Modelling of Plasma Surface Interaction

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Abstract. Molecular dynamics (MD) simulations are used to investigate chemical reactions that take place on surfaces exposed to ion bombardment and neutral radicals extracted from plasmas. Such chemical reactions occur in a nano-meter-scale thin top layer of the material and their characteristics significantly differ from those of ordinary chemical reactions in thermodynamical equilibrium. As applications of MD simulations to microscale fabrication and thin film formation processes, recent MD simulation results on organic polymer etching by hydrogen/nitrogen plasmas and surface diffusion of Si on highly hydrogenated Si surfaces are reviewed.

1. Introduction
Molecular dynamics (MD) simulations are used to investigate chemical reactions that take place on surfaces exposed to ion bombardment and neutral radicals extracted from plasmas. Such chemical reactions occur in a nano-meter-scale thin top layer of the material and their characteristics significantly differ from those of ordinary chemical reactions in thermodynamical equilibrium. We have developed MD simulation techniques and interatomic potential models that can handle chemical reactions (i.e., change of covalent bonding) in plasma-surface interactions.

As applications of our MD simulations, we review in this article recent simulation results that have been obtained by the authors on organic polymer etching by hydrogen/nitrogen plasmas [1, 2, 3, 4] and surface diffusion of Si adatoms on highly hydrogenated Si surfaces. Fast suffice
diffusion of Si adatoms may account for crystallization processes observed in plasma enhanced chemical vapor deposition (PECVD) processes of microcrystalline Si [5].

Organic polymers are considered to be one of the most promising candidates for low-dielectric-constant (i.e., low-k) insulating materials for interconnect wiring of semiconductor devices. In plasma etching of organic polymers, hydrogen, nitrogen, or ammonia gases are typically used for plasma discharges [6, 7, 8, 9]. It has been reported that sputtering yields of organic polymers in such processes sensitively depend on the ratio of hydrogen and nitrogen radical densities. Qualities of a carbon-nitride layer formed on the polymer surface during such a process is likely to have some influence on the sputtering yields and other etching properties. In actual plasma processes, various radial species are simultaneously react with surface materials. Therefore it is difficult to examine individual chemical reactions caused by specific radial/ionic species. Using MD simulations, on the other hand, we can examine each chemical reaction caused by specific incoming radical/ionic species with the surface material within the framework of given models implemented in the simulator.

Another example we discuss in this article is a possible crystallization process that is likely to take place during PECVD processes of microcrystalline silicon (µc-Si) for solar cells [10, 11]. Although it is well-known that a large amount of hydrogen dilution is needed for the manufacturing of µc-Si thin films by PECVD processes, the growth mechanism of microcrystalline Si has not been completely understood to date. While it is difficult to observe surface reactions such as microcrystalline growth processes in atomic scales, MD simulation of surface reactions can contribute to an understanding of such phenomena. Here we perform MD simulation of fast Si diffusion on a highly hydrogenated Si surface in order to examine the possibility that such fast diffusion accounts for crystallization of Si during the PECVD processes.

2. Simulation of organic polymer etching

To understand etching characteristics of a typical organic polymer surface during hydrogen-nitrogen plasma etching processes at the atomic level, we have used MD simulations [1, 2, 3]. In simulations, we injected nitrogen atoms, nitrogen molecules, or ammonia molecules into a model surface made of poly(1,4-phenylene) (i.e., poly(paraphenylene or PPP for abbreviation) with relatively low energies (25-50 eV). The set of interatomic potential functions used in the present simulations is a modified version of the potential functions initially developed by Yamada and Hamaguchi [12]. Details of the modified functions will be presented elsewhere.

In MD simulations, the equation of motion is solved for each atom in the system. To integrate the equation of motion for each atom, we employ the velocity Verlet algorithm. A typical time step employed here is 0.125 femtoseconds (fs), and the period of one injection event is 1.2 picoseconds (ps). The initial PPP substrate is shown in Fig. 1. The horizontal cross section (in the x-y plane) of the simulation box is 2.2×1.9 nm². Periodic boundary conditions are imposed in the x and y directions. The typical initial substrate has four monolayers, each of which consists of four chains of five phenyl rings. Therefore, the initial substrate has 480 carbon (C) atoms and 320 hydrogen (H) atoms in total. The atoms in the lowest monolayer are rigidly fixed, which prevents drift of the entire substrate by particle bombardment.

In our MD simulations, if any atom (injected or recoiled) passes through the lowest monolayer of the substrate, we consider that the substrate thickness employed in this particular event is not enough, discard this event, add another polymer layer to the substrate from the bottom, equilibrate the new substrate at the room temperature, and restart the injection anew.

In the simulations presented here, the simulation cycle of a single injection was typically repeated 2000 times, which corresponds to the dose of 4.8 × 10¹⁶. For the sake of simplicity, we assumed that reactivities of ions and charge neutral species for the same atomic species be essentially the same. Therefore all atoms were assumed to be charge neutral and highly energetic impinging species were simply interpreted as beam ions.
A typical time scale in which a MD simulation can practically follow the dynamics of a system of a large number of atoms is a few pico seconds after an injection of each beam species. Therefore, although slow chemical sputtering (e.g., thermal desorption) of surface species is also known to play a crucial role in organic polymer etching [6], we note that such an effect is not taken into account in the present work.

From the simulations, we have found that atomic nitrogen (N) beams most effectively nitrogenize the organic polymer due to its high reactivity among the three types of beams examined in the present simulation study. The carbon-nitride layer formed on the substrate surface during the process can increase the sputtering yields and act as a source of carbon-nitride clusters for sputtered species (i.e., etch products) when it is subject to energetic ion bombardment.

Figure 2 shows etched species after \(4.89 \times 10^{16} \text{cm}^{-2}\) injections of N atoms. Similarly Figure 3 shows etched species after the same number of injections of N\(_2\) atoms. NUM\(_C\) represents the number of C atoms contained in each desorbed cluster. For both N and N\(_2\) injection cases, the main desorbed species is CN for NUM\(_C\)=1 and is C\(_2\)N\(_2\) for NUM\(_C\)=2.

3. Simulation of surface diffusion

Recently fast deposition technologies for Si are in high demand for the fabrication of highly efficient solar cells. One of the promising technologies for solar cells uses \(\mu\)-Si. As mentioned earlier, fast surface diffusion of Si deposition precursors on highly hydrogenated Si surface could account for the crystallization processes that have been observed in PECVD processes of Si with high hydrogen dilution.

In this section, we review the recent MD simulation work by two of the authors (M. M. and S. H.) where the motion of a Si adatom on the hydrogen-terminated (111) Si crystal was examined [5]. Although the typical deposition precursor of silane based PECVD processes is known to be SiH\(_3\), we here consider only Si adatoms on the surface for the sake of simplicity. Indeed it has been found that that an adsorbed SiH\(_3\) on a highly hydrogenated Si surface tends...
to lose some of its hydrogen atoms quickly through hydrogen abstraction reactions and therefore does not remain as SiH$_3$ on the surface for an extended period.

The Si atom on the surface is given an initial “push” in a horizontal direction, i.e., the kinetic energy of 1eV with the initial velocity parallel to the surface. The direction of the initial velocity in the horizontal plane is chosen randomly.

As shown in Fig. 4, the model substrate consists of 672 Si atoms and 224 H atoms. The bottom substrate layer is fixed to prevent the drift and macroscopic deformation of the crystalline substrate. The model surface area is approximately $5.37 \times 5.37\text{nm}^2$ and the periodic boundary conditions are imposed in the horizontal directions, as in the case of PPP substrates discussed in the previous section. Initially the substrate is thermalized at 600K for 10ps. On the thermalized
substrate, a Si atom is placed with the horizontal initial velocity corresponding to 1eV and the whole system is simulated under the constant total energy conditions (i.e., in so-called NVE ensemble).

For surface diffusion MD simulations, the motion of each Si adatom was calculated for 1.8 ns with 600 randomly chosen initial conditions, i.e., initial velocity directions and initial positions. It has been observed that approximately 31 % of the examined 600 Si adatoms leave the surface (i.e., are desorbed) within 10 ps and almost all of the rest, i.e., approximately 69% of the total, remain on the surface until the very end of the simulation, i.e., $t=1.8$ ns. Among the 415 initial Si adatoms that continue to stay on the surface throughout the simulation, 257 of them have formed the full covalent bonds with the substrate Si atoms at appropriate lattice sites by $t=1.8$ ns while the other 158 initial Si adatoms continue to remain as adatoms, i.e., weakly bound to the substrate atoms until the end of the simulations. Here we call the former group the trapped atoms and the latter the untrapped atoms.

The mean squared displacement (MSD) on the surface is defined as

$$< \Delta r_{2D}^2(t) >= < (r_{2D}(t) - r_{2D}(0))^2 >,$$

where $r_{2D}(t)$ represents the horizontal position of the test particle (i.e., Si adatom) at time $t$ and the bracket $<>$ represents statistical average. The MSDs of the untrapped group and trapped group are evaluated and shown by dark and light colored curves as functions of time in Fig. 5 [5]. It is clearly seen that almost all Si adatoms of the trapped group become “trapped” by $t=10$ps.

At sufficient large time($t \geq 1$) ns, the MSD of the untrapped group is shown to increase linearly with time in Fig. 5, which indicates that long-time motions of surface adatoms are diffusive.
From Einstein’s relation, the 2-dimensional diffusion coefficient $D$ is derived from the MSD as

$$D = \frac{1}{4t} < \Delta r_{2D}^2(t) > .$$

The diffusion coefficient for adatoms (i.e., untrapped group) thus derived from the MSD in the time domain of $t \geq 1.0$ns of Fig. 5 is $D = 1.28 \times 10^{-8}$ cm$^2$/s [5].

4. Conclusions
We have briefly reviewed recent MD simulation work for organic polymer etching and fast surface diffusion of a Si adatom on a highly hydrogenated Si surface. The former is a technology that needs to be perfected for the fabrication of fast interconnect wiring in semiconductor chips and the latter relates to PECVD processes of $\mu$c-Si for solar cell technologies.

In organic polymer etching simulations, N, N$_2$, and NH$_3$ atoms/molecules were vertically injected into a PPP substrate with given injection energies [4]. At relatively low injection energies examined here (50eV or less), it was observed that atomic nitrogen (N) beams most effectively nitrogenize the organic polymer due to its high reactivity among the three types of beams examined in the present simulation study. The carbon-nitride layer formed on the substrate surface during the process can increase the sputtering yields and act as a source of carbon-nitride clusters for sputtered species (i.e., etch products) when it is subject to energetic ion bombardment. This is because the highly dense network of carbon and nitrogen in the carbon-nitride film (and therefore the “hardness” of the film) efficiently convert the kinetic energy of incoming beam into the energy to break the bonds in the film. We have listed the yields of various sputtered species for N and N$_2$ injections.

MD simulations of surface diffusion of Si adatoms during silane (SiH$_4$)-based PECVD
processes have shown that the coefficient of surface diffusion of a Si adatom on a highly hydrogenated Si surface at 600K is indeed much larger than those of typical clean Si surfaces known in the literature. Such high surface diffusion can account for the growth of µc-Si in the PECVD processes.

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