# Atomic-level simulation of non-equilibrium surface chemical reactions under plasma-wall interaction

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**Abstract**

Molecular dynamics (MD) simulations are used for the study of non-thermal-equilibrium reactions that take place on the substrate surface during plasma etching processes. In MD simulations, the motion of each atom is solved numerically based upon pre-determined interatomic potential functions and data of interest (such as sputtering yields, deposition rates, etch products, etc.) are evaluated from statistical averaging of relevant instantaneous data obtained from the simulations. In the present work, MD simulations of organic polymer etching by hydrocarbon beams were performed and atomic-scale morphology of the substrate surface during the etching and its relation to sputtering yields were examined.

*Key words:* molecular dynamics simulation; etching; deposition; plasma processing; organic polymer

## 1. Introduction

Plasma etching is now a standard technology for the fabrication of sub-micron structures on material surfaces in the semiconductor industry [1]. In the present work, we discuss classical molecular dynamics (MD) simulations for reaction dynamics of plasma etching. Especially we focus on MD simulations of organic polymer etching by hydrocarbon plasmas [2–6]. Organic polymers have been extensively studied as candidates for low dielectric-constant insulating materials in semiconductor chips.

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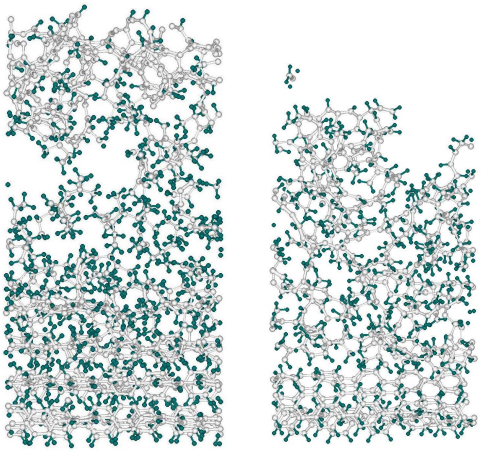
## 2. MD simulation of surface sputtering

In our MD simulations, substrate atoms are placed in a simulation cell with periodic boundary conditions in the horizontal directions. The cross sectional area of the simulation cell is approximately $2.2 \times 1.9$ nm$^2$. Energetic atoms, molecules, or radical species are injected from randomly selected horizontal locations just above the target in a selected direction, usually normal to the surface. The simulation period for each injection is 2-3 ps. The model substrate is poly (1,4-phenylene) [also known as polyparaphenylene (PPP)]. All atoms are assumed to be charge neutral and the interatomic potential functions are those proposed by Brenner [7] for covalent bonds, together with two-body Van der Walls force, as given in Ref. [8]. The typical number of atoms used in the simulations presented here is in the range of 1000-2000. For details on the simulation methods, the reader is referred to Ref. [2].



(a) (b)

Fig. 1. Horizontal views of PPP substrate surfaces after $2.4 \times 10^{16}/\mathrm{cm}^2$ injections of (a) $H_2$ and (b) $CH_4$ molecules, obtained from MD simulations. The substrate temperatures are set to be 450K for (a) and 600K for (b). The green and white spheres represent hydrogen and carbon atoms. The bond between two C atoms is depicted by a white bar and that between C and H atoms by a green bar.

## 3. Simulation results

Figure 1 (a) shows a typical PPP substrate surface after $2.4 \times 10^{16}/\mathrm{cm}^2$ injections of 50 eV $H_2$ molecules at substrate temperature 450 K, obtained from MD simulations. As is shown here, hydrogen atoms provided by the injected beam break carbon bonds. In this particular figure, a large portion of the substrate polymer is about to be removed from the surface. At high surface temperatures, desorption of such large clusters accounts for a large part of its etching rate.

Figure 1 (b) shows a typical substrate surface after $2.4 \times 10^{16}/\mathrm{cm}^2$ injections of $CH_4$ molecules at substrate temperature 600 K, obtained from MD simulations. In the case of $CH_4$ injections, chemical effects of hydrogen combined with collision effects by the large momenta carried by heavier carbon atoms allow effective etching of the polymer surface. At high substrate temperatures, sputtering yields are found to be larger due to the structural weakness arising from thermal oscillations. However, as discussed in Ref. [6], experimentally observed sputtering yields at high substrate temperatures are in general much larger mostly likely due to thermal desorption effects, which are not included in the MD simulations. The sputtering yields $Y_{\mathrm{C}}^{\mathrm{s}}$ under $CH_4$ injections for C atoms (i.e., the number of C atoms leave the surface per injection) obtained from MD simulations are $Y_{\mathrm{C}}^{\mathrm{s}} = 1.50$, 1.60, and 1.73 for the substrate temperature of 300K, 450K, and 600K, respectively. Note that, at each injection, a single C atom is added to the substrate, so the net decrease in the number of carbon atoms of the substrate per injection, i.e., the net erosion yield [2], is given by $Y_{\mathrm{C}}^{\mathrm{s}} - 1$.

## 4. Summary

We have presented some of our recent results of MD simulations of polymer etching by hydrocarbon beam injections. It is shown that the presence of hydrogen, combined with large momentum carried by heavy atoms in the beam, can etch PPP surface due to the combined physical and chemical effects of sputtering. We have also shown by MD simulations that the sputtering yields depend on the substrate temperature. However, as discussed in Ref. [6], since slow thermal relaxation processes such as thermal desorption cannot be included directly in MD simulations, the dependence of a sputtering yield on the substrate temperature obtained from MD simulations is much weaker than that from typical polymer etching experiments [9,10]. Development of effective means to include thermal desorption effects in MD simulations is a subject of future study.

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