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# Theoretical simulations of atomic and polyatomic bombardment of an organic overlayer on a metallic substrate

K.D. Krantzman <sup>a,\*</sup>, R. Fenno <sup>a</sup>, A. Delcorte <sup>b</sup>, B.J. Garrison <sup>c</sup><sup>a</sup> Department of Chemistry and Biochemistry, College of Charleston, 66 George Street, Charleston, SC 29424-0001, USA<sup>b</sup> PCPM, Université Catholique de Louvain, Louvain-la-Neuve, Belgium<sup>c</sup> Department of Chemistry, Penn State University, University Park, PA, USA

## Abstract

Our previous molecular dynamics simulations on initial test systems have laid the foundation for understanding some of the effects of polyatomic bombardment. In this paper, we describe simulations of the bombardment of a more realistic model system, an overlayer of *sec*-butyl-terminated polystyrene tetramers on a Ag{111} substrate. We have used this model system to study the bombardment with Xe and SF<sub>5</sub> projectiles at kinetic energies ranging from 0.50 to 5.0 keV. SF<sub>5</sub> sputters more molecules than Xe, but a higher percentage of these are damaged rather than ejected intact when the bombarding energy is greater than 0.50 keV. Therefore, at energies comparable to experimental values, the efficiency, measured as the yield-to-damage ratio, is greater with Xe than SF<sub>5</sub>. Stable and intact molecules are generally produced by upward moving substrate atoms, while fragments are produced by the upward and lateral motion of reflected projectile atoms and fragments from the target molecule. SF<sub>5</sub> is ineffective on this model system because of the densely packed lattice and the high mass of the substrate atoms. Experiments have determined that enhancements in yield with polyatomic projectiles are smaller on thin organic films compared to those found on thick organic targets.

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## 1. Introduction

Secondary ion mass spectrometry (SIMS) experiments have well established that polyatomic projectiles have the potential to greatly increase the sensitivity of static SIMS [1]. However, there are still many unresolved questions about how polyatomic projectiles enhance the yield of secondary

ions. For example, experiments show that the degree of enhancement varies greatly and depends on both the characteristics of the projectile and of the target. Furthermore, along with producing a larger emission yield, a polyatomic projectile will often induce more damage to the sample [1–4].

Our previous molecular dynamics simulations of the keV bombardment of organic films on atomic and metallic substrates have provided mechanistic insights into how polyatomic projectiles affect both the yield of desorbed molecules and the damage to the sample as compared to atomic

\* Corresponding author. Fax: +1-843-953-1404.

E-mail address: [krantzmank@cofc.edu](mailto:krantzmank@cofc.edu) (K.D. Krantzman).

projectiles [5–8]. Molecules that have multiple contact points to the surface are ejected intact when several substrate atoms hit different parts of the molecule, resulting in the cooperative uplifting of the molecule [5,9–11]. Our simulations show that the projectile must be able to penetrate the surface and break apart within the substrate in order to produce multiple collision cascades that can collaborate to lift intact molecules from the surface. Efficient transfer of energy is facilitated by substrates with open lattice structures and mass matching between the projectile and substrate atoms. However, these initial simulations were performed on test systems too small to be compared directly with experiment. Although useful as a guide, it is not clear that conclusions drawn from our simulations at bombarding energies less than 1.0 keV can be used to interpret SIMS experiments. With the increase in the available computational power, we have been able to extend these simulations to a more realistic model system. In this paper, we present the results of our simulations of the bombardment of a thin organic film on a metallic substrate with Xe and SF<sub>5</sub> projectiles at energies comparable to experimental values.

## 2. Method

The classical method of molecular dynamics simulations is used to study the system of interest and the application of this method is explained comprehensively elsewhere [9]. Briefly, the position and velocity of each atom as a function of time is determined by numerically integrating the classical equations of motion. The force on each atom is calculated from the gradient of the potential energy function, which is a careful blend of empirical pairwise potentials and sophisticated many-body potentials. Details of the simulations are described by Delcorte et al. [10,11]. The model system, shown in Fig. 1, is composed of 13 *sec*-butyl-terminated polystyrene tetramers physisorbed on a Ag{111} substrate of 7350 atoms. Simulations were performed with normal incident Xe and SF<sub>5</sub> projectiles at kinetic energies of 0.50, 1.0, 2.0 and 5.0 keV. The results at every incident energy are averaged over 150 trajectories, each with a differ-

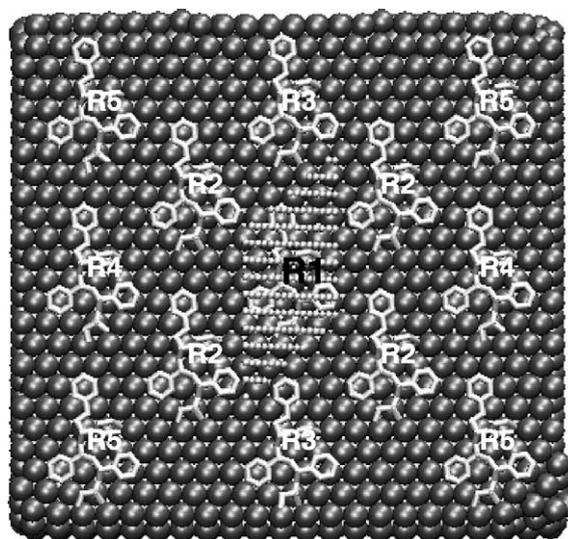


Fig. 1. Top view of the model system used in the simulations. Thirteen *sec*-butyl-terminated polystyrene tetramers are adsorbed on a Ag{111} substrate. Results are averaged over the 150 impact points shown as white dots. The labels R1, R2, etc. correspond to the distance of each molecule from the impact zone.

ent initial impact point on the surface. The impact points, which are shown in Fig. 1, are evenly distributed over an impact zone chosen to sample all symmetrically equivalent points on the surface.

## 3. Results

In each trajectory, the bombardment of the primary particle results in the ejection of intact molecules, molecular fragments and substrate atoms. A snapshot at 600 fs of a sample trajectory with SF<sub>5</sub> at 5.0 keV is shown in Fig. 2. When SF<sub>5</sub> impacts the surface, it strikes the molecule in the target zone, which breaks into many fragments. These fragments collide with neighboring molecules as they move away from the surface and fragment them. Reactions between these fragments and neighboring molecules occur to form new hydrocarbon clusters. Energy is also transferred to atoms in the silver substrate, which gently lift intact polystyrene tetramers from the surface at later times.

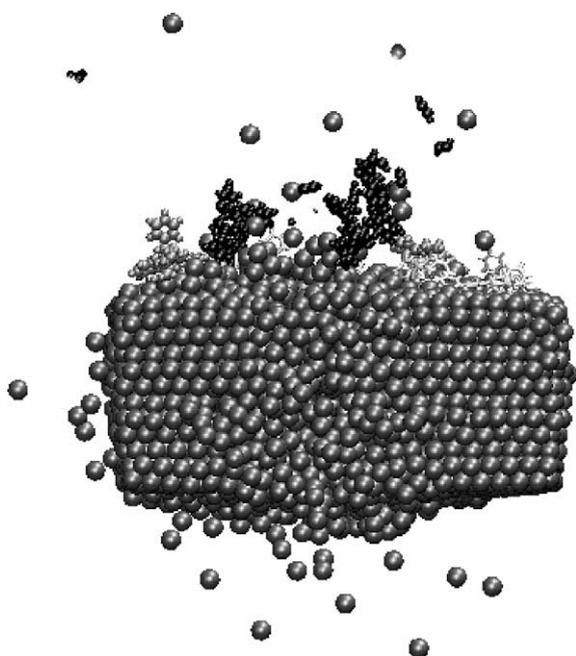


Fig. 2. Illustration of a sample trajectory at 600 fs produced by 5.0 keV  $\text{SF}_5$  bombardment. The silver spheres represent the substrate atoms and the white lines represent the polystyrene tetramers that remain on the surface. The black spheres represent polystyrene molecules are ejected as fragments. The smaller gray spheres represent two polystyrene molecules at positions R2 and R5, which are ejected stable and intact at times later in the trajectory.

Whole molecules that are ejected with internal energies less than the value estimated for dissociation, 28 eV [10,11], are predicted to reach an experimental detector intact and be measured as signal. The yield, a measure of the useful signal, is defined as the number of ejected stable polystyrene molecules. In Fig. 3(a), the average yields with Xe (closed circles) and with  $\text{SF}_5$  (closed triangles) are plotted as a function of incident kinetic energy. The yield increases as a function of energy with both projectiles, but Xe shows a greater increase with energy. At 1.0 keV and below, the yield is greater with  $\text{SF}_5$  than with Xe. At energies above 1.0 keV, the yield with Xe is larger. Therefore, there is a negative enhancement with  $\text{SF}_5$  at higher bombarding energies.

One experimental measure of the effectiveness is the efficiency, defined as the ratio of the yield to the damage cross-section. The damage, a measure

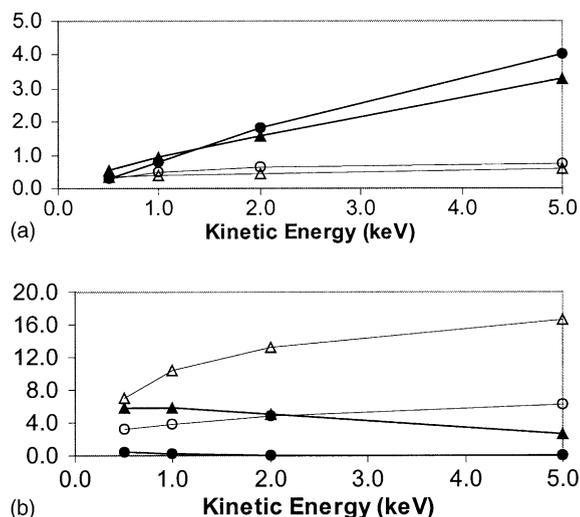


Fig. 3. A comparison of sputtered species from bombardment with Xe and  $\text{SF}_5$  as a function of incident kinetic energy. Circles represent values with Xe and triangles represent values with  $\text{SF}_5$ . (a) Yield (filled) and efficiency (open). (b) Average number of ejected polystyrene fragments (open) and projectile atoms (filled).

of the total damage to the surface, is defined in the simulations as the total number of molecules that are no longer available for detection after bombardment and includes all molecules that are ejected whole or as fragments. With this definition, the efficiency, a measure of the true effectiveness of the polyatomic projectile, is calculated as the ratio of the number of yield molecules to the number of removed molecules. In Fig. 3(a), the average efficiencies with Xe (open circles) and with  $\text{SF}_5$  (open triangles) are plotted as a function of incident energy for each projectile. At energies equal to 1.0 keV and higher, the increase in damage to the sample with  $\text{SF}_5$  is greater than the increase in yield. Therefore,  $\text{SF}_5$  is less efficient than Xe at these higher incident energies. Similar results are obtained from simulations with projectiles impacting at off-normal incidence.

The plots with open points in Fig. 3(b) are the average numbers of ejected polystyrene fragments. Both projectiles show an increase in the number of fragments with incident energy. The increase in the number of fragments produced by  $\text{SF}_5$  compared to Xe is greater than the increase in damage. For example, at 5.0 keV,  $\text{SF}_5$  produces 2.6 times more

fragments than Xe, but only 1.5 times more damaged molecules.

The average numbers of reflected projectile atoms are plotted in Fig. 3(b) with closed points. The fraction of reflected projectile atoms depends greatly on the mass ratio between the projectile atoms and the atoms in the substrate. Xe (131 amu) has a mass comparable to Ag (108) and very few atoms are reflected. A much greater fraction of S and F atoms are reflected and the amount shows a strong dependence on the incident energy. At 0.50 keV, 100% of the projectile atoms are reflected, while only 50% are reflected at 5.0 keV.

In Fig. 4(a), the percentages of molecules that are ejected as yield and damaged and the sum are plotted as a function of distance from the impact zone for both projectiles at 5.0 keV. Nearly 100% of the target molecule at R1 is removed from the surface as either yield or damage, while only a very small amount of molecules on the perimeters of the crystal at R5 are affected by the impact. The percentage of molecules that are ejected as yield is greatest from position R2, which is the surround-

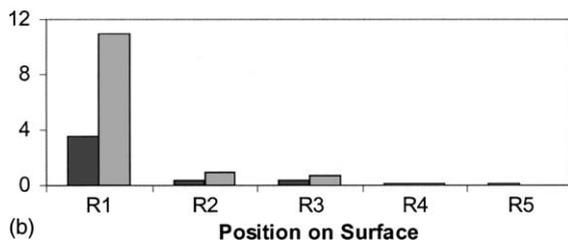
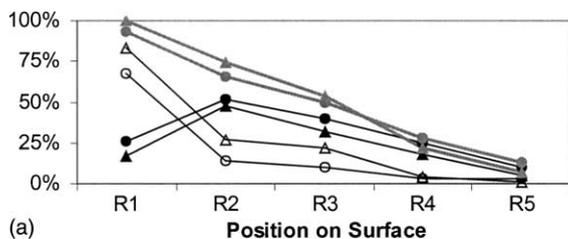


Fig. 4. A comparison of sputtered species with Xe and SF<sub>5</sub> at 5.0 keV as a function of the initial position on the surface. (a) Percentage of molecules at each surface position removed as yield (filled) or as damage (open). The total percentage of molecules removed is shown in gray. Circles represent values with Xe and triangles represent values with SF<sub>5</sub>. (b) Average number of total polystyrene fragments ejected.

ing area nearest to the impact zone. Interestingly, SF<sub>5</sub> removes a higher percentage of molecules than Xe in the areas closer to the impact zone. Farther out from the impact zone, at positions R4 and R5, Xe removes a higher percentage of molecules. Therefore, it appears that Xe distributes energy over a wider area of substrate atoms than SF<sub>5</sub>.

In Fig. 4(b), the average number of total PS fragments is plotted as a function of surface position for each projectile at 5.0 keV. The majority of fragments are from the target molecule in the impact zone at R1. SF<sub>5</sub> is larger than Xe and hits a greater number of atoms in the target molecule upon impact. Consequently, SF<sub>5</sub> produces a greater number of total fragments because it breaks the target molecule into more fragments. Fragments from the target molecule are a primary source of damage to the surrounding molecules, and therefore, SF<sub>5</sub> produces more damage than Xe.

#### 4. Conclusions

We have performed molecular dynamics simulations of the bombardment of a thin organic film on a metallic substrate with Xe and SF<sub>5</sub> projectiles at incident energies comparable to experimental values. The efficiency, defined as the ratio of the number of ejected whole molecules to the total number of molecules ejected, is greater with Xe than with SF<sub>5</sub>. From the simulations, we can conclude that for systems of thin organic films on metallic surfaces, the yield of intact molecules is governed primarily by the mass matching between projectile atoms and the substrate atoms. In this particular case, heavy metallic cluster projectiles such as Au<sub>n</sub> clusters should be more effective than polyatomic projectiles such as SF<sub>5</sub> and C<sub>60</sub> that are composed of light atoms.

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