Dependence of plasma-induced modification of polymer surfaces on polyatomic ion chemistry

Inkook Jang and Susan B. Sinnott[a]
Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611-6400

Fluorocarbon plasmas are widely used to chemically modify surfaces and deposit thin films. The deposition of mass selected fluorocarbon ions is useful for isolating the effects specific to polyatomic ions. In this study, the detailed chemical modifications that result from the deposition of beams of polyatomic fluorocarbon ions ($C_3F_5^+$ and CF_3^+) on polystyrene surfaces at experimental fluxes are identified using classical molecular dynamics simulations. These simulations elucidate how and why more efficient fluorination of the surface is achieved by CF_3^+ ion beam deposition, but $C_3F_5^+$ ions are more efficient at growing fluorocarbon thin films. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1764597]

Fluorocarbon plasmas are commonly used in several industries to chemically modify the surface properties of materials. Nevertheless, there is much that is still not known about the chemical reactions that occur between the surface and the components of the plasma.[1–5] It has been determined that the effects of plasma processing are highly localized to the topmost layers of the surface and several types of particles, such as ions, electrons, neutral atoms, and molecules, can coexist in the plasma environment. It is also well accepted that polyatomic ions and neutrals within low-energy plasmas have a significant effect on the surface chemistry induced by the plasma.

In this study, the classical molecular dynamics simulations numerically integrate Newton's equations of motion with a third-order Nordsieck predictor corrector[6] using a time step of 0.2 fs. The simulations consider the continuous deposition of 240 $C_3F_5^+$ (CF_2–C^+F–CF_2) and 400 CF_3^+ on two identical polystyrene (PS) surfaces. Each ion in the continuous beam is deposited at a randomly chosen location within the active region of the surface with a random orientation relative to the surface. The ions in both beams have a translational kinetic energy of 50 eV/ion, and their incident angle is normal to surface. Total fluences and ion currents are 1.8×10^{16} F atom/cm^2 and 80 nA, respectively. After the ion deposition process is complete, the systems are thermally equilibrated for 25 ps prior to analysis. The total simulation time is 0.5–0.9 ns.

The polymer surface used in the simulations is eight layers of syndiotactic crystalline PS for a total surface thickness of 60 Å. The three bottom layers of the surface and atoms within 5–10 Å from the four sides of the slab have Langevin stochastic and frictional forces applied to maintain the surface temperature at 300 K.[6] This imitates the heat dissipation process of real surfaces. The rest of the atoms in the system have no constraints placed on them. Periodic boundary conditions are applied within the plane of the surface to mimic an infinite surface.

To facilitate these realistic, large length ($5 \times 3 \times 6$ nm) and time-scale (0.5–0.8 ns) MD simulations, a C–H–F many body empirical potential was developed based on Brenner's second-generation reactive empirical bond-order (REBO) potential for hydrocarbons.[7] In the C–H–F potential development, two-body parameters for C–F and F–F are adopted from Tanaka's C–F potential, and H–F parameters are determined by us from *ab initio* calculations.[8,9] In addition to the REBO potential for short-range covalent interaction, long-range van der Waals interactions are also included in the form of a Lennard-Jones potential that is only active at distances greater than the covalent bond lengths.[6]

No distinct pure FC film layers are predicted to form on the time scales of these simulations. Rather, numerous fluorocarbon ions and dissociated ion fragments are embedded in the PS, some of which form covalent bonds to PS carbon atoms. The polymer backbone structures are randomized and, consequently, their volume increased by the ion bombardment. The F atoms spread more widely and deeply as a result of CF_3^+ ion beam deposition than $C_3F_5^+$ ion beam deposition because of smaller size and higher velocity of the CF_3^+. However, the highest density of F occurs at a depth of 10–15 Å for both $C_3F_5^+$ and CF_3^+ ion beam processes. More F atoms chemically bond to the PS during CF_3^+ ion deposition than during $C_3F_5^+$ ion deposition, as shown in Fig. 1. In general, ions or ion fragments that form covalent bonds with polymer substrate have smaller penetration depths than nonbonded, embedded species. This explains why the penetration depths of F atoms for CF_3^+ deposition are similar to the values in the case of $C_3F_5^+$ deposition. Thus, with regard to the depth of surface modification, CF_3^+ deposition is approximately equivalent to $C_3F_5^+$ deposition under conditions of experimental fluence where the CF_3^+ ions have higher incident velocities than the $C_3F_5^+$ ions.

However, the manner in which the $C_3F_5^+$ and CF_3^+ ions modify the PS surfaces is distinctly different in other respects. This is indicated by Fig. 1, which shows the density of the ions and ion fragments that remain within the PS surface. Intact C_3F_5 is the most abundant species in the modified PS surface after $C_3F_5^+$ ion deposition, with the amount present equal to about 11% of the incident $C_3F_5^+$. In the case of CF_3^+ deposition, F is the most abundant species in the modified PS surface, such that 6% of all incident F atoms end up bonded to PS chains. These F atoms attach to the PS chains by replacing H atoms or capping the ends of broken chains.

[a]Author to whom correspondence should be addressed; electronic mail: ssinn@mse.ufl.edu

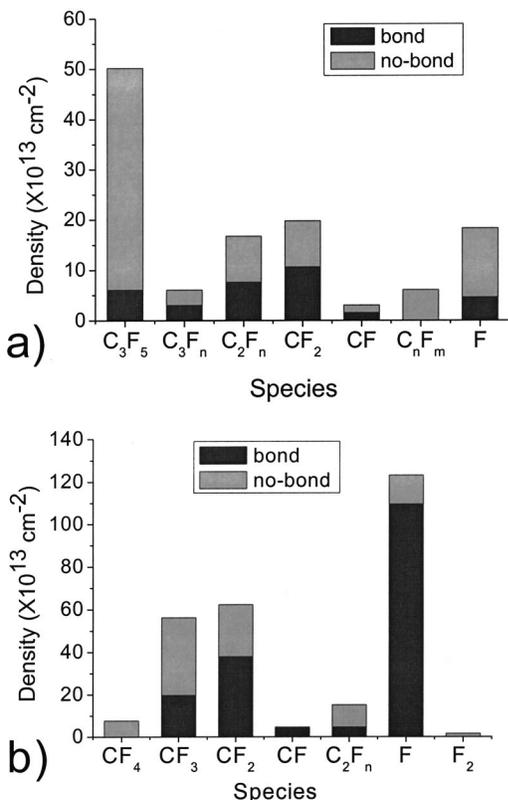FIG. 2. (Color) Snapshot from the MD simulations showing CF_2 fragments cross-linking PS chains.

FIG. 1. Density of indicated species that remain bonded to carbon atoms in, or are embedded within, the PS surfaces. "Bond" means that the species form covalent bonds with C atoms in the PS chains and "no-bond" means the species are simply embedded in the surface on the time scales of the simulations. (a) $C_3F_5^+$ ion deposition, where C_3F_5 is not included in C_3F_n, and $n>3$ and $m>5$ for C_nF_m, (b) CF_3^+ ion deposition.

In the case of CF_3^+ ion deposition, CF_3, CF_2, and F are the major scattering species, which agrees with reported experimental results[10–12] that show that relative amounts of CF_3, CF_2, CF, and F depend on the incident energy of the ion, and more CF and less CF_3 emerges as scattering fragments at higher incident energy. While the simulations do predict that somewhat fewer CF scattering fragments are produced than experimental results at the same incident energy, this difference is attributed to the fact that a softer surface is considered in the simulations than in the experiments. In the case of $C_3F_5^+$ deposition, C_3F_5, C_2F_3, and CF_2 are the major scattering species. This result indicates that most of the ion dissociation occurs by breaking one of the C–C bonds in the incident $C_3F_5^+$. Some experiments under similar conditions find that CF_3 is a major scattering fragment and no significant amount of CF_2 was detected, in disagreement with our results,[12] while others find that CF_2 is a major fragment and little CF_3 is detected, in good agreement with our results.[4] In these simulations, the ground state of $C_3F_5^+$ ($CF_2-C^+F-CF_2$) is used. However, a higher energy state isomer, such as $CF_3-C^+=CF_2$ or CF_3-CF-C^+F is possible, and these have CF_3 moieties. In a previous study, we explored the effect of different structures of $C_3H_5^+$ on the results of deposition on polystyrene, and found that if the incident ion contains CH_3 moieties, CH_3 fragment are preferentially produced as major species by dissociation.[4]

CF_x radicals (especially CF_2) have been considered as the most important species in fluorocarbon film deposition from plasma.[13–15] Spectroscopic analysis indicates that CF_2
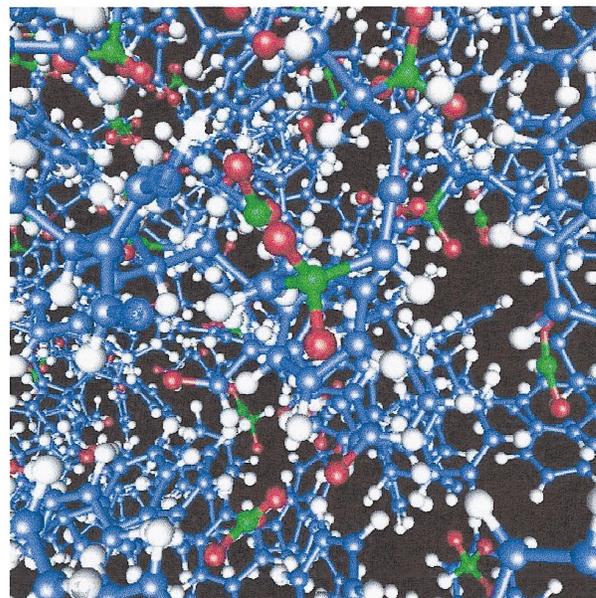
fragments are major building blocks of fluorocarbon films.[16,17] However, there is some controversy about the role of CF_2 radical in fluorocarbon film formation. Some researchers correlate adsorbed CF_2 with gaseous phase thermal CF_2 radicals in plasma.[13,14,17,18] This suggests that direct deposition of gas phase CF_2 radicals plays a major role in fluorocarbon film growth. However, other researchers argue that there is no direct correlation between gaseous phase CF_2 and fluorocarbon film growth.[5,16,19] Cunge and Booth et al. suggested that CF_2 on the surface is generated by energetic polyatomic ion deposition.[5] In these simulations, CF_2 fragments are found to be the second most abundant and reactive species produced, regardless of the type of ion in the beam. In the case of $C_3F_5^+$, over 50% of the deposited CF_2 fragments form covalent bonds with the PS chains while in the case of CF_3^+, 61% of the deposited CF_2 ions form covalent bonds with the PS chains. Furthermore, because CF_2 has two active sites, it can act as a cross-linking agent between neighboring PS chains, as illustrated in Fig. 2. Although the substrates in these simulations are polymeric rather than Si or SiO_2, these results are consistent with reported spectroscopy results[4,20] and support the argument that fluorocarbon films are not formed exclusively by direct interaction of gaseous CF_2 with the surface.

The simulations also show how F atoms dissociated from CF_3^+ incident ions play a very important role in fluorination of the polymer surface through direct incorporation into the polymer chains. This suggests that surface fluorination occurs as a result of CF_3^+ deposition even in the earliest stages of surface modification before stable fluorocarbon film growth has started. Overall, Fig. 1 illustrates that CF_3^+ deposition is more efficient at PS fluorination than $C_3F_5^+$ deposition. However, it also indicates why experimentally,[4] $C_3F_5^+$ is more efficient at producing fluorocarbon thin films. In particular, many larger fragments produced by $C_3F_5^+$ ion deposition, such as C_2F_n and C_3F_5, contain more than one C atom and may have more than one active site. Although some of these fragments are predicted to remain on, or embedded in, the surface without forming covalent bonds to the

PS, these embedded species are expected to form bonds to the PS or with other fragments over longer times than are accessible in these classical MD simulations. These larger fragments can thus readily react and connect with other fluorocarbon ions or fragments to grow polymer-like structures than smaller fragments. In contrast, F atoms, the most dominant fragment in CF_3^+ deposition, deactivate potential film nucleation sites within the PS. This prediction is consistent with the general concept of fluorocarbon plasma processing, that polymerization is dominant in high C/F ratio feed gas while surface reaction and etching is dominant at low C/F ratios.[21]

In conclusion, these classical molecular dynamics simulations show how and why CF_3^+ and $C_3F_5^+$ play different roles in plasma deposition processes on hydrocarbon polymers. The findings can be generalized to state that larger polyatomic ions produce a wider variety of precursors for film growth than smaller polyatomic ions and thus should be more effective at growing films. Additionally, they suggest that CF_2 is likely to be an important precursor for film growth from fluorocarbon polyatomic ions, in general.

[1] S. H. Wheale, C. P. Barker, and J. P. S. Badyal, Langmuir **14**, 6699 (1998).
[2] A. von Keudell, Thin Solid Films **402**, 1 (2002).
[3] E. T. Ada, O. Kornienko, and L. Hanley, J. Phys. Chem. B **102**, 3959 (1998).
[4] M. B. J. Wijesundara, Y. Ji, B. Ni, S. B. Sinnott, and L. Hanley, J. Appl. Phys. **88**, 5004 (2000).
[5] G. Cunge and J. P. Booth, J. Appl. Phys. **85**, 3952 (1999).
[6] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, New York, 1987).
[7] D. W. Brenner, O. A. Shenderova, J. A. Harrison, S. J. Stuart, B. Ni, and S. B. Sinnott, J. Phys.: Condens. Matter **14**, 783 (2002).
[8] J. Tanaka, C. F. Abrams, and D. B. Graves, J. Vac. Sci. Technol. A **18**, 938 (2000).
[9] C. F. Abrams and D. B. Graves, J. Appl. Phys. **86**, 5938 (1999).
[10] W. R. Koppers, M. A. Gleeson, J. Lourenco, T. L. Weeding, J. Los, and A. W. Kleyn, J. Chem. Phys. **110**, 2588 (1999).
[11] W. R. Koppers, J. H. M. Beijersbergen, T. L. Weeding, P. G. Kistemaker, and A. W. Kleyn, J. Chem. Phys. **107**, 10736 (1997).
[12] T. Ast, D. E. Riederer, S. A. Miller, M. Morris, and R. G. Cooks, Org. Mass Spectrom. **28**, 1021 (1993).
[13] M. J. Sowa, M. E. Littau, V. Pohray, and J. L. Cecchi, J. Vac. Sci. Technol. A **18**, 2122 (2000).
[14] M. Inayoshi, M. Ito, M. Hori, T. Goto, and M. Hiramatsu, J. Vac. Sci. Technol. A **16**, 233 (1998).
[15] J. H. Wang, J. J. Chen, and R. B. Timmons, Chem. Mater. **8**, 2212 (1996).
[16] K. Takahashi, A. Itoh, T. Nakamura, and K. Tachibana, Thin Solid Films **374**, 303 (2000).
[17] D. C. Gray, H. H. Sawin, and J. W. Butterbaugh, J. Vac. Sci. Technol. A **9**, 779 (1991).
[18] N. M. Mackie, V. A. Venturo, and E. R. Fisher, J. Phys. Chem. B **101**, 9425 (1997).
[19] M. Nakamura, M. Hori, T. Goto, M. Ito, and N. Ishii, J. Vac. Sci. Technol. A **19**, 2134 (2001).
[20] M. B. J. Wijesundara, L. Hanley, B. R. Ni, and S. B. Sinnott, Proc. Natl. Acad. Sci. U.S.A. **97**, 23 (2000).
[21] C.-M. Chan, *Polymer Surface Modification and Characterization* (Hanser/ Gardner, New York, 1994).