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MD simulation analysis of synergetic effects on surface reaction in Si and SiO_2 etching by Cl plasmas

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Abstract: Molecular dynamics (MD) simulations have been performed to study the etching of silicon (Si) and silicon dioxide (SiO_2) surfaces by chlorine (Cl) ions and radicals possibly with an addition of oxygen (O) ions and radicals. Although the Si etching yield is typically much larger than that of SiO_2, Si and SiO_2 exhibit similar etching rates due to the much lower Si number density in SiO_2. The addition of O ions or radicals to the Cl etching was found to replenish preferentially etched O atoms in SiO_2 but hardly affected the Si selectivity.

Keywords: Etching, MD simulations

1. Introduction

Over the last decades, typical sizes of semiconductor devices continuously shrunk, reaching atomic scales. At such scales, device manufacturing becomes more challenging and a deeper understanding of the etching mechanisms is required. Plasma etching[1] is a key technology for nanoscale etching of various materials, including silicon (Si) or silicon dioxide (SiO_2).

In plasma etching, atoms are removed from the material surface by the impact of energetic ions and chemically reactive species emitted from the plasma. As surface etching is typically due to synergetic effects between chemical reactions with incident chemically reactive species and collision cascades induced by the impacting energetic ions, it is also called reactive ion etching (RIE). Surface etching reactions can be promoted by ion beam etching (IBE) if the incident ions are chemically reactive.

A previous study of nanoscale structure etching of a Si material by a Cl plasma with a SiO_2 mask[2] showed that, although the etching yield of Si is much larger than that of SiO_2, the SiO_2 mask was typically etched more than the Si substrate. It showed that, for the etching of nanoscale structure, transient effects such as the initial swelling of the Si substrate can significantly affect the etched profiles. It was also observed that oxygen (O) was preferentially removed (i.e., etched) from the SiO_2 mask. Due to this O depletion, the mask surface becomes Si-rich, which affects its structure and impacts the etched profile, especially for IBE.

In this work, we study the etching of Si and SiO_2 surfaces exposed to Cl ions and radicals, and possibly with an addition of O ions and radicals, using molecular dynamics (MD) simulations. The etching rate of each material is first evaluated for IBE and RIE. We then examine the effect of oxygen by adding O^+ ions or O radicals. For each case, the etching rate of the Si and SiO_2 materials are compared, and the Si selectivity is evaluated.

2. Simulation model

In MD simulations, Newton's equation of motion is numerically solved for each atom for given interatomic forces models. The interatomic potential functions used in this study are essentially the same as the Stillinger-Weber-type potential functions given in Ref. [3].

This study was performed in a similar way to a previous study[2]. The Si substrate (Fig. 1a) was made of a collection of Si atoms arranged in a diamond crystalline structure with a lattice constant $a_{\mathrm{Si}} = 5.43$ Å. It had a size of 3.26 nm, 3.26 nm, and 2.17 nm in the x, y, and z directions, respectively. Similarly, the SiO_2 material (Fig. 1b) was made of a collection of Si and O atoms arranged in a β-cristobalite crystalline structure of lattice constant $a_{\mathrm{SiO_2}} = 6.978$ Å. It had a size of 4.19 nm, 4.19 nm, and 2.79 nm in the x, y, and z directions. Both materials were thermalized at 300 K.

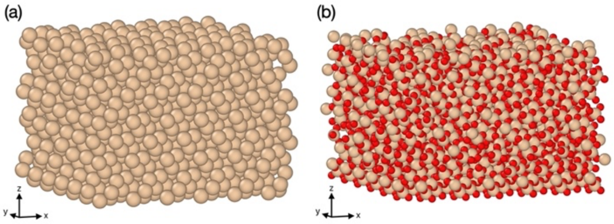

Figure 1: 3D representations of the (a) Si and (b) SiO_2 materials used in this study. The beige and red spheres represent Si and O atoms. Both materials are in thermal equilibrium at 300 K.

The material was placed at the bottom of the simulation box having the same dimensions as the material in the horizontal direction. Periodic boundaries were applied in the horizontal directions to simulate an infinitely wide material. To prevent the material from moving downward during the simulation, the bottommost layers were fixed.

The material surface is exposed to incident Cl^+ ions and possibly Cl radicals, O^+ ions, and O radicals in a cyclic way. Incident ions, Cl^+ or O^+, were injected with a given energy and at normal incidence, i.e., along the z-axis. For the sake of simplicity, no charge effect of incident ions was considered in this study, and all ions were modelled as the corresponding neutral species. On the other hand, radicals, Cl or O, were injected with a given low incident energy and with a random downward incident angle. The kinetic energy of incident radicals was set low, comparable to the thermal energy.

The total numbers of injected Cl^+ ions, O^+ ions, Cl radicals, and O radicals for a specified time interval are denoted by $N_{\mathrm{Cl^+}}$, $N_{\mathrm{O^+}}$, N_{Cl}, and N_{O}, respectively. The ratio of the number of injected Cl radicals to that of Cl^+ ions is denoted as $\Gamma = N_{\mathrm{Cl}}/N_{\mathrm{Cl^+}}$. In the case $\Gamma = 0$, no Cl radicals are injected, and we call the process IBE. When $\Gamma \neq 0$, we call the process an RIE.

At the beginning of each injection cycle, the injected atoms are added above the material surface at random places across the surface such that they are just out of interaction range with the surface and other injected atoms. During the first 500 fs, constant-energy (NVE) conditions were applied to update the positions and velocities of all atoms. Cooling was then applied for the next 1.5 ps to thermalize the system to 300 K. At the end of the 2 ps injection cycle, all atoms not belonging to the material were removed before a new injection cycle was started.

3. Results and discussion

The etching of Si and SiO_2 flat surfaces was first studied for a Cl^+ IBE and a Cl-based RIE for the materials described above. In IBE, the materials were exposed to a single Cl^+ ion ($N_{Cl^+} = 1$) with an incident energy of 100 eV during each injection cycle. In RIE, the material was exposed to ten Cl radicals ($N_{Cl} = 10$) with an incident energy of 0.1 eV during odd injection cycles, and to a single Cl+ ion ($N_{Cl^+} = 1$) with an incident energy of 100 eV during even injection cycles. It corresponds to $\Gamma = 10$.

The effect of O^+ ions and O radicals for both Cl^+ IBE and Cl-based RIE was then studied. It was done by adding a second step for IBE, or a third step for RIE, to the injection cycle during which O^+ ions or O radicals were injected. For O^+ ions, a single O^+ ion ($N_{O^+} = 1$) with an incident energy of 100 eV was injected. For O radicals, ten O radicals ($N_O = 10$) with an incident energy of 0.1 eV were injected.

For each case, the surface height change Δ is computed as a function of the ion dose. The surface height is defined as the height z where the material number density is equal to $10^{22}\mathrm{cm}^{-3}$. The etching rate is obtained as the slope of the surface height change Δ during steady-state etching. The Si selectivity is obtained as the ratio of the Si etching rate to the SiO_2 etching rate.

The first observation from the surface height change Δ is that, when exposed to Cl ions or radicals, the Si surface initially swelled before being etched. This initial swelling of the Si surface is due to the incorporation of the incident Cl atoms into the Si material. On the other hand, the SiO_2 surface hardly swelled, and the SiO_2 material was etched from the beginning of the Cl exposure.

The etching rate as well as the Si selectivity is shown in Figure 2 for each case. Firstly, when the materials are exposed only to Cl^+ ions, i.e., for IBE, a similar etching rate was observed for both materials. Although the etching yield of Si, i.e., the average number of atoms removed from the material surface by a single Cl^+ ions, is much higher than that of SiO_2, this similarity of the etching rate is due to the much lower Si number density of SiO_2 than Si. When the materials were also exposed to Cl radicals, i.e., for RIE, the etching rate of both materials increased by a factor of around 2 due to the formation of $SiCl_x$ species on the material surface. Unlike the case of energetic Cl^+ ions, which physically etch the material by causing collision cascades in the material, thermal Cl radicals chemically interact with surface atoms. Surface atoms are therefore more weakly bonded with the material bulk and therefore more easily etched by energetic Cl^+ ions.

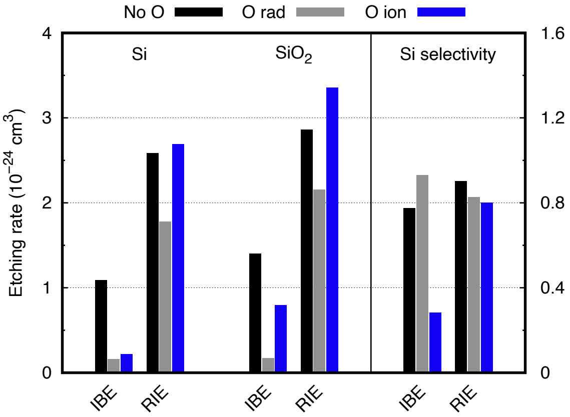

Figure 2: Etching rate and Si selectivity of Si and SiO_2 surfaces for the studied cases. The Si selectivity corresponds to the ratio of the Si etching rate to the SiO_2 etching rate.

For both IBE and Cl-based RIE, preferential removal of O atoms from the SiO_2 surface was observed, making the surface Si-rich. The O deficiency near the SiO_2 surface caused by it can be mitigated by injecting O to replenish the depleted O. Here, we consider the injection of energetic O^+ ions and thermal O radicals separately.

When exposed to O radicals (Fig. 2, case “O rad”), both materials show a lower etching rate for both IBE and RIE. Having low energy, O radicals were mostly deposited on the material surface and hardly penetrated the inside of the material. We now first consider the IBE case. In the case of the SiO_2 material, incident O radicals are partially replenishing the lost O atoms, lowering the material etching rate. On the other hand, for the Si material, the surface was oxidized by the incident O radicals, forming a SiO_2 layer on top of the Si material. Ultimately, the etching rate of both materials will be the same as their surface will have the same chemical composition. A similar mechanism takes place for RIE. However, the presence of Cl radicals caused a decrease in the effect of O radicals. Unlike the IBE, the Si selectivity did not change.

When O^+ ions were injected (Fig. 2, case “O ion”), the etching rates of both materials were lower than the cases without O^+ ions for IBE but higher for RIE. Having larger incident kinetic energy, Cl^+ ions penetrated the material much deeper than thermal Cl radicals and, therefore, affected a deeper region of the material. For IBE, a lower etching rate was observed for both materials. However, the decrease in etching rate was found to be much smaller for SiO_2 than Si, causing the Si selectivity to decrease significantly. On the other hand, in the presence of Cl radicals, i.e., for RIE, the etching rate slightly increased although the Si selectivity did not change much.

4. Conclusions

In this study, the etching rates of Si and SiO_2 surfaces exposed to a Cl plasma were evaluated by MD simulations. It was found that, under the studied conditions, both materials are etched at similar rates when exposed to incident Cl^+ ions and Cl radicals. This is due to the lower Si number density in SiO_2 than in Si, which balances the lower etching yield of SiO_2 compared with that of Si.

An addition of O^+ ions or O radicals was found to strongly affect the etching rates of both materials. Lost O atoms in SiO_2 were partially replenished by incident O ions or atoms while the Si material surface was oxidized by incident O atoms. However, little effect on the Si selectivity was observed, except for O^+ ions in IBE.

A better Si selectivity may be achieved by using lower ion energy or adjusting the amount of injected O atoms.

5. Acknowledgments

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6. References

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