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On Universality in Sputtering Yields Due to Cluster Bombardment

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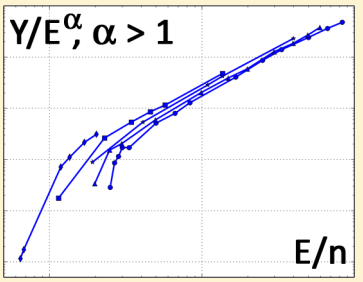
ABSTRACT: Molecular dynamics simulations, in which atomic and molecular solids are bombarded by Ar_n (n = 60−2953) clusters, are used to explain the physics that underlie the "universal relation" of the sputtering yield Y per cluster atom versus incident energy E per cluster atom (Y/n vs E/n). We show that a better representation to unify the results is $Y/(E/U_0)$ versus $(E/U_0)/n$, where U_0 is the sample cohesive energy per atom or molecular equivalent, and the yield Y is given in the units of atoms or molecular equivalents for atomistic and molecular solids, respectively. In addition, we identified a synergistic cluster effect. Specifically, for a given $(E/U_0)/n$ value, larger clusters produce larger yields than the yields that are only proportional to the cluster size n or equivalently to the scaled energy E/U_0. This synergistic effect can be described in the high $(E/U_0)/n$ regime as scaling of Y with $(E/U_0)^{\alpha}$, where $\alpha > 1$.



SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis

Energetic cluster beams are used in a number of experiments including surface cleaning, surface smoothing, and the analytical technique of secondary ion mass spectrometry (SIMS).[1] There is a seemingly infinite number of combinations of cluster composition, number of atoms in the cluster n (cluster size), beam kinetic energy E, and beam angle that one can implement. The issue is how to compare the results in an organized fashion in order to determine the optimal set of conditions for each application. One measure of the results of an experiment is the yield of material Y that is ejected per incident projectile. For cluster projectiles, there is the dependence of Y on the cluster size n, which is entangled with the dependence of Y on E.[2] The typical shape of the Y on E dependence for bombardment by clusters of size less than a few thousand particles within a broad range of incident kinetic energy (∼1−1000 keV) consists of a power onset, wide linear region and final drop.[2,3] Generally, the spread in the data points can be reduced by presenting the yield per projectile atom Y/n versus energy per projectile atom E/n on a log−log plot.[2,4] This property of the Y/n on E/n dependence was observed for atomistic (Ag, Au, Si) and molecular (octane, polystyrene, Irganox) solids sputtered by cluster projectiles (Au_n, C_{60}, Ar_n), all of which are used in experimental and computational studies to optimize the SIMS technique.[3,5,6] The Y/n versus E/n relation has been called "universal", and this assignment is somewhat supported by experimental and computational results, although there are two arms: one for organic solids and another for inorganic solids observed in this dependence.[6,7] The underlying physical interpretation is not, however, clear. The interpretation of the data is further muddled by either plotting together yields from clusters of different elemental composition or for solids of different chemical composition. Finally, because of the experimental energy range for clusters of ∼5−20 keV, different regions of the Y/n versus E/n graph as presented in the literature usually contain data from only a few cluster sizes. Specifically, small clusters are used for high E/n values and large clusters for small E/n values. There is often a gap in the middle or transition region. The goal of this study is to elucidate the essential physics behind the apparent universal Y/n versus E/n relationship and eventually apply the conclusions to experimental applications. In order to achieve these objectives, a systematic study has been designed.

Molecular dynamics (MD) simulations have been successfully used to understand many aspects of the energetic cluster bombardment process. We have therefore performed a number of MD simulations in which atomic and molecular solids were bombarded by Ar_n clusters in order to disentangle the important physical elements of the "universal relation". The substrate systems included in this study are the coinage metals Ag, Pt, Au, and Al,[8] and the molecular solid octane.[9] The elements come from three different rows of the periodic table and have a wide disparity of masses. The cohesive energies span almost a decade being 0.68, 2.95, 3.39, 3.81, and 5.85 eV for octane, Ag, Al, Au, and Pt, respectively. The elements Al, Ag, and Au have lattice constants within 1% of each other. We employed argon clusters because they are a popular cluster source for both surface smoothing and SIMS.[10,11] In addition, the results are not affected by possible chemical reactions between the atoms in the cluster beam and the substrate.

The basic characteristic of the yield Y versus total incident kinetic energy E for cluster bombardment of solids is given in Figure 1a, for different sized Ar_n clusters bombarding a Ag(111) surface as determined from the MD simulations. We present here the yield in units of volume Y_v according to the protocol that has been adopted in experiment to display the results. In the higher energy regime, the yield is approximately propor-

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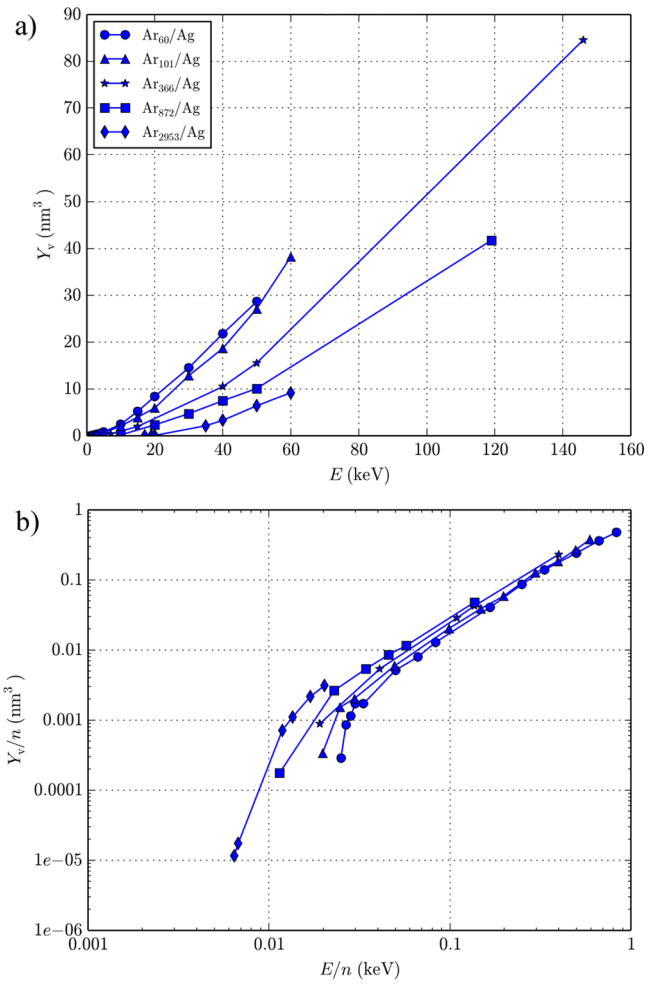

Figure 1. (a) Dependence of volume sputtering yield Y_v on total incident kinetic energy E for Ar_n cluster bombardment of a Ag(111) surface. (b) Same data plotted as Y_v/n versus E/n.

tional to the total kinetic energy, although the slope depends upon the cluster size n. At low energies, there is an onset region indicating a threshold for ejection. For a given total energy E, the smaller clusters produce larger sputtering yields. These characteristics have been observed in data from numerous simulations and experiments.[2−6,11−16] The experimental results of Ag and Au samples bombarded by small Au_n (n = 3−13) clusters showed that the agreement among sets of data for various cluster sizes n look better if Y/n^2 versus E/n is plotted in log−log format.[17] Anders et al., based on computational studies of self-sputtering of an amorphous Ar substrate by Ar_n (n = 1−1000) clusters, proposed Y/n versus E/n to reduce the spread in data points.[2] The latter approach has been adopted in subsequent studies. In this manner, the dependence of sputtering yield Y_v on the total incident kinetic energy E is shown in Figure 1b as Y_v/n versus E/n. For the high E/n regime, the slopes of the curves are similar. The differences in threshold region for low E/n values are magnified in the log−log plot. For all values of E/n, the highest Y_v/n value is for the largest cluster, an observation that is described in more detail below.

The interpretation of the new axes in Figure 1b is not necessarily obvious, especially the ordinate Y/n. The abscissa quantity E/n is generally interpreted as the energy per cluster atom but has also been interpreted as a quantity proportional to the square of the velocity[5] of the cluster. At this point we believe the essential interpretation is energy per cluster atom, although the initial energy loss of the cluster has been described by the cluster acting as a single bead experiencing frictional forces.[18−20] Even though there may be subtleties with the E/n interpretation, they are not as perplexing as the reasons behind the yield per atom dependence. Assuming the Y/n dependence on E/n to reduce the spread in the data points, one can notice that the shape and relative positions of the curves in Figure 1b will be the same if the vertical axis is Y/E. This is because for a given E/n value, the total energy E is proportional to the number of cluster atoms n. The interpretation now is that for a given E/n value in the high E/n regime of the Y/E versus E/n dependence, the total yield scales with the total energy E, which makes more physical sense rather than Y/n, because the total energy E is the primary factor affecting the value of the yield Y. As proposed by others[2,18,21] the important energy is the one that is relative to the cohesive energy of the solid per atom U_0. Since using the cohesive energy per atom U_0, the sputtering yield Y must also be given in atoms rather than the current experimental convention of presenting it in the units of volume.[6]

The plot of $Y/(E/U_0)$ versus $(E/U_0)/n$ in log−log format is given in Figure 2a for four metals and a variety of Ar cluster

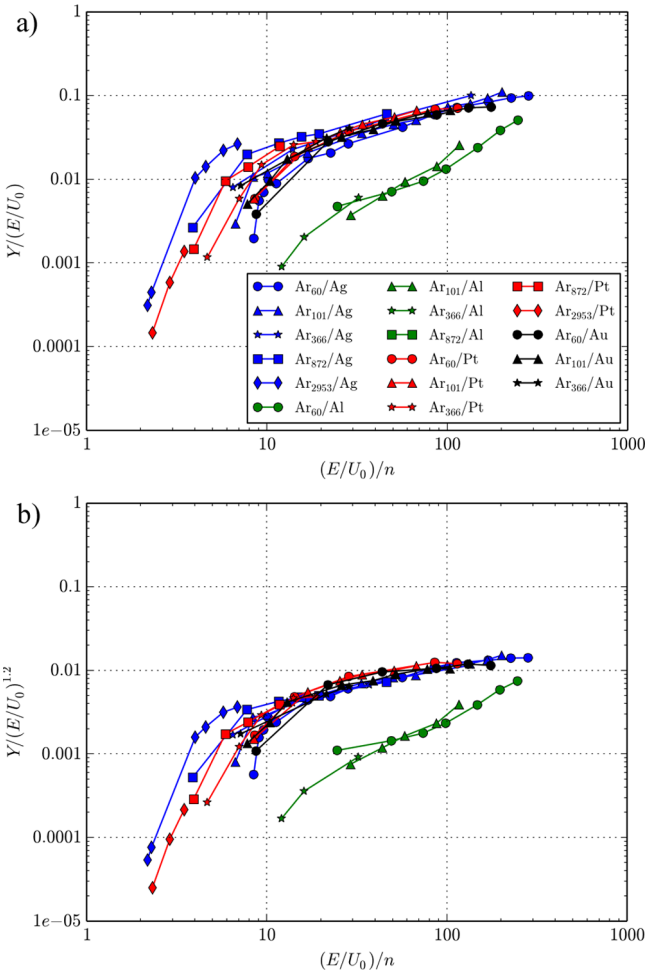

Figure 2. (a) Dependence of the sputtering yield Y per scaled total energy E/U_0 on the scaled total energy E/U_0 per projectile atom n for Ar_n cluster bombardment of Ag(111), Al(111), Pt(111), and Au(111) surfaces. (b) Same data plotted as $Y/(E/U_0)^{1.2}$ versus $(E/U_0)/n$.

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sizes n. The curves for the three metals, Ag, Pt and Au, are in near concurrence with each other, whereas the values for Al are about an order of magnitude lower. The energy partitioning in these systems is quite different. There are three channels into which the energy can go, including kinetic energy of the sputtered metal atoms, kinetic energy of the reflected Ar atoms, and deposition into the solid. For Ag, Pt, and Au, the energy partitioning is very similar in the $(E/U_0)/n > 10$ region with 10−15% of the energy going to kinetic energy of sputtered metal atoms, 5−10% of the energy going to kinetic energy of reflected Ar atoms, and the remaining 70−80% going to deposition into the solid. The energy partitioning for Al is distinct, with the percentages being <5%, ∼0%, and >95%, respectively. That is, almost all of the primary energy for Ar cluster bombardment of Al deposits into the solid. We believe two factors are important, namely, the relative mass of the cluster atom and substrate atom and the openness of the solids. The metals Ag, Pt, and Au all have atomic masses much greater than Ar, whereas the mass of Al is less than Ar. In addition, the openness of the Al crystal is greater than the other metals since it has the same lattice constant as Ag and Au, but the atomic number of the Al atoms is considerably smaller. Essentially, the size of the Al atoms are smaller than the Ag, Pt and Au atoms. The lighter mass and the greater openness of the Al system allows the Ar atoms to penetrate deeper into the solid, depositing more energy into the solid with less going into the energy of the sputtered and reflected particles. Consequently, the yield is less. This first test case of four coinage metal systems shows that including the scaled energy E/U_0 in the $Y/(E/U_0)$ versus $(E/U_0)/n$ dependence improves the agreement between the results for different systems, although there are still missing sample dependent factors.[7] Missing factors include items such as relative mass of the cluster and substrate atoms, structural effects and related penetration depth of the energy, and potentially other physical properties or processes.

The data shown in Figures 1b and 2a still show that the larger clusters give larger Y_v/n and Y/E values for a given E/n value and a given data set. The actual dependence for which the spread in data points is reduced the most is $Y/(E/U_0)^{1.2}$ versus $(E/U_0)/n$, as shown in Figure 2b. There is a synergistic effect with the larger clusters, an observation also noted in previous studies and often called the nonlinear effect.[22,23] For larger clusters, less energy is lost into solid, and thus more energy goes into sputtering. In addition, our simulations show that systems with larger yields tend to have more clusters of atoms in the ejected material. The effective cohesive energy for clusters is less than the sum for the individual atoms. We do not expect the exponent value of 1.2 to be universal, but we do expect that a larger cluster will produce a larger yield than the yield that is only proportional to the cluster size n. Taking into account the assignment of $Y/(E/U_0)$ for the vertical axis and regardless of the underlying mechanism, this synergistic effect can generally be described as scaling of Y with $(E/U_0)^{\alpha}$, where $\alpha > 1$, for a given $(E/U_0)/n$ value. For example, the synergistic cluster effect for small clusters (n = 3−13) bombarding a metal substrate[17] has $\alpha = 2$.

The last check is whether this new set of variables works for molecular solids where the volume yields are about 2 orders of magnitude larger than for atomic solids.[5,6,11,13−16] Shown in Figure 3a are the Y/n versus E/n curves for Ar_n cluster bombardment of octane and Ag surfaces in which the yield is given in volume units of nm^3. For our simulations, the volume yields differ by an order of magnitude. Shown in Figure 3b is $Y/(E/U_0)$ versus $(E/U_0)/n$ dependence for the same systems. The yield for octane is in molecular equivalents and includes intact and fragmented molecules. The definition of the cohesive energy U_0 of the molecular solid is not straightforward, as the sputtering process involves breaking weak intermolecular interactions and strong intramolecular bonds.[6] Since we observe little molecular fragmentation in the octane system,[9] we use the molecular value of 0.68 eV as U_0 for an octane molecular equivalent. All data points agree within a decade of each other. This observation supports our statement of achieved unification in data, because the original volume yields differ by an order of magnitude and so differ the cohesive energies for investigated molecular and organic solids. The high $(E/U_0)/n$ portion of the curves for octane is flatter than for Ag, a trend also seen experimentally.[6,11,13−16] Our simulations show that as $(E/U_0)/n$ increases for the octane system, a significant amount of the incident energy goes into internal excitation and fragmentation of the molecules, thus less energy is available for ejection, and the yield does not increase with energy.

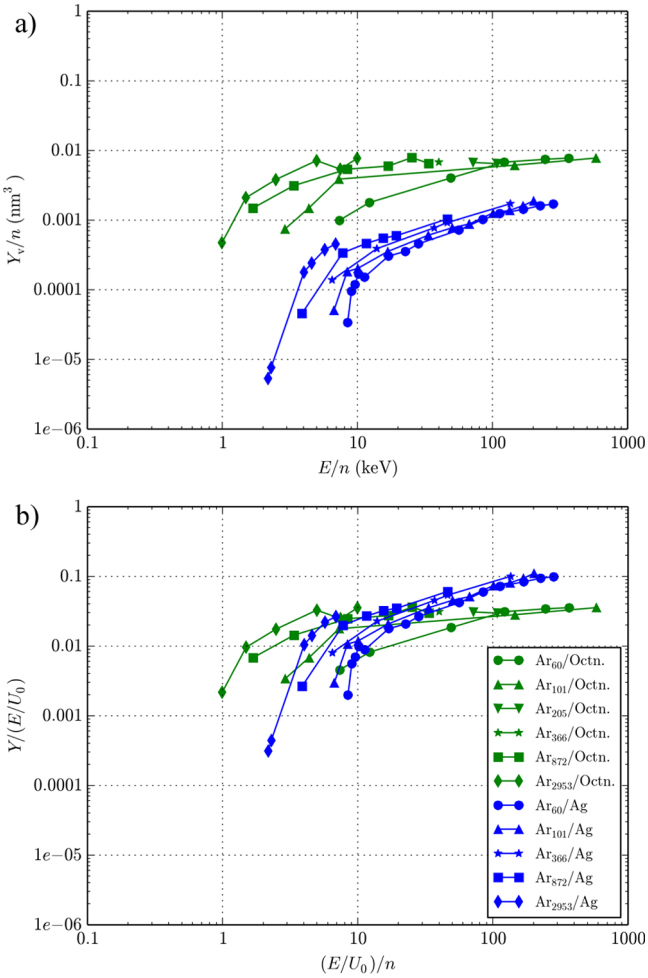

Figure 3. (a) Dependence of Y_v/n in volume units of nm^3 on E/n for Ar_n cluster bombardment of octane and Ag(111) surfaces. (b) Same data plotted as $Y/(E/U_0)$ versus $(E/U_0)/n$.

In summary, we have explored the underlying physics that is associated with so-called universal representation of Y/n versus E/n for sputtering yield due to cluster bombardment. The data actually fall in better concurrence when $Y/(E/U_0)$ versus $(E/U_0)/n$ is used, where U_0 is the cohesive energy of the sample per atom or molecular equivalent, and the yield Y is given in

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units of atoms or molecular equivalents for atomistic and molecular solids, respectively. The $Y/(E/U_0)$ versus $(E/U_0)/n$ representation is, however, still missing some significant sample and possibly projectile properties and as such does not allow to completely unify the results for all systems. The most notable factors missing from the representation are the relative mass of the projectile and substrate atoms, and structural effects, both of which influence the amount of energy E that can be utilized for sputtering. If either most of the primary energy is back reflected or deposited below the depth that can contribute to sputtering as shown by the Al results, the sputtering yield is reduced. We have also identified a synergistic effect for larger clusters. Specifically, for a given $(E/U_0)/n$ value, larger clusters produce larger yields than the yields that are only proportional to the cluster size. This synergistic effect can generally be described in the high $(E/U_0)/n$ regime as scaling of Y with $(E/U_0)^{\alpha}$, where $\alpha > 1$.

METHODS

The calculation protocol was described in detail previously.[24] The coinage metal samples[8] used in MD calculations were cuboid and measured from approximately 30 × 30 × 17 to 35 × 35 × 27 nm. In all cases, the (111) face was used. The crystalline octane samples[9] were hemispherical with a radius from approximately 12.5 to 17.5 nm. The size of the sample depended on the cluster size and incident energy. The samples were bombarded by Ar_n clusters of n = 60, 101, 205, 366, 872, and 2953 atoms at normal incidence. An average from 10 trajectories per set of conditions was used to obtain the data points for the coinage metal simulations. For the octane simulation, only one trajectory per set of conditions was used for this purpose because of extensive computational cost of the calculations. Our studies on the octane system showed, however, that the sputtering yields obtain from single trajectories differ by no more than 10% from each other.

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Notes

The authors declare no competing financial interest.

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