Molecular Dynamics Simulations of Si and SiO₂ Selective Etching

S. Hamaguchi and H. Ohta

Department of Fundamental Energy Science,
Kyoto University,
Gokasho, Uji, Kyoto 611-0011, Japan.

Abstract

Molecular dynamics (MD) simulations of silicon and silicon dioxide etching by energetic halogen (fluorine or chlorine) atoms are performed using newly constructed sets of classical interatomic potentials for Si-O-F and Si-O-Cl systems. The classical interatomic potentials are obtained by fitting potential energy data obtained from ab initio quantum mechanical calculations to Stillinger-Weber type three-body potential functions. The obtained sputtering yields and selectivities are in good agreement with experimental observations.

1. Introduction

Silicon (Si) etching is one of the most widely used plasma processes in the current semiconductor chip manufacturing. To create desirable patterns on a chip surface, high etch yield ratios (i.e., selectivities) of Si against other materials are required. In the present paper, we discuss the ratio of Si and SiO₂ etch yields, using molecular dynamics (MD) simulations of atomic processes on Si and SiO₂ targets.

In classical MD simulations, each atom is modeled as a particle interacting with other particles via pre-determined interatomic potentials. Motions of such particles are assumed to follow Newton’s equation of motion. In actual atomic systems, atomic interactions are determined by the electronic states and exact determination of such interactions requires quantum mechanical calculations. However in plasma etching simulations, we may employ classical MD simulations for the following reasons. First, to numerically simulate plasma etching processes, which typically involve surface bombardment with relatively high kinetic energy, one needs to follow motions of a large number of particles after each atomic impact. Furthermore, to obtain statistically reliable measurable quantities such as etching yields, one needs to repeat simulations with different initial conditions many times. Therefore, it is practically impossible to employ computationally expensive quantum mechanical (i.e., ab initio) MD simulations for such systems. Second, due to the relatively high ion impact energies, such surface reactions may be less sensitive to the exact interatomic potential functions than ordinary chemical reactions in thermodynamical equilibrium. One of the goals of our MD simulation study is to clarify to what extent classical MD simulations can reveal the nature of surface reactions in plasma processing.
To dates, various authors have performed classical MD simulations for Si etching by halogen beams [1-6]. In order to simulate SiO$_2$ etching by halogens, we have constructed sets of classical interatomic potentials for Si-O-F and Si-O-Cl systems by fitting potential energy data obtained from *ab initio* quantum mechanical calculations to Stillinger-Weber type three-body potential functions [1,7-10]. The details of the interatomic potentials for Si-O-F and Si-O-Cl systems are found elsewhere [10].

2. MD simulation

In our MD simulations, an atom (either halogen or Ar) is directed to the target surface in the normal direction with a given energy from a randomly selected location just above the target surface. We assume that the impinging atoms and the target surface are charge neutral since ions are neutralized right before hitting the target due to an Auger emission process. The target surface (either Si crystal or SiO$_2$ beta-cristallite) is initially kept at 300°K. For the sake of simplicity, all the injected particles are monomers in the present simulations. Details of our simulation method are found in Ref. [6].

After each ion injection, motions of all atoms in the simulation box (which typically contains about 1000 atoms) are monitored for about 0.7 ps. Then the system is artificially cooled to 300°K for 0.3ps. This cooling process is unrealistic but necessary in order to repeat many injection runs efficiently. In actual processes, such cooling occurs much more slowly (typically from several µs to ms). Therefore the surface we obtain in simulations may be rougher than the actual surface. This surface roughness can cause large clusters of atoms (i.e., molecules or radicals) to be desorbed from the surface in simulations. Although such events are not so frequent, desorption of a small number of large clusters contribute significantly to the sputtering yields. Therefore, we define here the sputtering yield $Y$ (of Si) as the number of Si atoms desorbed from the target surface (Si or SiO$_2$) in the form of a cluster containing only a single Si atom (e.g., SiCl$_x$ or SiCl$_x$O$_y$ with $x, y \geq 0$) per atomic injection. In this sense, yield $Y$ defined here gives a lower bound of the actual sputtering yield [6].

<table>
<thead>
<tr>
<th>Si</th>
<th>Ar</th>
<th>Cl</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>20eV</td>
<td>0</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>30eV</td>
<td>0</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>50eV</td>
<td>0.011</td>
<td>0.26</td>
<td>0.42</td>
</tr>
<tr>
<td>100eV</td>
<td>0.084</td>
<td>0.46</td>
<td>0.51</td>
</tr>
<tr>
<td>150eV</td>
<td>0.15</td>
<td>0.67</td>
<td>0.62</td>
</tr>
</tbody>
</table>

(a)

<table>
<thead>
<tr>
<th>SiO$_2$</th>
<th>Ar</th>
<th>Cl</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>50eV</td>
<td>0.0031</td>
<td>0.020</td>
<td>0.12</td>
</tr>
<tr>
<td>100eV</td>
<td>0.039</td>
<td>0.11</td>
<td>0.20</td>
</tr>
<tr>
<td>150eV</td>
<td>0.067</td>
<td>0.15</td>
<td>0.22</td>
</tr>
</tbody>
</table>

(b)

Table 1: Sputtering yields $Y$ of (a) the Si target and (b) SiO$_2$ target as functions of the kinetic energy of different impinging species (Ar, Cl, and F).
<table>
<thead>
<tr>
<th>ratio</th>
<th>Ar</th>
<th>Cl</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>50eV</td>
<td>3.5</td>
<td>13</td>
<td>3.5</td>
</tr>
<tr>
<td>100eV</td>
<td>2.2</td>
<td>4.2</td>
<td>2.6</td>
</tr>
<tr>
<td>150eV</td>
<td>2.2</td>
<td>4.5</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Table 2: The ratios of sputtering yields for the Si target to those for the SiO$_2$ target

Fig. 1: Typical steady-state SiO$_2$ surface conditions under 150 eV (a) Cl and (b) F beam etching. White, gray and black spheres represent Si, Cl (or F) and O atoms, respectively.

3. Results and discussion

Table 1 summarizes the Si sputtering yields $Y$ (defined above) obtained from MD simulations for both Si and SiO$_2$ targets [6]. The yield values are obtained by averaging over 640 impacts (which are equivalent to 20 monolayers of impinging atoms for our simulation box). These values are consistent with available experimental data [6]. Using the etching yields given in Table 1, we have also calculated the yield ratios (i.e. selectivities), which are given in Table 2. The etching by Cl gives much higher selectivities than that by F or Ar, especially near the SiO$_2$ etching threshold.

Figure 1 shows typical steady-state surface conditions of the SiO$_2$ target under Cl and F beam etching. The impinging kinetic energy is 150 eV in both cases. The steady state is obtained after sufficient surface bombardment. (Physical quantities such as sputtering yields...
are measured only after the surface reaches steady state.) It is shown in Fig. 1 that smaller F
atoms penetrate the target more deeply than Cl atoms. In addition, F atoms are also more
reactive with the target in the sense that Si-F and O-F binding energies are much higher than
Si-Cl and O-Cl binding energies. These account for the high sputtering yields by F
bombardment as F atoms can more easily terminate Si bonds in both Si and SiO₂ targets,
which makes Si atoms less firmly bound to the target surface.

References