

Study of angular influence of $C_3H_5^+$ ion deposition on polystyrene surfaces using molecular dynamics simulations

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The influence of incident angle on the interaction of polyatomic hydrocarbon ions ($C_3H_5^+$) with polystyrene surfaces is examined using classical molecular dynamics simulations. The forces are determined using the reactive empirical bond order method developed by Tersoff and parametrized by Brenner. The total incident energy is 50 eV and the angles considered are 0° (normal to the surface), 15° , 45° , and 75° . At each angle, the outcomes of 80 trajectories are compiled and averaged. The results show that intact ions scatter from the surface in only 2% of the trajectories and that the ions dissociate in 61% of the trajectories at normal incidence. At 75° , intact ions scatter away in 56% and they dissociate in only 30% of the trajectories. The largest total amount of carbon is deposited at normal incident angles. However, more ions or ion fragments are predicted to remain near the surface (penetrate 3.5–5.5 Å) at 45° . This is because ion fragments tend to penetrate more deeply (6–7 Å) into the surface at smaller angles. Consequently, some inclined angles are found to be most efficient for the deposition of the precursors necessary for polymer thin-film growth.
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I. INTRODUCTION

Plasma processing is widely used for surface modification and the deposition of thin films. It is both efficient and environmentally friendly because it is possible to confine the effects to a depth of a few Å and solvents are not needed. Plasma processing can alter the chemical and physical properties of the treated surface in a significant manner and result in a range of new surface properties. Therefore, it is widely used to coat or manufacture biomedical devices, optical devices, contact lenses, and chemical sensors.^{1–4}

In spite of the many applications of plasma processing, there is much that is not known about the reaction mechanisms between components of the plasma and the surface.^{3,5,6} Although much experimental research has been done to understand plasma–surface interactions, experimental studies cannot provide direct information about the relevant reaction mechanisms. Computer simulations of plasma–surface interactions are therefore frequently used to better determine the most likely reactions.^{7–9} Many different reactions are possible because many different kinds of particles (ions, electrons, polyatomic ions, etc.) are present in the system and interact collectively with the substrate. Therefore, multiple processes, such as thin-film growth and substrate etching occur simultaneously.^{3,10–13} To better isolate the effects of polyatomic ions in low energy plasma deposition on thin films, the deposition of mass selected polyatomic ion beams are studied.^{12,14–18}

Computer simulations of polyatomic ion bombardment on various materials have been studied by several groups using molecular dynamics (MD) methods.^{4,18–21} MD simulations are an ideal computational approach to study polyatomic ion bombardment because most of the important events in the

deposition process occur within a few picoseconds. Therefore, the simulations provide direct mechanistic information about the reactions.⁷ In previous work, we examined the deposition of CH_3^+ and $C_3H_5^+$ on polystyrene (PS) surfaces at kinetic energies of 20–100 eV and compared the results to experimental findings for the analogous fluorocarbon ions CF_3^+ and $C_3F_5^+$ on PS.^{4,18} In the previous studies, the ions were only deposited at angles normal to the PS surface. The experiments and simulations showed that $C_3F_5^+/C_3H_5^+$ ions were more effective at growing films than the CF_3^+/CH_3^+ ions when they were deposited at similar energies per atom (~ 6 eV/atom). Fragmentation of both types of ions increased when the ion energies were increased to 50 eV in both the experiments and simulations. The simulations provided insight into the dependence of the reaction products and penetration depths on the incident energies, ion structures, and the identity of the penetrating fragments.

The effect of changing the deposition angle of atoms, ions, and clusters on surface modification has been studied by many groups.^{22–35} These studies find that metal ions are steered toward the top of existing islands by long-range attractive forces at angles greater than 50° and that the degree of surface roughness increases as the angle increases from the surface normal. They also show that the rapidity by which the ion is captured, or is free to move within the surface, changes with angle. When growth is considered for long periods of time, increasing angle has been linked to the formation of porous films that contain columnar structures. Finally, the degree of ion scattering from surfaces is found to increase as the angle increases.

In this article, we examine the influence of incident angle on the deposition of $C_3H_5^+$ on PS surfaces at total kinetic energies of 50 eV/ion using classical MD simulations.

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TABLE I. Percentage of occurrence of the indicated events averaged over 80 trajectories at different incident angles.

Event	0°	15°	45°	75°
Simple scattering from the surface	2.2	7.5	11.3	51.3
Scattering from the surface with a captured surface atom(s)		1.3	2.5	5.0
Embedding within the surface	22.5	23.8	15.0	
Incorporation with the surface	15.7	23.8	26.3	13.8
Dissociation (losing one or more H atoms)	27.9	13.8	15.0	13.8
Dissociation $CH_2+C_2H_3$	23.6	21.3	21.3	11.3
Dissociation $CH_3+C_2H_2$	1.1	1.3		
Dissociation $CH_2+C_2H_2+H$	4.5	3.8	1.3	2.5
Dissociation $CH+C_2H_3+H$	3.4	1.3	1.3	1.3
Dissociation $CH+C_2H_2+H+H$			1.3	
Dissociation CH_2+C_2H+H+H			1.3	
Dissociation CH_2+CH_2+H		2.5	1.3	1.3
Dissociation $CH_2+CH+CH+H$			1.3	

II. COMPUTATIONAL DETAILS

In classical MD simulations Newton's equations of motion are integrated numerically; the timestep used in this work is 0.2 fs.³⁶ Short-range interatomic forces are calculated using the reactive empirical bond order potential for hydrocarbons developed by Tersoff,³⁷ parametrized by Brenner,³⁸ and refined within the last few years.³⁹ Unlike molecular mechanics models, this potential can predict new bond formation and bond breaking which are important processes in polyatomic ion deposition and surface modification. It has been successfully used to obtain insight into various processes such as molecular-surface collisions,⁴⁰ cluster-surface impacts,⁴¹ and the chemical vapor deposition of diamond.⁴² Long-range van der Waals interactions are included through a with Lennard-Jones potential that is active only at distances greater than the covalent bond lengths.⁴³

Because of the empirical, classical nature of these potentials, electronic effects such as electronic excitations or charging of the atoms is not included. Therefore, ions with positive charges are treated as reactive radicals rather than true ions with an actual charge. It is recognized that the presence of a positive charge will influence the chemical reactions that occur during deposition. However, it is also true that many incident ions are rapidly neutralized as they approach the surface. The expectation is that the simulation results are qualitatively correct and can provide insight into the processes taking place during polyatomic ion deposition on PS.

The PS surfaces used in the simulations contain eight layers for a total thickness of 50 Å. The bottom layer of the surface, and atoms within 5 Å from the four sides of the slab, have Langevin frictional forces³⁶ applied to maintain the surface temperature at 300 K. This imitates the heat dissipation process of real surfaces. The rest of the atoms in the system have no constraints and are designated as "active." Periodic boundary conditions are also applied within the plane of the surface to mimic an infinite surface and effectively double the number of thermostat atoms at the edges of the surface.

The impacting $C_3H_5^+$ ions are deposited at different loca-

tions within the active region of the surface at various orientations relative to the surface. The incident angles are 0°, 15°, 45°, and 75° from the surface normal and the total kinetic energies of the ions are fixed at 50 eV. Deposition at every angle is examined in 80 trajectories and the simulations run from 0.2 to 1.2 ps before it is determined that the results have reached a steady state.

III. RESULTS AND DISCUSSION

The simulations are performed with the ground state structure of $C_3H_5^+$ ($CH_2-C^+H-CH_2$). It was previously predicted that the ground state structure is most prevalent experimentally despite the fact the ions have significant internal energy that could lead to excited state structures.¹⁸ The etching effects are predicted to be negligible even though hydrogen atoms are knocked loose from the surface at all the angles considered. Instead, the ions deposit intact, fragment, or scatter from the PS surface. The averaged results for all the angles considered are summarized in Table I.

Table I shows that the number of ions that scatter from the surface increases as the angles increases from the surface normal, in agreement with findings in the literature for other systems.²² At 75°, ions are scattered away in 56% of the trajectories without any dissociation. In contrast, ions scatter from the surface in only 2% of the trajectories at normal incidence. Overall, at smaller angles (closer to the surface normal), ions are more likely to dissociate. At normal incidence, the ions dissociate in 61% of the trajectories, whereas they dissociate in only 30% of the trajectories at 75°. At all angles, $CH_2+C_2H_3$ is the most common dissociation reaction (see Fig. 1). At 15°, the ions deposit intact in 48% of the trajectories, the largest percentage of any of the angles considered, while the ions deposit intact in 38% and 41% of the trajectories at 0° and 45°, respectively. The ion fragments indicated in Table I react with the surface atoms after dissociation in most cases. Therefore, the exact structures of the fragments may be different from the structures shown in Table I after equilibration. At normal incidence, more trajectories result in the scattering of hydrogen atom(s) from the

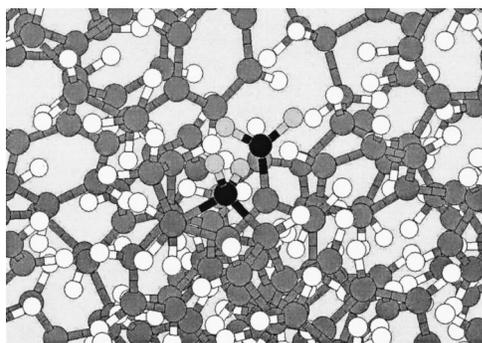


FIG. 1. Snapshot from the MD simulations showing the products of the dissociation of the $C_3H_5^+$ ion into CH_2 and CH_3 fragments that bond to the PS surface. (Black spheres are carbon atoms from the ion, dark gray spheres are carbon atoms from the PS, light gray spheres are hydrogen atoms from the ion, and white spheres are hydrogen atoms from the PS.)

polyatomic ions or the PS than is the case at larger angles. This indicates that the kinetic energy of the ions is transferred more efficiently to breaking bonds at normal incidence. Similarly, more carbon-carbon bonds in the ions are broken at normal incidence.

Figure 2 summarizes the number of ion fragments that are bonded to, or embedded in, the PS surface 0.8–1.2 ps after deposition. The embedded fragments penetrate the PS surface but do not form bonds with the PS carbon atoms on the time scales of these simulations. Following the notation used in Ref. 18, “C” and “H” represent carbon and hydrogen from the polyatomic ion while “h” is hydrogen from the PS surface. On the whole, the smallest amount of deposition occurs at 75° . From Figs. 2(a)–2(c), it is clear that incident angle does not greatly effect the total number of C_3H_y species that remain on the PS surface up to 45° . Slightly more C_3H_5 is deposited at 15° and 45° than 0° because of the greater amount of dissociation that occurs at normal incidence. However, slightly more C_3H_n is deposited at 0° and slight more $C_3H_n h_m$ is deposited at 15° . At 75° , the amount of scattering is so large that significantly fewer large fragments are deposited on or embedded in the surface. These trends are also true for C_2H_y fragments, as indicated in Figs. 2(d)–2(e). Slightly more C_2H_n and $C_2H_n h_m$ result at 0° but the second greatest amount varies between 45° and 15° .

More hydrocarbon fragments that contain only one carbon atom (especially CH_2) remain on the PS surface after deposition at 15° and 45° than 0° , as indicated in Figs. 2(f)–2(h). Slightly more CH_2 and CH_n is deposited at 45° while slightly more $CH_n h_m$ results at 0° . The majority of the CH_2 fragments form one or two bonds with carbon atoms from the PS backbones (as shown in Fig. 1). This indicates that CH_2 fragments play a major role in the cross linking of the PS surface. At 0° , many CH_y fragments bond to hydrogen atoms that were originally bonded to PS carbon atoms. At 75° , only a few trajectories result in the dissociation of the polyatomic ions, so not many fragments are formed. These results are consistent with the finding that CF_y (especially CF_2) ions or radicals generated in fluorocarbon plasmas play a central role in polymer film formation.^{44–47} Consequently, if the reactiv-

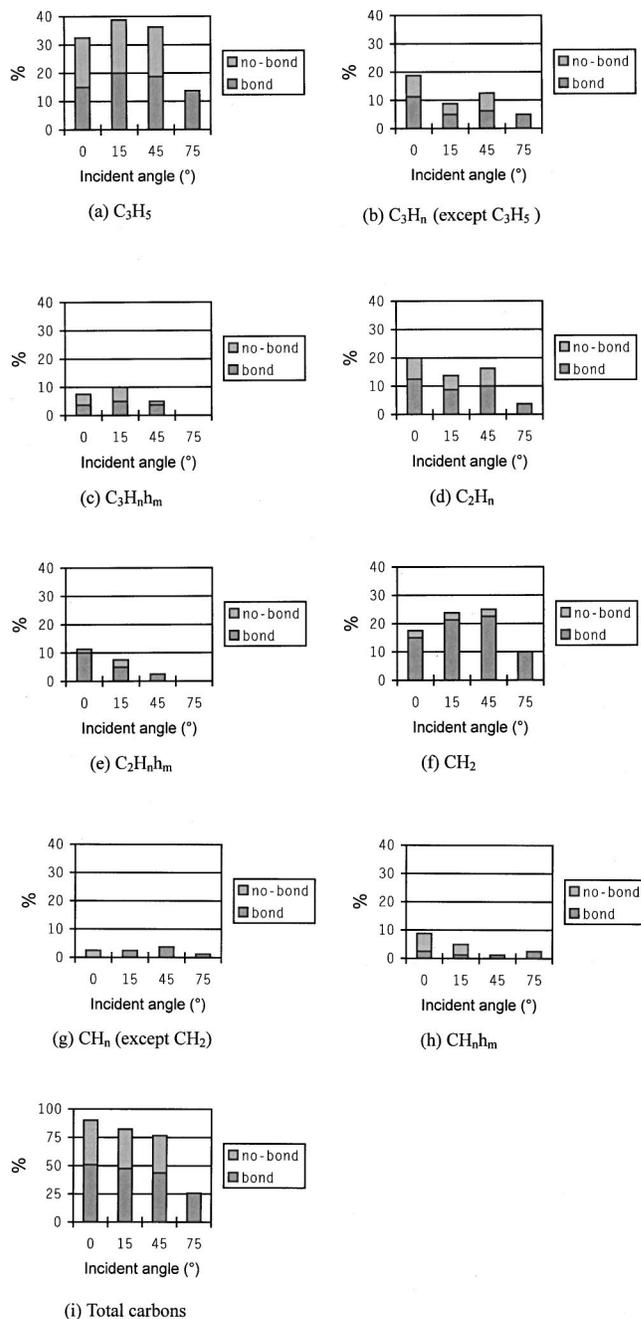


FIG. 2. Percentages of the indicated product species that remain bonded to carbon atoms in the PS surface or are embedded in the PS surface. The results represent the averaged data from 80 trajectories. “Bond” means that the indicated species formed bonds with carbon atoms in the PS.

ity and behavior of polyatomic hydrocarbon and fluorocarbon fragments in plasma are similar to each other, these results indicate that polymer surface modification in fluorocarbon plasma or by ion beam deposition may be more efficient at small incident angles.

The number of carbon-carbon and carbon-hydrogen PS bonds that are broken as a result of the deposition of the ions decreases as the deposition angle increases, as shown in Fig. 3. The largest decrease occurs at 75° , while an average of 0.9–1 bonds are broken for 0° , 15° , and 45° . Bond breaking

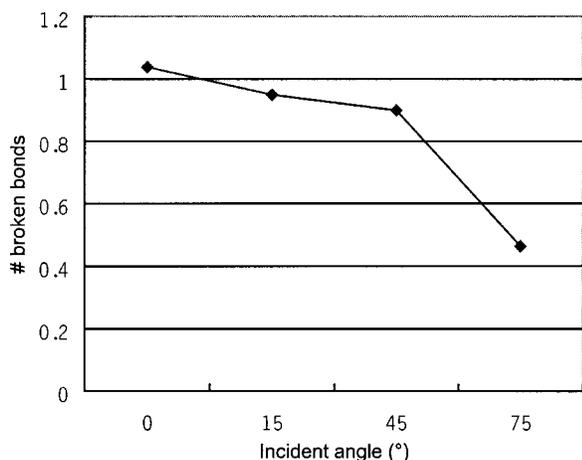


FIG. 3. Average number of broken bonds per trajectory in the PS surface as a result of $C_3H_5^+$ deposition at the indicated angles over the 80 trajectories.

within the PS leads to cross linking with the ions or fragments, as discussed and shown in Fig. 1, but can also lead to cross linking between polymer backbones.⁴⁸ Thus, deposition at small angles can lead to appreciable cross linking despite the fact that not all of the kinetic energy of the ion is directed into the surface.

Figure 2(i) summarizes the total amount of carbon deposited on the PS surface over the 80 trajectories per angle. While ion bombardment at normal incidence deposits the greatest amount of carbon, ion bombardment at 15° and 45° results in the deposition of only slightly less carbon on the surface. However, bombardment at 75° results in significantly less (about one fourth of the amount at 0°) carbon deposited on the surface.

Figure 4 shows the average penetration depth for the ions or significant ion fragments as a function of deposition angle. Figure 4 indicates that more fragments that contain carbon atoms remain near the surface at 45° (ions penetrate the PS 3.5–5.5 Å) compared to normal incident angles (ions penetrate the PS 6.2–7.2 Å) or 15° (ions penetrate the PS 6.0–

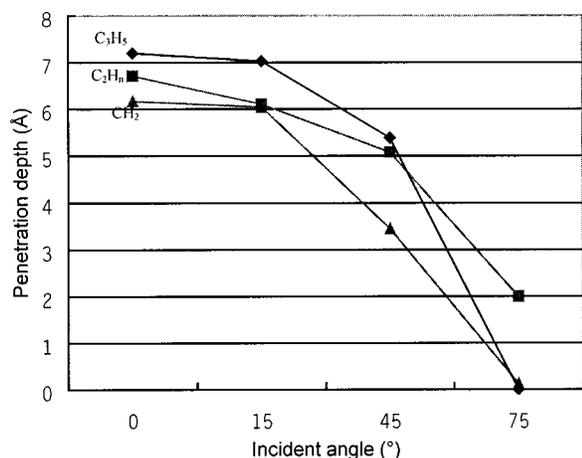


FIG. 4. Average penetration depths of major species (C_3H_3 , C_2H_n , and CH_2) from the incident ions as a function of angle. Zero-penetration depth means that the indicated species is adsorbed right on the surface.

7.0 Å). Therefore, these simulations predict that a medium inclined angle is best for thin-film deposition close to the surface. Although the penetration depth for ions and major fragments is very small at 75°, too large an angle results primarily in scattering and the number of ions or major fragments considered in Fig. 4 for 75° is small (as indicated in Table I and Fig. 2).

Larger penetration depths lead to a larger number of bonds broken in the PS surface, so the data contained in Figs. 3 and 4 are correlated. However, Fig. 2 shows that there is little difference in the number of carbon atoms bonded with PS carbon atoms at 0°, 15°, and 45° on the time scales of the simulations. Instead, about half of the carbon atoms merely embed within the PS surface without forming covalent bonds to the PS backbones. It is likely that the embedded fragments would form bonds with the PS chains or react with succeeding incident ions if continuous bombardment simulations had been performed or if the trajectories ran for longer times.

IV. CONCLUSIONS

Classical MD simulations are used to investigate the effect of incident angle on the interaction of $C_3H_5^+$ with a PS surface. Overall, normal incident angles lead to the most reactive collisions. In 98% of the trajectories, the $C_3H_5^+$ ions or their fragments remain on the PS surface. In contrast, 56% of incident ions are scattered away from the PS surfaces without dissociation at 75°. The total number of deposited carbon that remains at the surface is largest at normal incident angles. However, more ions or fragments remain near the surface at 45°. In addition, the amount of CH_2 fragments that remain at the surface is largest at 45° with the majority of these fragments bonded to the carbon backbones of the PS. Therefore, the simulations predict that the largest amount of CH_2 fragments, an important precursor for polymer film growth in plasma, is deposited near the surface at 45°. Therefore deposition at an inclined angle such as 45° should be more efficient for shallow surface modification than deposition at normal incidence even though more scattering would occur.

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