

# Plasma Beam Irradiation into Organic Polymer Surfaces

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## Abstract

Aiming at understanding of interactions between plasmas and carbon-based material surfaces, we have carried out molecular dynamics (MD) simulations of hydrocarbon plasma injections into a poly (1,4-phenylene) surface using interatomic potential functions for hydrocarbon systems. Our simulation results show that injected carbon atoms deposit on the surface and form a new bonding network. When hydrocarbon beams are injected, on the other hand, we find surface erosions by hydrogen atoms takes place, which is consistent with experimental observations conducted under similar conditions as well as previously reported other MD simulation results for carbon-containing different substrate materials.

## Keywords:

plasma processing, plasma-surface interaction, molecular dynamics simulation, low-k material, organic polymer

## 1. Introduction

Carbon-based materials are some of the most promising and sought-after materials for various applications. For example, the first walls and diverter plates of magnetic nuclear fusion devices are often made of carbon-based materials. Such surfaces are directly exposed to fusion plasmas and can influence the plasma characteristics through adsorption and desorption of impurities. For industrial applications, plasmas have been widely employed to process carbon-based materials in order to fully exploit their potential advantages, too. Nitrogen ion implantation into carbon nanotubes and diamond surfaces has been studied in an effort to have these materials function as semiconductors. Other examples include organic polymers with low dielectric constants (low-*k*), which are considered to be promising candidates for insulating materials that can reduce RC delay for future integrated circuits (IC) chips [1-3]. Plasma processes of such organic polymers to realize microscopic structures are now also widely studied. In such processes, a mixture of hydrogen and nitrogen atoms (or alternatively ammonia) is used as the source gas of plasmas.

Classical molecular dynamics (MD) simulation is a useful tool to investigate such beam-surface interactions. For its applications to (H,C) systems (*i.e.*, systems that consists of H and C atoms only), Brenner proposed an interatomic potential model [4]. This potential model has been widely used for studies of, for example, chemical vapor depositions (CVD) of diamond films [4], Young's moduli of carbon fibers [5], and erosion of hydrogenated amorphous carbon surfaces [6]. With regard to polymer surfaces, ion deposition on

polystyrene surfaces was studied [7,8]. However, due to the lack of interatomic potential models for systems including nitrogen atoms in addition to hydrogen and carbon atoms, few simulations of plasma-surface interactions concerning nitrogen atoms have been carried out although nitrogen atoms play important roles in various applications as described above.

To understand physical/chemical mechanisms of surface reactions during such processes, we have constructed an interatomic potential model for (H,C,N) systems [9]. We are now in the process of applying this model to MD simulations of plasma etching for low-*k* organic polymer surfaces. In the case of a hydrogen-nitrogen plasma, the majority of such incoming clusters include nitrogen atoms. However, the surface must be also bombarded by some hydrocarbon clusters, which are recycled from the substrate surface into the plasma. In the present study, as the first step toward the full understanding of organic polymer etching by hydrogen/nitrogen plasmas, we examine one of the simplest cases, *i.e.*, interactions between hydrocarbon beams and hydrocarbon polymers using Brenner's potential, which is given in Ref.4. The results obtained here will be compared with results obtained under our potential model in the near future.

## 2. Molecular dynamics simulation

As the substrate for our MD simulations presented here, we select poly (1,4-phenylene), which is a chain of phenylene rings [Fig. 1]. The polymers are assumed to be arranged in an almost parallel manner, as shown in Fig. 2. In this figure, white and black spheres represent carbon and hydrogen

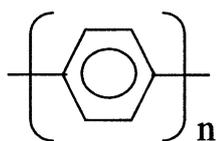


Fig. 1 Poly (1,4-phenylene), *i.e.*,  $[C_6H_4]_n$ . This material is also called as polyparaphenylene (PPP).

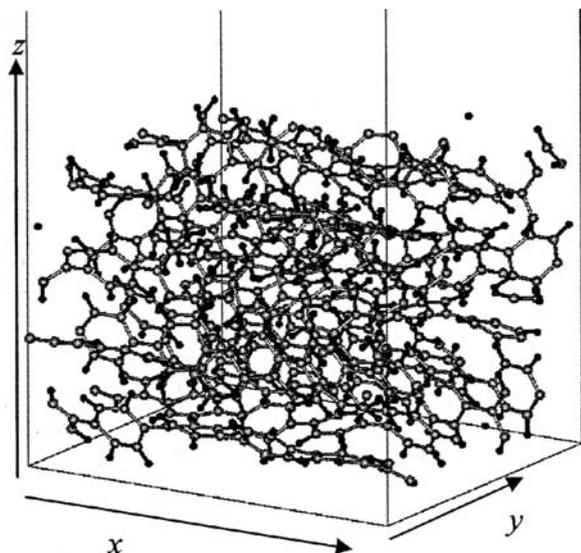


Fig. 2 The initial model substrate of PPP used here. The black and white spheres represent hydrogen and carbon atoms. The black and white bars represent covalent bonds between H and C atoms and between C and C atoms.

atoms. Covalent bonds among particles are represented by bars where white (black) bars correspond to carbon-carbon (carbon-hydrogen) covalent bonds. The mass density of this model substrate is  $1.33 \text{ g/cm}^3$ , which is consistent with the known mass density of poly (1,4-phenylene) [10]. The horizontal cross section of this simulation cell (which is roughly the substrate surface area in our simulation) is approximately  $2.2 \times 1.9 \text{ nm}^2$ . Boundary conditions are the following: in the horizontal directions [ $x$  and  $y$  directions], boundary condition is periodic. The bottom layer is fixed. The typical initial substrate we used for this work has four layers of PPP polymers and each layer consists of 4 chains of 5 phenylene rings per layer. In other words, the initial substrate consists of 480 C atoms and 320 H atoms. However, we dynamically adjust the thickness of the substrate by adding extra polymer layers from the bottom if necessary, so that no atoms would pass through the bottom layer. In our simulations, we inject C, CH,  $CH_2$ ,  $CH_3$ ,  $CH_4$ , H and  $H_2$  with kinetic energy of 50 eV normally to the substrate surface from above. The velocity Verlet method is used for numerical integration of the equations of motion. The time increment is set to be 0.5 fsec.

### 3. Results

Figure 3 shows the substrate surface after carbon atom

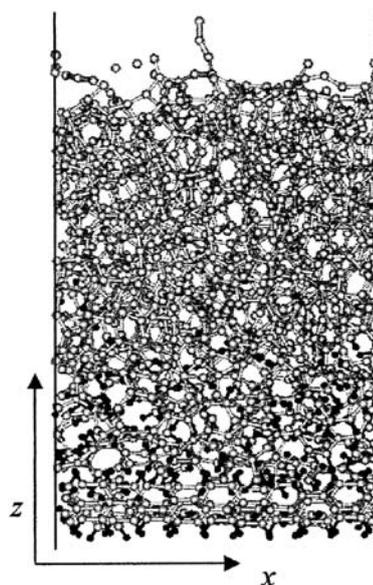


Fig. 3 A side view of the substrate surface after carbon atom injections of  $2.4 \times 10^{16} \text{ atoms/cm}^2$ .

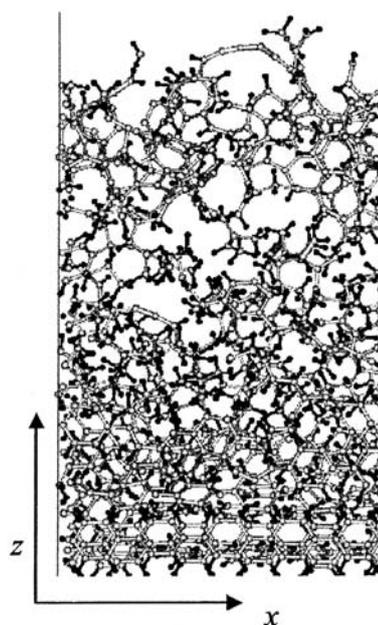


Fig. 4 A side view of the substrate surface after  $H_2$  molecule injections of  $2.4 \times 10^{16} \text{ H}_2 \text{ molecules/cm}^2$ .

injections whose injection dose is  $2.4 \times 10^{16} \text{ atoms/cm}^2$ . The thickness of each bar is proportional to the order of covalent bond. As shown in the figure, injected carbon atoms deposit on the surface. In addition to the most dominant  $sp^2$  type carbon-carbon bonds, the  $sp^3$  type bonds are also observed in this layer. We also observe that very few hydrogen atoms are contained in this layer.

Figure 4 shows the substrate surface after hydrogen molecule injections of  $2.4 \times 10^{16} \text{ H}_2 \text{ molecules/cm}^2$ . Unlike the case of carbon atom injections, atoms are relatively sparsely arranged in the top part of the substrate and carbon-

carbon bonding networks are not firmly formed. Furthermore it seems a large layer-like segment of the surface material can be easily separated from the rest of the substrate.

Figure 5 shows the substrate surface after  $\text{CH}_4$  cluster injections of  $2.4 \times 10^{16}$   $\text{CH}_4$  molecules/ $\text{cm}^2$ . Similar to the case of  $\text{H}_2$  molecule injections, hydrogen atoms of incident  $\text{CH}_4$  erode the surface. However, in this case, the separation of a segment is not observed. This is because large momenta of incident carbon atoms physically break the eroded substrate.

As to other hydrocarbon injections, we have observed that, as the number of hydrogen atoms in the injected cluster  $\text{CH}_x$  ( $x = 1-3$ ) increases (decreases), the resultant surface after sufficient bombardment becomes closer to that of  $\text{CH}_4$  cluster (C atom) injections. The resultant surface conditions for H atom injections are similar to those for  $\text{H}_2$  molecule injections.

Figure 6 shows the sputtering yields for C,  $\text{H}_2$  and  $\text{CH}_4$  injections, which are defined as  $Y_\alpha = N_\alpha^{\text{out}} - N_\alpha^{\text{in}}$  with  $N_\alpha^{\text{out}}$  and  $N_\alpha^{\text{in}}$  being the numbers of removed and injected  $\alpha$  ( $= \text{C}$  or  $\text{H}$ ) atoms per injection. Thus a positive (negative) value of  $Y_\alpha$  corresponds to sputtering (deposition) of the species. The horizontal axis represents injection dose [In our simulations, 100 injections are equivalent to the dose of  $2.4 \times 10^{15}$  / $\text{cm}^2$ ]. The circle and triangle in the figures represent the sputtering yields of hydrogen or carbon atoms averaged over each  $2.4 \times 10^{15}$  / $\text{cm}^2$  injections (gray dashed lines) around the indicated value of dose.

Figure 6a shows that, in the case of C atom injections, H atoms in the top part of the substrate are sputtered (i.e., removed) in the early stage of injections (filled circles with a solid line, dose  $\sim 0-7.2 \times 10^{15}$  / $\text{cm}^2$ ). On the other hand, Fig. 6b shows that almost all injected C atoms are deposited in the substrate (filled triangles). After almost all hydrogen atoms are removed from the top layer of the substrate,  $Y_{\text{H}}$  reaches zero around when the injection dose reaches about  $7.2-9.6 \times 10^{15}$  / $\text{cm}^2$ . This contrasts with the cases where injected hydrogen and carbon atoms tend to be deposited in the substrate for  $\text{H}_2$  and  $\text{CH}_4$  injections. However, as we saw in Figs. 4 and 5, due to the erosion by hydrogen atoms, sputtering yields gradually increase.

For  $\text{CH}_4$  injections, unlike C or  $\text{H}_2$  injections, the sputtering yield as a function of the injection dose oscillates, as shown in Fig. 6. We have observed that, in the case of  $\text{CH}_4$  injections, relatively large (but much smaller than the layer-like segment we observed in the case of  $\text{H}_2$  injections) clusters such as  $\text{C}_{19}\text{H}_{12}$  are sometimes removed from the surface. When such large clusters are removed from the surface, sputtering yields drastically increase from its average value. The fluctuation of the sputtering yields seen in Fig. 6 is the results of such large etch products. Sufficient statistical average over larger number beam injection events will further reduce such statistical noise in simulation data.

#### 4. Discussion

In etching experiments of organic low- $k$  polymers, hydrogen and nitrogen plasmas are usually used. In such

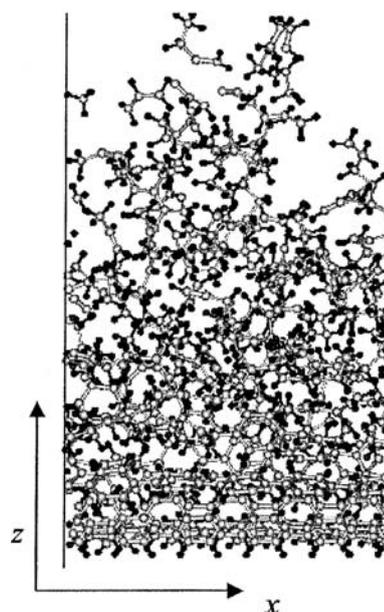


Fig. 5 A side view of the substrate surface after  $\text{CH}_4$  cluster injections of  $2.4 \times 10^{16}$   $\text{CH}_4$  molecules/ $\text{cm}^2$ .

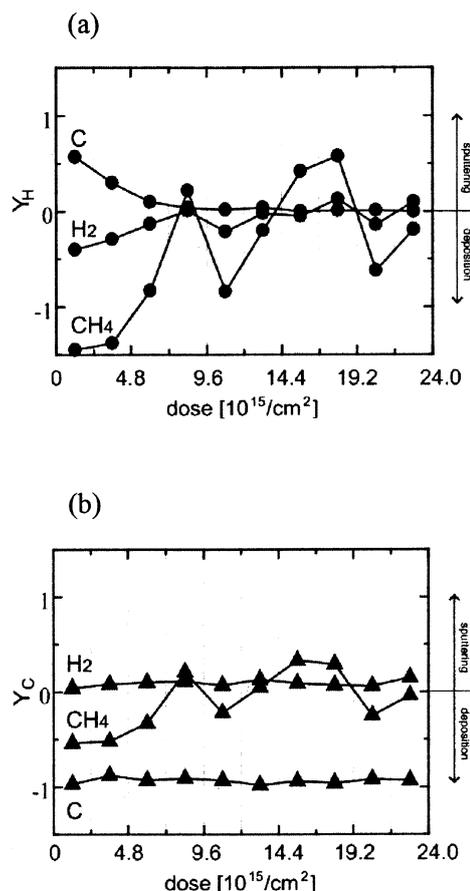


Fig. 6 Sputtering yields of a) H and b) C atoms as functions of injection dose. The sputtering yield is defined as  $Y_\alpha = N_\alpha^{\text{out}} - N_\alpha^{\text{in}}$  with  $N_\alpha^{\text{out}}$  and  $N_\alpha^{\text{in}}$  being the numbers of removed and injected  $\alpha = \text{H}$  or  $\text{C}$  atoms per injection. Sputtering yields shown here are averaged values over every  $2.4 \times 10^{15}$  / $\text{cm}^2$  of injections around the indicated value of dose.

experiments, low energy nitrogen atom injections are also performed [3] and injected nitrogen atoms tend to deposit in the substrate surface. As we saw in Figs. 3 and 6b, we have observed in our MD simulations that injected low energy carbon atoms tend to deposit in the substrate, which is similar to the behavior of nitrogen atoms in polymer etching experiments by hydrogen/nitrogen plasmas. Furthermore, as observed in nitrogen radical exposure experiments [1,3], sp<sup>3</sup> carbon bonds as well as sp<sup>2</sup> bonds are observed. The similar roles played by N and C atoms may be attributed to their similar masses and relatively close bond energies among N-N, N-C, C-C as well as N-H and C-H.

On the other hand, it is also known experimentally [3] and numerically [6] that H radicals erode polymers and hydrogenated amorphous carbon surfaces, and therefore increase their etching rates. This erosion effect by hydrogen atoms is observed also in our simulation, where it is shown that injected hydrogen atoms break the carbon-carbon bonding networks. Further, injections of hydrogen-rich molecules, such as CH<sub>4</sub>, effectively destroy the surface, which is similar to experimental observation that NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> usually function as etchants. Since the injections of C atoms alone do not etch the surface whereas the CH<sub>4</sub> injections seem to effectively etch the surface, the polymer etching mechanism by CH<sub>x</sub> or NH<sub>x</sub> beams must be combined effects of erosion by hydrogen atoms and the destruction by energetic carbon atoms.

## 5. Summary

In Summary we have performed MD simulations of PPP etching by hydrocarbon beams. Based on the simulation data, we have estimated sputtering and deposition yields and examined surfaces structures during the polymer etching processes. The simulation results also exhibit some

characteristics similar to those observed in polymer etching by hydrogen/nitrogen plasmas. We shall carry out simulations under conditions closer to those of actual organic low-k polymer etching experiments in the near future, using the newly developed C/H/N potential functions. In these simulations, nitrogen atoms and various nitrogen compounds will be injected into the surface and different roles played by carbon and nitrogen atoms will be clarified.

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