

# Angle of incidence effects in a molecular solid

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## Abstract

We investigate the influence of the angle of incidence on the sputter yield when bombarding a molecular solid, benzene, with  $C_{60}$ . Our simulations show that at normal incidence, essentially all of the projectile energy is deposited into the substrate within  $\sim 2.5$  nm of the surface. However, at  $75^\circ$  incident angle, only 35% of the projectile energy is deposited within a depth of less than 1.5 nm of the surface while 65% of the projectile energy is reflected. Therefore, important aspects of the collision process which are dependent upon energy deposition, such as sputter yield, ejection depth, and molecule dissociation, may change as the incident angle changes.

*Keywords:* Molecular Dynamics, cluster,  $C_{60}$ , SIMS, incident angle

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## 1. Introduction

Molecular dynamics (MD) simulations have been shown to be an effective tool for gaining insight into the physical phenomena that occur during cluster bombardment. Numerous simulations have illuminated aspects of the crater formation and subsequent ejection of material. At this stage, simulations are generally performed by aiming the projectile normal to the surface in order to simplify the subsequent analysis of ejected particles while experiments are performed at an off-normal angle of incidence. The importance of incident angle is well-established for atomic bombardment, but the effect for cluster bombardment is not completely established.

There have been a few studies that have discussed the influence of incident angle on sputter yield. Hill and Blenkinsopp observed an increase of Si yield when Si is bombarded with 15 keV  $C_{60}^+$  as the incident angle is increased from  $0^\circ$  to  $60^\circ$  [1]. Likewise, Krantzman et al. performed corresponding simulations to the experiments of Hill and Blenkinsopp and observed a higher sputter yield of Si at  $45^\circ$  than at normal incidence. At both incident angles, all of the carbon atoms in the projectile become deposited in the substrate by forming SiC bonds, but for the  $45^\circ$  angle simulation more energy is deposited near the surface creating the larger Si yield [2]. Conversely, Postawa et al. observed a decrease in Ag yield for 15 keV  $C_{60}$  bombardment of Ag {111} with incident angles ranging from normal incidence to  $60^\circ$  with respect to the normal. Here the substrate atoms have a much larger mass than the projectile atoms, so less projectile energy is transferred to the surface at more grazing incident angles which explains the decrease in yield [3]. Lastly, Sanada et. al. used a  $C_{60}$  beam at varying angles to clean polymer and organic surfaces, which were then analyzed using x-ray photoelectron spectroscopy. They found that using the more grazing angles such as  $75^\circ$  results in more effective cleaning without damage of polymer samples than near-normal incident angles,  $0^\circ$  and  $15^\circ$  [4].

The difference in yield trends with off-normal angle of incidence for the various substrates relates to where energy is deposited. For heavy targets, an off-normal angle of incidence may result in back-scattering in which case the effective incident energy is reduced as the incident angle becomes

more grazing. On the other hand, the energy is deposited deeper into the substrate at normal incidence, and it may put the energy too deep to efficiently contribute to the sputter yield. Given the importance of molecular solids in SIMS applications, here we perform simulations of 5 keV  $C_{60}$  bombardment of a molecular solid, benzene, at incident angles ranging from normal incidence to  $88^\circ$  with respect to the normal. We investigate the effect of angle of incidence on crater shape and size, the amount of projectile energy deposition, and total ejection yield.

## 2. Simulation Method

The molecular dynamics method and simulation preparation used have been described elsewhere [5-7]. Briefly, Hamilton's equations of motion are integrated to determine the positions and velocities of each atom as a function of time. The system used contains 198,720 benzene molecules in an orthorhombic structure. We used a coarse-grained approach to eliminate hydrogen atoms from the simulations. The coarse-grained technique describes a benzene molecule as six CH beads each with a mass of 13 amu rather than six carbon atoms and six hydrogen atoms. This technique has proven to significantly decrease simulation time as a simulation of 500 eV  $C_{60}$  on atomistic benzene took 6 months to calculate for 25 ps, but an identical simulation using the coarse-grained benzene took only 4 days to calculate [6]. The interactions among all the particles have been published elsewhere [8]. The C-C potential between carbons in the fullerene projectile were described using the Brenner REBO potential designed for hydrocarbons [9]. The 5 keV  $C_{60}$  projectiles had varying incident angles of  $0^\circ$ ,  $15^\circ$ ,  $30^\circ$ ,  $45^\circ$ ,  $60^\circ$ ,  $75^\circ$ , and  $88^\circ$  with respect to the normal.

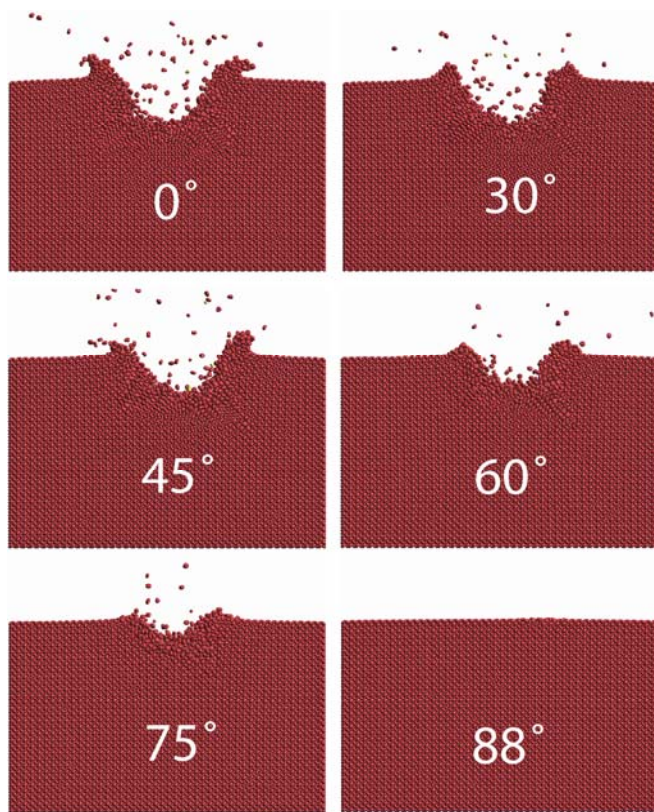
## 3. Results and Discussion

Snapshots of the crater formed by each trajectory are shown in Figure 1 after a time of 10 ps. For the angles,  $0^\circ$  through  $30^\circ$  the craters formed are similar in shape and size, thus the  $15^\circ$  trajectory is omitted. At  $45^\circ$ ,  $60^\circ$ , and  $75^\circ$  the craters are shallower, but still maintain a hemispherical shape. For the trajectory run with an  $88^\circ$  incident angle, there is no apparent crater at 10 ps. In fact, the surface looks barely disturbed. For the angles  $0^\circ$  to  $30^\circ$ , almost all of the projectile energy is deposited into the sample as seen in Figure 2a, and then beginning with  $45^\circ$ , some of the projectile energy begins to be reflected back into the vacuum, thus reducing the effective incident energy. The observed ejection yield vs. the incident angle is shown in Figure 2b, and we see that there is no significant difference in yield between  $0^\circ$  and  $30^\circ$  degrees, however, at  $45^\circ$  the yield begins to decrease. The yield trend is directly correlated with the amount of energy deposited to the substrate. As more energy is deposited to the surface, there is a higher ejection yield. These results are similar to those seen by Postawa et al. [3] in that as the effective incident energy is decreased, the observed ejection yield also decreases.

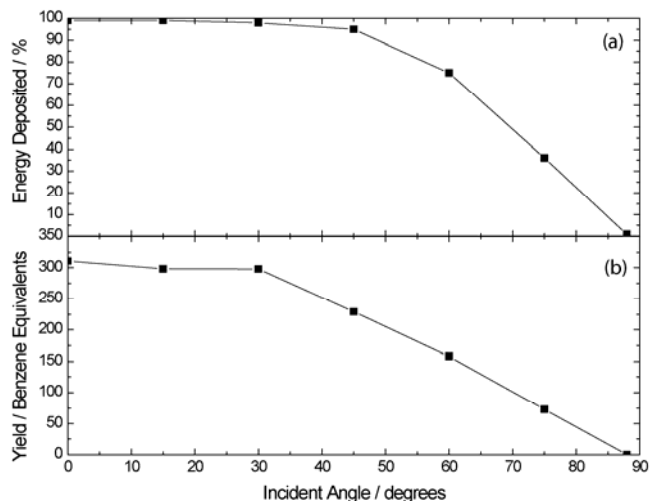
The results suggest that using a grazing incident angle would be beneficial for cleaning polymers and organic films as reported by Sanada et. al. [4]. The shallow crater formed by the projectile aimed at  $75^\circ$  indicates that only material within 2 nm of the surface is removed, while at normal incidence, material is disrupted at a depth of greater than 4 nm. In addition, the low level of energy deposition and back-scattering of material would lead one to believe that any molecular damage would be ejected rather than left in the substrate which may occur for a projectile aimed at normal incidence.

These calculations have been performed at 5 keV whereas many of the experiments are performed at 20-40 keV. The effect of incident angle has been studied for 40 keV  $C_{60}^+$  bombardment of cholesterol films.[10] Here, the highest yield was observed at an incident angle of  $45^\circ$  with only a small decrease in yield as the angle approaches  $75^\circ$ . A question is whether the yield trend observed in simulations can be extrapolated to higher kinetic energies and therefore be compared to experimental studies. Recently we have developed the mesoscale energy deposition footprint (MEDF) model for

taking short-time information from a simulation to predict where the energy is deposited and hence to estimate the yield [11, 12]. Although this model has only been developed to date for normal incidence, we can use some of the concepts for these simulations. For normal bombardment at 5 keV on the coarse-grained benzene system, the energy is deposited at almost exactly the correct depth to be used effectively for ejection. As the incident energy of the projectile increases, the energy is deposited too deeply, and some of the energy is deposited in the bulk of the crystal [12]. For the more off-normal angles of 60° and 75° at 5 keV, however, the energy is deposited too shallow thus producing low ejection yields. As the incident energy of the projectile increases, we assume the energy will also be deposited deeper into the crystal, but for some depth increase, the deposited energy will still contribute to enhanced yield. Thus, a straightforward extrapolation of our results to higher energies is not currently possible. Short-time simulations are underway to determine the incident energy effect of the yield vs. angle trend.



**Figure 1.** Snapshots at 10 ps of a 2 nm slice of the sample centered around the point of impact for projectiles aimed at 0°, 30°, 45°, 60°, 75°, and 88° with respect to the normal.



**Figure 2.** (a) The percentage of projectile energy deposited to the substrate as a function of incident angle. (b) The calculated yield at 26 ps as a function of incident angle.

#### 4. Conclusions

Simulations of 5 keV  $C_{60}$  at incident angles, 0°, 15°, 30°, 45°, 60°, 75°, and 88° show that between normal incidence and 30°, there is virtually no difference in terms of crater formation and yield. For more grazing angles, 45° to 88°, the crater become very shallow, and the yield is decreased.

The next step of this project is to test the angle of incidence effects when the sample is bombarded with 5 keV Au<sub>3</sub> and both projectiles at higher energies.

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