Giant Metal Sputtering Yields Induced by 20–5000 keV/atom Gold Clusters

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Very large nonlinear effects have been found in Au_1 to Au_5 cluster-induced metal sputtering yield measurements over a broad projectile energy interval from 20 keV/atom to 5 MeV/atom. The sputtering yield maxima were found at the same total energy but *not* at the same energy/atom as expected. For Au_5 a yield as high as 3000 was reached at 150 keV/atom while the Au_1 yield was only 55 at the same velocity. [S0031-9007(98)06358-3]

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More than twenty years ago it was discovered that dimers of heavy ions bombarding solids gave rise to nonlinear effects in the bombarded materials, i.e.; the effect of the two atoms arriving together exceeded by a considerable amount the sum of the effects of the two constituent atoms arriving individually [1]. Nonlinear effects were in particular studied in sputtering. They were found to be related to dense energy depositions in the target through the projectile collisional nuclear stopping power $(dE/dx)_{\mathrm{nucl}}$. In the case of Au → Au, the variation with energy of the sputtering yield, i.e., the number of atoms expelled per incoming projectile, displays a much more pronounced maximum [2] than predicted by the linear cascade sputtering theory of Sigmund [3]. Dimer (and a single trimer) irradiations were performed with Se_2 and Te_2 [1] and Sb_2, Sb_3, and Bi_2 [4,5] on high-Z targets like Ag and Au. At that time, only a rather limited amount of experimental results was obtained due to the lack of suitable cluster beams. Thompson [6] emphasized the transition from linear to spike cascade effects. A quantitative thermal spike model [7] was proposed, as well as more qualitative shock wave approaches [8,9]. A molecular flow model [10] aims at explaining results for condensed noble gases at relative temperatures substantially higher than encountered here. Molecular dynamic simulations have also been performed, but are all concerned with low energies in comparison to the present results [11,12]. A recent review [13] concluded that for metal targets where the nuclear stopping power $(dE/dx)_{\mathrm{nucl}}$ determines the sputtering yields, much more extended data sets were needed. The sputtering effects induced in insulators and semiconductors depend largely on other mechanisms [14] and are outside the scope of the present paper.

Recently, the experimental situation changed drastically with the possibility to accelerate cluster beams such as gold and carbon, through tandem accelerators [15,16]. Among other experiments these beams were used to study nonlinear effects in secondary emission of ions and particularly secondary cluster ions [17–19]. In such measurements it is not possible to discern between mechanisms leading to enhanced emission or to enhancements in the ionization probability of the emitted species. Apart from the large intrinsic interest in studying nonlinear effects over a broad energy range to gain a better understanding of the underlying mechanisms, such yield data are hence also needed for the interpretation of other emission phenomena like secondary ion and electron yields, in particular to investigate whether measured nonlinear effects in ion yield are simply a part of the total yield. Here we present sputtering yield measurements of gold targets bombarded by Au_n ($n = 1$ to 5) clusters in the energy range 20 to 5000 keV/atom.

The gold cluster beams were produced by the Aramis tandem accelerator (CSNSM, Orsay) [20], whose maximum terminal voltage is 2 MV. The ion beams originated from a standard sputtering ion source. The energies ranged from 20 keV to 2.8 MeV with this accelerator. Below 100 keV, beams were obtained using Au_n^- ions injected into Aramis without any stripping gas at the terminal. For these conditions the final cluster energy is equal to the injection energy. A few experimental points above 3 MeV were obtained with a beam delivered by a liquid metal gold cluster ion source located in the high voltage terminal of the 15 MV Orion-Tandem accelerator (Institut de Physique Nucléaire, Orsay) [21]. The accelerated ions were selected by magnetic deflection through a small angle before passing a 3 mm diameter collimator at the entrance of the experimental chamber. Beam currents were measured just after this collimator with a simple Faraday cup equipped with a secondary electron repeller. The currents were always larger than 50–100 pA for Au_1^+, Au_2^+, and Au_3^+, but 10 pA or less for Au_4^+ and Au_5^+. Electrostatic deflection plates were used to check if the clusters were intact when arriving at the experimental chamber. For Au_2^+, Au_3^+, and Au_3^- beams it was found that the charged fragment component in the beams was negligible at the normal operating pressure of less than 5×10^{-7} hPa. The

pressure in the beam tube had to be increased by an order of magnitude before significant fragmentation occurred. For Au_4^+ and Au_5^+ the fragment beams were too weak to be measured.

The mass eroded from the target was measured with the quartz microbalance method [22]. After the beam current measurements, the Faraday cup is retracted from the beam line to let the ions hit a thick gold layer covering an oscillating quartz. Our quartz microbalance [23] utilized a 0.5 mm thick quartz crystal oscillating at 6 MHz. A decrease of the gold thickness due to sputtering gives rise to a proportional increase of the oscillation frequency. Water cooling at room temperature was used during all the measurements in order to keep the quartz temperature constant. The gold thickness (initially 1000 ± 50 nm, vapor deposited onto the quartz oscillator surface) was always much larger than the maximum range of the projectiles in gold, in order to stop the projectiles within the gold layer to prevent the quartz crystal from being radiation damaged. The sputtering yields were directly deduced from the mass removed from the gold covering the quartz. The sensitive quartz surface had a diameter of 8 mm although the beam diameter was limited to 3 mm by the aperture. It was verified with centered gold depositions of increasing diameters that the frequency response of the quartz did not vary by more than 2% between diameters of 3 and 8 mm. A similar result may be deduced from the differential sensitivity measurement made by Oliva-Florio *et al.* [24]. We checked before each set of experiments that the beam spot was centered on the quartz surface. The focused beam had an elongated shape in the vertical direction ensuring that the beam in that direction was homogeneously distributed over the 3 mm aperture. For weak beams (Au_4 and Au_5) it was necessary to focus the beam in the horizontal direction to better than the 3 mm to obtain sufficient intensity and the beam spot was not fully homogeneous. In these cases yield measurements were performed with maximum beam current centered on the target, which will give too high a yield, and with the beam displaced 1 mm to the side, which will give too low a yield. The two values differed by no more than 25% and the average was used and assigned an error of half the difference. Further, no erosion was observed with the beam electrostatically deflected away from the target, excluding the possibility of erosion by neutrals.

Figure 1(a) shows the gold sputtering yields per atom, Y/n, as a function of the energy per atom of the projectiles, i.e., at the same velocity for all clusters. The error bars take into account uncertainties in the quartz response due to beam inhomogeneity, in the beam current measurement, and in the thickness measurement. They are not shown explicitly for Au_1 and Au_2 projectiles as their size is about the same as that of the symbols in the figure. For atomic projectiles, the maximum yield is roughly at the same energy as the maximum of the nuclear energy loss (calculated with the TRIM code [25] to be at ~800 keV for Au → Au) and agrees within 10% with the gold results

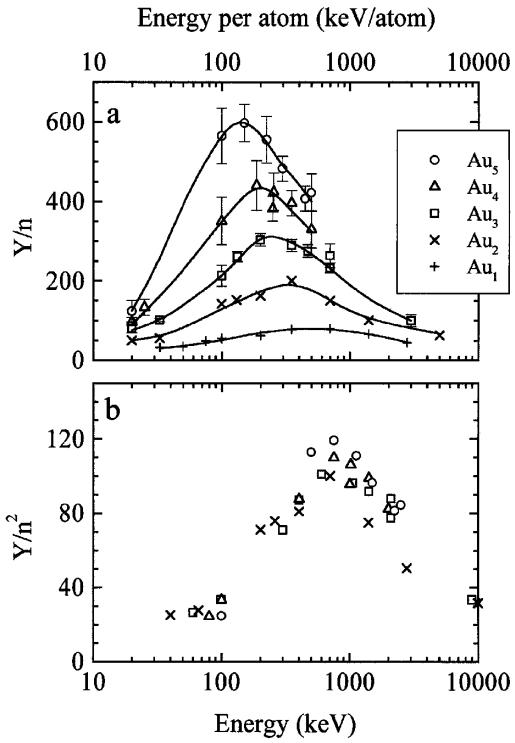

FIG. 1. (a) Gold cluster sputtering yields per atom, Y/n, for Au_1 to Au_5 cluster projectiles as a function of the energy per atom of the projectiles. The solid lines are guides for the eye to follow the energy dependence for each cluster size. (b) The same data as above (except for Au_1) shown as Y/n^2 and given as a function of *total* cluster energy.

of Bay *et al.* [2]. Taking into account the fact that the nuclear energy loss of bismuth into gold (calculated as above with TRIM) is higher than for gold in gold, and that the spike contribution is hence also larger, our results for Au_1 are consistent with (but 15% lower than) the Johar and Thompson [5] yields of gold induced by bismuth [26]. The overall tendency is that our data are a bit low compared to published data. The maximum sputtering yield measured with Au_5^+ projectiles at 150 keV/atom is 3000 ± 200, while the Au_1 yield is 55 at the same velocity. The figure thus shows the strong nonlinear enhancement of the sputtering yields induced by clusters $[Y(Au_n \rightarrow Au) \gg nY(Au \rightarrow Au)]$. There is no evidence of electronic sputtering, in agreement with the results of Bay *et al.* [2] which extend up to 20 MeV (electronic stopping constitutes some 15% of the total stopping at 1 MeV/atom and dominates the energy deposition above 3 MeV/atom). Figure 1(a) shows that the position of the maximum yield shifts to lower energy per atom as the cluster size increases, whereas in the absence of nonlinear effects all curves should fall on top of each other when plotted as a function of energy per atom. When the data are plotted as a function of the total energy [Fig. 1(b)] all the curves ($n = 2$ to 5) display the same maximum at about 800 keV. Our choice of ordinates in Fig. 1(b)

(Y/n^2, rather than normalizing the curves' maxima) is only indicative of an experimental trend. Since the nuclear stopping power of Au_n clusters is proportional to n at a given *velocity* (not energy) [27], our data rule out any empirical scaling with a power of $(dE/dx)_{\mathrm{nucl}}$ such as suggested in Ref. [6]. This result will be a crucial test for any theory of the cluster energy deposition mechanism, but clearly points to a spike mechanism.

Sigmund and Claussen assumed the sputtering yield to be a sum of the established linear collision cascade yield [3] and a contribution from a thermal spike surface evaporation [7]. The calculated linear yield (which contains no free parameters) fits existing yield data for Au on Au very well at energies far above and below the maximum of the nuclear stopping power [2,13]. The thermal spike in their model is assumed to be cylindrical and perpendicular to the surface in the version of the theory that we apply here. The only free parameter is the initial spike radius ρ_0. Sigmund and Claussen took $\langle\rho_0^2\rangle$ to be of the order of the mean square lateral straggling of the collision cascade. Taking a constant cylindrical track width $\langle\rho_0^2\rangle = 240$ Å^2, Sigmund and Claussen obtained rather good agreement with the experimental values of Ref. [5]. All the experimental points of Ref. [5] were obtained at energies well below the maximum of the nuclear energy loss, where the sputtering yields are still relatively small in comparison to those obtained in the present work. Using energy independent values of $\langle\rho_0^2\rangle$ we cannot obtain a similar agreement with the results of Fig. 1, mainly because the theory leads to a maximum at the same energy/atom for all clusters. The basic concept of an evaporation spike model is, however, attractive and we note that formally the results of Ref. [7] could be used with ρ_0 as a parameter increasing with both cluster size and energy. So reversing the procedure we deduced values of $\langle\rho_0^2\rangle^{1/2}$ from each experimental yield value (Fig. 2). There is an overall tendency for $\langle\rho_0^2\rangle^{1/2}$ to increase with energy, as expected [7], and the values appear physically reasonable, keeping in mind the relation between ρ_0 and the lateral straggling of the cascade. We have tried several power law variations of $\langle\rho_0^2\rangle^{1/2}$ with energy. A linear increase with energy, which could be justified by assuming an energy-independent shape of the spikes leads to too fast a vanishing of the thermal spike contribution with increasing energy. Other attempts using power laws were also in vain and we can conclude only that the relationship between $\langle\rho_0^2\rangle^{1/2}$ and the energy is somewhere in between a constant value and a linear variation. For a fixed velocity $\langle\rho_0^2\rangle^{1/2}$ is found to increase with cluster size. Although intuitively reasonable this possibility was not mentioned in Ref. [7]. The impressive data alignments of Fig. 1(b) remain unaccounted for. To have a complete thermal-spike theory of nonlinear sputtering yields we need a precise model for the relation between lateral straggling and spike radius as well as a calculation of lateral straggling of cluster-induced cascades as a function of energy.

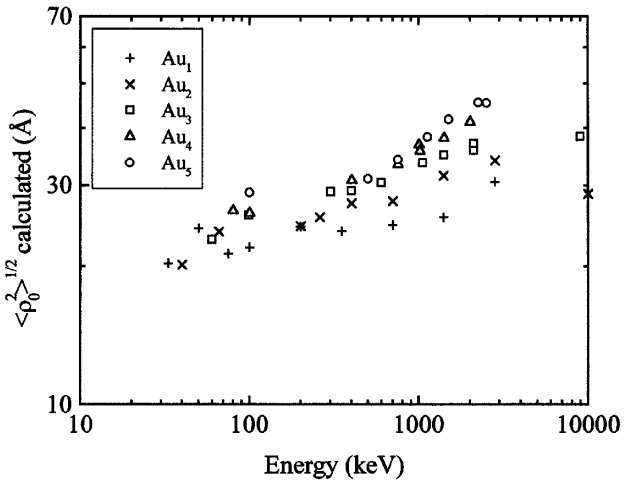

FIG. 2. Deduced values of the initial width of the cylindrical track, $\langle\rho_0^2\rangle^{1/2}$, as a function of the total cluster energy. For comparison, the radius of a Au_5 cluster is less than 3 Å.

Gold clusters have been found to induce very large sputtering yields from gold targets exceeding those ever observed before from a metal target. Nonlinear effects amounting to a factor of 10 have been observed. The nonlinearity is not given as a simple power of the nuclear stopping power. One can further speculate on the observation of saturation for such nonlinear effects when larger-cluster irradiations become possible at these energies. A simple extrapolation from Fig. 1(b) indicates that a ~800 keV energy Au_n cluster should have a sputtering yield of $\sim 100n^2$, meaning that a part increasing with n^2 of its energy would be consumed just to overcome the surface-binding energy (3.78 eV). For sputtering as clusters, the surface-binding energy is smaller but nearly compensated by their internal kinetic energy. The kinetic energy of the atoms sputtered through the linear cascade is a further 2.8% of the total energy [28]. Then, a 800 keV cluster having a size of $n = 45$ would consume 100% of its energy for sputtering. But, as a matter of fact, only a small fraction of the total projectile energy might be available for sputtering. Therefore, saturation of the nonlinear effect should be actively pursued through performing experiments with still larger clusters than Au_5.

In addition to very large nonlinear effects, we have found experimentally that the maximum in the sputtering yield moves to lower velocities as the cluster size increases. The dependence on total energy (rather than on the energy per atom) of the sputtering yield is the second main finding of this work. It indicates that the thermal spike theory of cluster sputtering needs to be amended in order to accommodate results obtained with irradiation by heavy clusters over a broad energy range.

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