Combined simulations and analytical model for predicting trends in cluster bombardment

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1. Introduction

The ability to computationally model the use of cluster beams in secondary ion mass spectrometry (SIMS), at experimentally significant incident energies in the range of 10–120 keV, is limited due to the fact that these higher energies require large samples in order to contain the entire bombardment event. Along with the computational challenges for performing these simulations is the lack of predictive analytical theories which utilize material properties to estimate the relative yield of ejected material. To overcome these challenges, a new approach has recently been developed that uses information from short time (\(\approx 0.5\) ps) molecular dynamics simulations along with an analytic model to predict trends in ejection behavior for \(\text{C}_60\) and \(\text{Au}_3\) bombardment of water ice [1,2]. The advantage of this approach is that the properties of the cluster and substrate material are included in the MD simulations, thus the explicit dependence of the sputtering yield on these properties does not need to be known. Since the development of the mesoscale energy deposition footprint (MEDF) model [1,2], it has been applied to several simulation systems. In this paper we describe the model and summarize the applications to a variety of systems.

2. Computational details

The mesoscale energy deposition footprint (MEDF) model was developed based on the work of Jakas et al. [3] and has been described in detail previously [1,2]. One can debate whether the clusters used in SIMS actually deposit energy in a track, but ultimately the validity of this approximation will be in how well the MEDF model works in predicting accurate yield trends in SIMS calculations. Briefly, the energy which has been transferred from the projectile to the sample is described using fluid dynamics. This energy creates a cylindrical track, with a radius of \(R_{\text{cyl}}\), of kinetically energized particles in the sample (see Fig. 1a). As time passes and the material is evacuated, there is a greater area of contact with the vacuum and additional material can be permitted to escape (Fig. 1b). Using this model, the yield is approximated as a conical region and can be estimated by the equation

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Y = \frac{h_0}{3} \left( \frac{p}{3} \right) R_{\text{cyl}}^3,
\]

where \(h_0\) is the number density of the sample, \(R_{\text{cyl}}\) is the radius of the excited track, and \(R_S\) is the extended radius which delineates the volume of additional material that can eject and is related to \(R_{\text{cyl}}\) by the equation, \(R_S = \left( \frac{\bar{E}}{E_{\text{exc}}} \right)^{1/2} R_{\text{cyl}}\) where \(\bar{E}\) is the average excitation energy above the cohesive energy of the sample. Inserting this equation into the yield equation gives, \(Y = \frac{h_0}{3} \left( \frac{p}{3} \right) R_{\text{cyl}}^3 \bar{E}\). From this equation, only the radius of excitation and the average amount of excitation is needed in order to get an estimate of the ejected volume and amount of yield which will result from a particular bombardment event.
There are several steps that are needed in order to analyze a particular system using this model, which warrants a description of the analysis process. These steps are described as follows:

- Determine at what time one is going to examine the energized track. In studies to date, we have chosen this time to be when 90% of the projectile energy has been deposited to the substrate. For the systems studied thus far, the 90% energy transfer time is on the order of 50–200 fs.

- At the 90% energy transfer time, create a contour plot of $\tilde{E}$ (see Fig. 2).
  - The fluid dynamics calculations assume that the track is only energized in the radial/horizontal direction, thus we omit kinetic energy associated with motion in the vertical direction.
  - The contour plots in Fig. 2 have been plotted for a slice 2 nm thick centered at the point of impact of the cluster. In more recent studies, we have used cylindrical averages to remove directional inhomogeneities.

- Determine the value of $R_{\text{cyl}}$ from the contour plots such as those shown in Fig. 2. This can be done by choosing the proper excitation scale. The average excitation is based on the binding energy of the particles, thus a total energy of zero corresponds to having sufficient energy to be free of any potential, and the corresponding $\tilde{E}$ will be equal to one since it is one full binding energy unit higher than equilibrium. Ideally the interface ($R_{\text{cyl}}$) between bound material (grey) and excited material would be uniform as in the illustrations in Fig. 1. As one can see from the contour plots in Fig. 2 however, this is not the case. Although we have used a color scale which makes a clear distinction between areas with average excitation greater than one, the value of $R_{\text{cyl}}$ is not easily defined and must be visually estimated. Thus we often calculate yields for values of $R_{\text{cyl}}$ slightly smaller and larger than our estimate in order to account for the imprecise nature of the evaluation of this value.

- Once the value of $R_{\text{cyl}}$ is estimated, determine the value of $\tilde{E}$ within the entire volume of the cylinder $R_{\text{cyl}}$ and depth $R_{\text{cyl}}$.

- Calculate the yield from the equation, $Y = \eta \pi / (3) R_{\text{cyl}}^3 \tilde{E}$. The bottom of Fig. 2 shows the predicted conical volume for 5-keV bombardment of Au$_3$ and C$_{60}$ on water ice along with the original positions of the molecules that eject. Although there is not perfect agreement, the ejected molecules do originate from approximately the same region.
Several systems of interest have been studied and are being used to investigate the MEDF model, by both ourselves and others. Some of these include amorphous water [1,2], silicon, silicon-carbide, diamond [4], benzene [5,6], and silver samples [7]. In the remainder of this paper, we will focus on some of the key outcomes of the model, and illustrate how the MEDF model has been used to extrapolate short time MD simulations to obtain relative yields for experimentally relevant conditions beyond the scope of current simulation.

3. Results

3.1. Amorphous water

The MEDF model was developed for 5-keV bombardment by Au$_3$ and C$_{60}$ of amorphous water ice as shown in Fig. 2 and discussed above. Several short time simulations were run using various incident energies in the range of 10–80 keV for Au$_3$ and C$_{60}$ on amorphous water. The MEDF predicted yields along with experimental results for similar systems is shown in Fig. 3 as a function of incident energy.

The error bars associated with the figure represent a fluctuation of ±0.3 nm in the calculation of $R_{cyl}$ and ±10% for the experimental results. The model predicts that the sputtering yield due to C$_{60}$ bombardment will rise rapidly relative to increasing incident energy whereas the yield due to Au$_3$ bombardment is almost independent of energy. From the contour plots the reason for this behavior is evident. The Au$_3$ deposits a large portion of its energy too deep for it to effectively promote ejection. The C$_{60}$ on the other hand deposits its energy in the near surface region, almost independent of energy. (It must be noted that the results for Au$_3$ agree with the experimental yield far greater than can be justified.) The deviation which occurs for C$_{60}$ but is absent in the Au$_3$ case, may be due to the fact that these simulations treated the water molecules as rigid and did not allow for any reactions to take place. Allowing energy from the bombardment event to go into reaction pathways may significantly alter the excitation energy profile of the events and thus affect the yield. Similar simulations have been performed which allow for some reactions to take place, and it was found that the C$_{60}$ creates a larger density of reacted material in the near surface region than the Au$_3$ (see Fig. 4) [8]. Therefore, any effects the reactions may have will be significantly magnified in the case of C$_{60}$ due to the fact that $R_{cyl}$ is on the order of 2 nm.

3.2. Silicon, silicon carbide and diamond

Simulations have been performed to investigate the dynamics of silicon, silicon carbide, and diamond bombarded with C$_{60}$ [4]. As one proceeds from Si to SiC to diamond, the number density almost doubles for each material, thus a simple analysis would give that the yield should increase accordingly. The cohesive energy, however, also increases indicating that the yield should decrease. The full MD simulations show that the largest yield, by almost a factor of two, occurs for SiC. The MEDF analysis delineates how the various factors influence the sputtering yield and illustrates how these two properties become competing terms in the yield equation.
3.3. Benzene and silver

A series of simulations using benzene and silver samples have been used to investigate the yield due to bombardment by various size clusters [6,7]. These simulations were performed using a range of fullerene clusters from C$_{20}$ to C$_{540}$ to determine if there is an optimally sized cluster for maximizing yield. The results of these calculations indicate that clusters like C$_{60}$ of intermediate size produce the highest yields for 5-keV bombardment on benzene and 15 keV on silver. Again, using the MEDF model, these results can be explained based on the characteristic way each cluster deposits its energy. The mid-sized clusters are able to deposit their energy at an optimal depth to produce ejection, while the smaller and larger clusters deposit energy either too shallow or too deep respectively. The MEDF model has also been used for the benzene sample to predict the trends at higher energies [5].

4. Conclusions

The use of the MEDF model as a tool for elucidating trends in cluster bombardment behavior has been presented. Using only the physical information obtained within the first 0.5 ps of a simulation, we are able to determine the general yield trends associated with varying clusters and energies, as well as elucidate a physical basis for the phenomena that occur. This model has successfully described the increased yield via C$_{60}$ versus Au$_3$ based on the deposition of energy within a sample. We have also been able to explain the increased total yield of silicon carbide versus silicon and diamond, and the optimal deposition behavior of mid-sized clusters such as C$_{60}$. Further development of this model is being carried out so that it can be utilized over a broader range of systems and projectiles.

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References