Molecular dynamics simulation of plasma-surface interactions during dry etching processes

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Abstract - Molecular dynamics (MD) simulations are used to study non-thermal-equilibrium reaction dynamics taking place on the surface during dry 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 this paper, we review our recent MD simulations results on organic polymer etching. Similar simulations were also performed for selective etching processes of silicon and silicon dioxide substrates.

I. INTRODUCTION

Plasma etching is now a standard technology for the fabrication of sub-micron structures on material surfaces in the semiconductor industry [1]. In plasma etching, kinetic energies of ions combined with high reactivity of various radical species generated in the plasma are used to cause non-thermal-equilibrium chemical reactions in a few-nanometer deep surface region of the substrate material. Anisotropic etching and high selectivity required in the fabrication processes result form these chemical reactions. The mechanisms of such chemical reactions, however, have not been well understood to date.

A theoretical understanding of the surface reactions may be achieved, at least partially, by analyses of atomistic models that are designed to represent molecular dynamics near the substrate surface. In the present work, we discuss classical molecular dynamics (MD) simulations for reaction dynamics of plasma etching. In the present work, we focus on MD simulations of organic polymer etching by hydrogen carbon plasmas [2,3,4,5]. Organic polymers have been extensively studied as candidates for low dielectric-constant insulating materials in semiconductor chips.

To simulate plasma-surface interaction, one usually needs to handle a large number of particles (i.e., atoms) and repeat simulation runs for sufficiently many times to reduce statistical noise. Therefore the use of more detailed *ab initio* (i.e., quantum mechanical) simulations is impractical for this type of study. On the other hand, for classical MD simulations, the reliability of simulation results is in general affected largely by the choice of interatomic potential functions for the particles constituting the system.

II. SIMULATION METHODS

In our MD simulations, substrate atoms are placed in a simulation cell with periodic boundary conditions in the horizontal directions. 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. Process data such as etch yields, deposition rates, and etch products are obtained as functions of the injection species, incident angle, incident energy, and substrate temperature. Usually the process data depend also on injection dose especially when some deposition processes take place. In what follows, we give more detailed descriptions on these procedures.

To integrate the equation of motion for each atom, we employed the velocity Verlet algorithm. A typical time step for the simulations presented here is 0.5 femtoseconds (fs). All atoms are assumed to be charge neutral and the covalent bonds, which are shorter-range interactions (2), are represented by the potential functions derived by Brenner [the 2nd parameter set in Ref. [6]. Longer range (10) van der Waals interactions [7] are also taken into account among carbon atoms. Beams from the plasma are represented by carbon atoms, hydrogen atoms/molecules, or various hydrocarbon clusters CHx (x=1-4) vertically injected into the model polymer substrate. The translational kinetic energy of each incident atom or cluster is set to be 50eV in the present work. We use random numbers to determine the horizontal position and orientation of each incident cluster. Incident clusters are introduced at time intervals of ΔT_{int} , which we typically set

as $\Delta T_{int} = 500$ fs for the 300 K substrate. (For polymer substrates with higher temperature, we use much longer simulation time intervals.) We have confirmed that the interval ΔT_{int} that we used for each simulation is sufficiently long to capture short-time effects caused by beam-surface interactions. The simulation is performed under constant-energy (i.e., microcanonical) conditions for the first 80% of the time period ΔT_{int} (i.e., $0 \le t \le 0.8\Delta T_{int}$). Then the substrate temperature is gradually reduced to the initial substrate temperature during the rest of the time interval (i.e., $0.8\Delta T_{int} \le t \le \Delta T_{int}$) to make the system ready for the next injection. In this artificial cooling phase, a frictional force which represents a hypothetical global coupling to a heat bath is added to the equation of motion to remove (or add) heat from (or into) the system and to have the system reach the initial substrate temperature T_0 at the end of each time interval. Prior to the next injection, sputtered particles, i.e., atoms or clusters having no interaction with the substrate, are removed from the system.

Since experimentally observed etching rates of various low-k organic polymers are known to be similar[1-4], we conjecture that their etching characteristics are essentially determined by those of phenyl rings in their backbones. Therefore, in the present study, we have selected one of the simplest organic polymers, i.e., poly (1,4-phenylene) [also known as polyparaphenylene (PPP)] as the material of our model substrate. PPP consists of chains of phenyl rings only. In the model surface, the polymer chains are placed nearly in one direction without cross-linking and we have confirmed that the constructed material has the known mass density $\rho = 1.33\,\mathrm{g/cm^3}$ [8] of PPP in thermal equilibrium. A typical PPP substrate at 300K obtained from MD simulations is shown in Fig.1, where the bars represent covalent bonds. In actual simulations presented here, the typical initial substrate has four monolayers, each of which consists of four chains of five phenyl rings, i.e., 480 C atoms and 320 H atoms in the model substrate in total. In beam injection simulations, however, if any particle (injected or collided) passes through the lowest monolayer, we consider that the thickness of the substrate employed in this particular event is not adequate, discard this event, add another polymer layer to the substrate from the bottom, equilibrate the new substrate at the given initial temperature, and restart injection anew. The cross sectional area of the simulation box is approximately 2.2×1.9 nm^2. The periodic boundary conditions are imposed in the horizontal directions, as mentioned earlier. The atoms in the lowest monolayer are rigidly fixed, which prevents drift of the entire substrate by the particle bombardment.
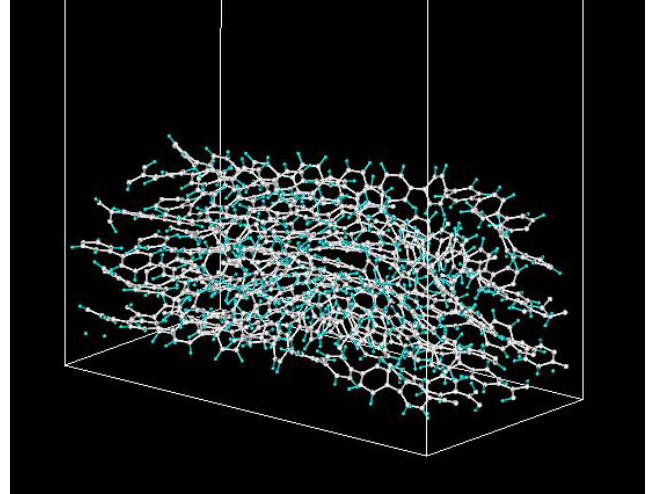

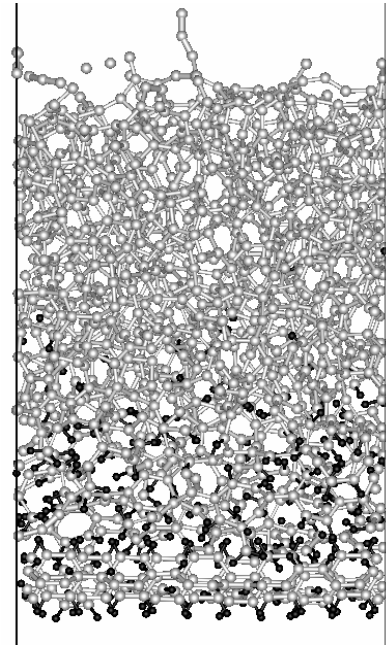Fig. 1: A PPP substrate at PPP obtained from MD simulations.

Fig. 2: A surface after 2.4×10^{16} cm^{-2} vertical injections of 50eV C atoms into a clean PPP surface at 300K. The white and black spheres represent carbon and hydrogen atoms and the thickness of each bar is set to be proportional to the bond order. Growth of a C layer on the polymer substrate is observed.

The kinetic energy carried by incident species are usually released in a "shallow" region of the surface,

i.e., a thin layer typically a few nano-meter deep. The released kinetic energy causes chemical reactions (i.e., breaking and reconnecting of bonds) in the nano-scale shallow region, which allows low-temperature processes, i.e., processes without heating the bulk substrate. For example, injection of 50eV carbon atoms into PPP substrates results in deposition of amorphous carbon layer, as shown in Fig. 2. It has been confirmed [2] that deposited carbon bonds shown in Fig. 2 are mostly of sp2 hybridization.

With hydrogen atoms, which tend to break carbon bonds, in the beam, the polymer surface becomes more prone to sputtering. Figure 3 shows sputtering yields for hydrogen (a) and carbon (b) atoms as functions of injection dose [2]. Here $Y_H^{(N)}$ is the net erosion yield for hydrogen, which is defined as the number of hydrogen atoms leave the polymer surface per injection, including those hydrogen atoms supplied by the injection beam. Since the substrate contains hydrogen, this quantity being positive means that hydrogen atoms of the substrate are removed by the impact. As shown in Fig. 3(a), in the case of CH_4 injection, hydrogen atoms supplied by the beam are initially deposited but, at a later stage, the substrate hydrogen atoms are also removed. Similarly, $Y_C^{(N)}$ represents the net erosion yield for carbon. In general, we define $Y_A^{(N)}$ of species A as $Y_A^{(N)} = Y_A - I_A$, where Y_A is the sputtering yield of A atom and I_A is the number of A atoms injected into the substrate per injection.

III. SUBSTRATE TEMPERATURE DEPENDENCE

In general, sputtering yields depend on the substrate temperature. This dependence is especially strong in the case of polymer substrates. There are mainly two possible mechanisms that cause such temperature dependence. One is the structural weakness of the substrate due to large thermal oscillation and the other is large thermal desorption due to the high substrate temperature. The former is likely to affect a fast process of sputtering, i.e., more surface atoms tend to be removed directly by and immediately after the beam injection impact if the binding forces among substrate atoms are weaker. Such phenomena can be easily captured in our MD simulation. On the other hand, the latter is a slow thermal process based on the balance between the binding energies of surface atoms and those of thermal fluctuations. Such processes are, however, cannot be simulated by MD simulations in a straightforward manner due to their extremely long time scale. Therefore, we here examine only the former effects by varying the substrate temperature in our MD simulations.
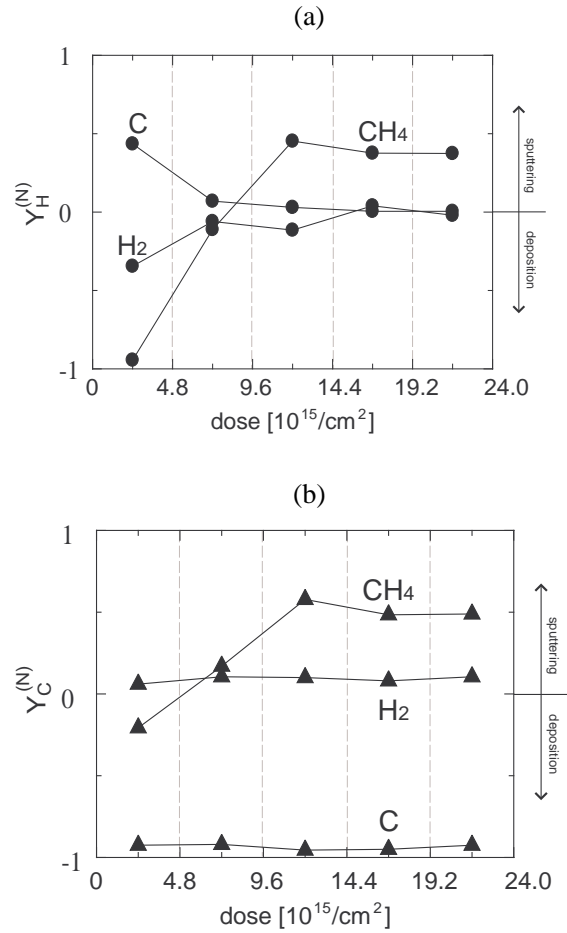
(a)

(b)

Fig 3: The sputtering yields (defined in the main text) for hydrogen (a) and carbon (b) of the polymer surface subject to each beam species as functions of injection dose.

Figure 4 shows a typical structure of the PPP substrate after 2.4×10^{16} cm^{-2} vertical injections of 50eV CH_4 atoms into a clean PPP surface at 600K [4]. It is seen that the upper part of the substrate surface is significantly modified and almost broken into hydrocarbon clusters. Such rough surfaces are frequently observed when the substrate temperature is high. The potential energy for Van der Waals attractive interaction that we have employed in the simulations presented here is 0.05eV, which is comparable to the surface temperature 600K used for the simulations given in Fig. 4. We note that, however, it is confirmed by our MD simulations that the PPP substrate at 600K is still stable and crystalline, similar to that shown in Fig. 1, without atomic bombardment. Therefore, we expect that polymer chains are bound to each other less firmly via Van der Waals interactions at a high substrate temperature and the surface can be significantly deformed by atomic bombardment under such conditions, which is likely to result in higher sputtering yields. Figure 5 shows the injection dose

dependence of the net erosion yields of the PPP substrate under 450K and 600K substrate temperatures conditions.
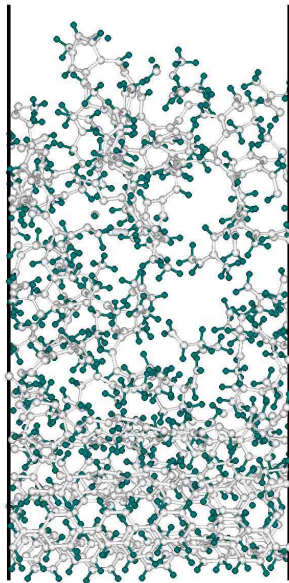

Fig. 4: A surface after 2.4×10^{16} cm^{-2} vertical injections of 50eV CH$_4$ atoms into a clean PPP surface at 600K.
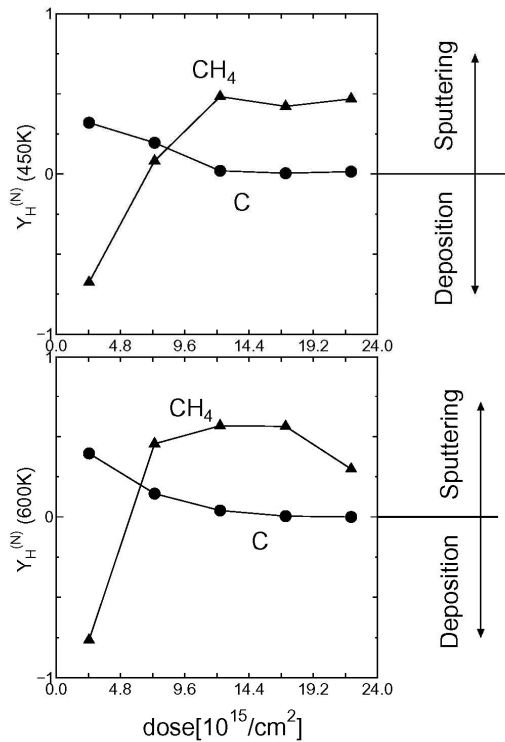

Fig. 5: Net erosion yields of H atom for C and CH$_4$ injections as functions of injection dose at 450 and 600K substrate temperatures

IV. CONCLUSIONS

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 also depend on the substrate temperature. Since our MD simulation does not include thermal desorption effects to the full extent, we expect this dependence arises from structural weakness of the polymer substrates due to the high substrate temperature. Stronger substrate temperature dependence of sputtering yields may arise if one includes the enhanced thermal desorption effects as well as the change of gas-phase chemistry caused by higher temperatures of the operating gases in contact with the substrate.

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