the model predicts well the qualitative dependence of the sputtering yield on the nanocrystal size.

Further high-precision experiments are required to test the predictions and reliability of simulation and modelling. On the other hand, the effect of a substrate will need to be properly taken into account in the analytical model and in molecular dynamics, significantly increasing computational demands for the latter. For increasing the transferability and quantitative performance of the analytical model, a correction modifying the damage profile according to the target surface will have to be implemented[13]. For irradiation with intermediate-mass ions, a model incorporating features from both cascade producing[9] and light ion[12] irradiation would be optimal.

Acknowledgments

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