

Effects of Van der Waals Interactions on SiO₂ Etching by CF_x Plasmas

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Abstract

We have performed Molecular Dynamics (MD) simulations of silicon dioxide etching processes by fluorocarbon plasmas. It is known that both etching and deposition caused by carbon atoms can take place simultaneously in such processes. In order to understand the atomic scale mechanisms of such processes, we have developed empirical interatomic potential models for MD simulations, which include covalent bonds and Van der Waals (VW) interactions among Si, O, C, F atoms. Especially, to clarify the effect of VW interactions, we have performed two different simulations with and without VW interactions. Deposition of fluorocarbon films is observed only in the case with VW forces. In the early stage of carbon deposition, small carbon clusters are formed sparsely without being bound with the substrate atoms through covalent bonds. Therefore such carbon clusters can easily depart from the surface without VW interactions. Although VW interactions are order-of-magnitude smaller than covalent bonds in terms of bond energy, we found it is VW interactions that keep such deposition precursors near the substrate surface to assist the growth of fluorocarbon films.

Keywords:

plasma processing, plasma-surface interaction, deposition, molecular dynamics, interatomic potential

1. Introduction

The atomic-scale understanding of plasma-surface interaction during plasma etching processes is of significant importance in the development of advanced dry etching technologies for microelectronics applications. Etching processes of silicon dioxide (SiO₂), which is widely used as insulator material for interconnect in microchips, are typically done with fluorocarbon plasmas (CF_x). One of the problems that are difficult to understand in such processes is the coexistence of both etching and deposition processes caused by carbon atoms. Surface reactions during the etching process, *i.e.*, “plasma-surface interactions”, may be understood in its simplistic form as a “beam-surface interaction,” without taking into account effects of background neutral species. The energy range of ions accelerated in the plasma sheath (the beam energy) is typically 10–1000 eV.

Recently numerical simulations by classical molecular dynamics (MD) methods have attracted a great deal of attention as a means to analyze plasma-surface interactions. Various such simulations have demonstrated that this classical approach, as opposed to *ab initio* quantum mechanical simulations, provides sufficiently good descriptions of surface reaction dynamics. Numerical studies based on classical MD simulations can often compensate shortage of experimental data and give physical insight into the atomic-scale reaction

mechanisms. [1,2,3,4]

In order to perform MD simulations of SiO₂ etching by fluorocarbon plasmas, we have developed a phenomenological model of the covalent bonds and Van der Waals (VW) interactions for Si/O/C/F systems. Details of this interatomic potential model will be published elsewhere.

2. Model and MD procedure

For MD simulations, our model consists of two types of interactions: the covalent bond and VW interaction. The former is strong (several eV) and of short range, effective only among neighboring atoms. By contrast, the latter is weak (10⁻² eV) and of longer range, which can reach more than third neighboring atoms (several Å). The total VW interaction energy per atom is typically about 10⁻¹ eV as about a dozen of atoms may exist in the interaction range.

Let us briefly outline our interatomic potential model for Si/O/C/F systems. During plasma etching, energetic ions hit the material surface and interact with it chemically and physically. Chemical reactions often involve breaking and reconnection of covalent bonds. To represent chemical reactions correctly in MD simulations, it is important to model interatomic potentials associated with covalent bonds with good accuracy. To construct our phenomenological

interatomic potential functions, we fit model functions to energy data obtained from *ab initio* quantum mechanical calculations. In this process, special attention was paid to ensure that the model potentials are designed to correctly reproduce stable molecules in thermal equilibrium. In other words, the bond energy, bond length, and frequency of harmonic oscillation of each covalent bond were carefully fit to *ab initio* data. In addition, our model includes an algorithm to select the bond order of each covalent bond appropriately, so that the model can represent the dependence of the π -bond energy for C-C, C-O, O-O atoms on the configuration of surrounding atoms. The de-localized double bond, the coordinate bond in CO molecule, and the $+\pi$ effect by a F atom (an effect that F atoms weaken neighboring π -bonds) are also taken into account. In the model, all isolated atoms and atomic clusters are assumed to be charge neutral.

Van der Waals (VW) interactions are also included in the potential model. The VW interaction is typically given by a two-body potential function of Lennard-Jones type. In the present model, for the sake of simplicity, we use the same VW attractive potential function for all atomic pairs and its potential depth is about 10^{-2} eV. The repulsive part of the VW potential is not included since it is already in the covalent bond potential. The VW potential function is shown together with the C-C pair potential function in Fig. 1, where the VW potential energy is magnified by a factor of 10, so that the shapes of both covalent bond potential and VW potential can be seen in the figure.

To emulate surface reactions caused by energetic ion (atomic) impact, atomic-scale MD simulations are performed in a cell with a fixed boundary at the bottom of the cell and periodic boundaries in the horizontal directions. The substrate consists of atoms arranged in a specific manner and is brought to thermodynamical equilibrium with a given (usually the room) temperature. In our simulations presented here, the substrate surface area is about 2.1×2.1 nm² and its depth is kept sufficiently deep as the code automatically adds extra atomic monolayers to the substrate from the bottom in such a

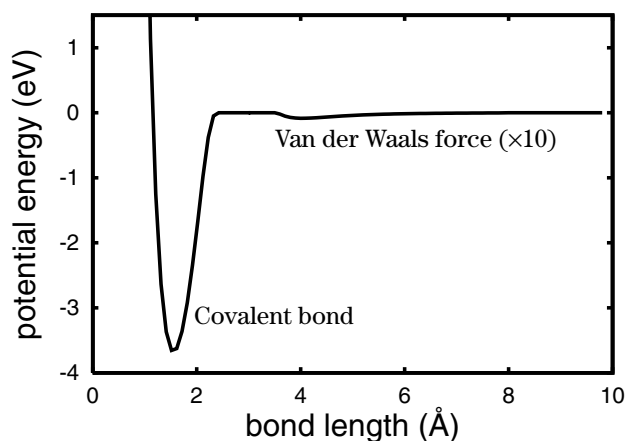


Fig. 1 Potential energy curve for the C-C bond including VW interaction. The VW potential energy is magnified by a factor of 10, so that it can be seen in this figure.

way that no atom will pass through the bottom layer during the simulation. The typical number of atoms employed to represent the substrate in our simulations is about two thousand. The pseudo β -cristobalite is used as the initial lattice of our SiO₂ substrate, where O atoms are inserted between Si atoms located at the diamond lattice sites.

Energetic atoms or clusters are directed normally to the substrate surface and the trajectory of each atom is traced numerically based on Newton's equation of motion. Each impact by energetic atom or a cluster is considered as an independent event. In a single event of impact, atomic motions are calculated under the constant energy conditions for 0.4 ps. Almost all reactions such as breaking and reformation of bonds by energetic impact take place during this period. After then an artificial temperature control (Berendsen thermostat [5]) is imposed on atoms constituting the surface (except for atoms bound with the surface weakly through VW interactions) during the next 0.1 ps, which represent energy dissipation from the surface. At the end of the cycle, the surface temperature is set to the initial surface temperature, *i.e.*, 300 K. Atoms that leave the substrate surface with a momentum in the upward direction are automatically detected and removed from the simulation cell.

3. Simulation results

First we performed MD simulation by using the potential model of covalent bonds only. As shown in Fig. 2 (a), no stable deposition was observed without VW interactions. In these simulations, atomic clusters, especially those containing many carbon atoms, are created and most of them end up leaving the surface even with extremely small upward momenta if they are not bound with the substrate through

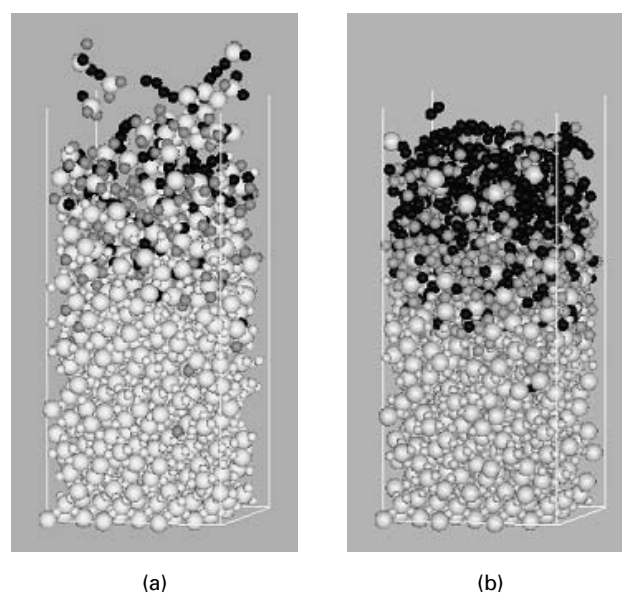


Fig. 2 Typical surface conditions during 100 eV CF beam impact: (a) without and (b) with VW interactions. Large white, small white, gray, and black spheres represent Si, O, F, and C atoms, respectively.

covalent bonds. As a result, carbon atoms remain in the substrate only sparsely. Under these conditions, etching reactions take place, which does not agree with experimental observations of beam etching performed under similar conditions. [6]

Second we introduced VW interactions in our simulations in addition to the covalent bonds. With VW interactions, deposition was observed, as shown in Fig. 2 (b). This agrees with observations in beam experiments [6]. For an atom located near or in the substrate, its total VW interaction energy is of order of 10^{-1} eV due to its relatively long interaction range (in which there are dozens of interacting atoms) although the pair-wise VW potential energy is only about 10^{-2} eV. The VW potential energy per atoms is, however, still lower by a factor of 10 than the corresponding covalent-bond potential energy.

Nevertheless VW interactions significantly increase the chance to trap unbound atoms and clusters. In order to confirm that the long-range nature of the VW interaction, rather than the potential depth of it, causes deposition, we also performed simulations using 10 % stronger covalent forces without VW interactions. We have found no deposition takes place under such conditions.

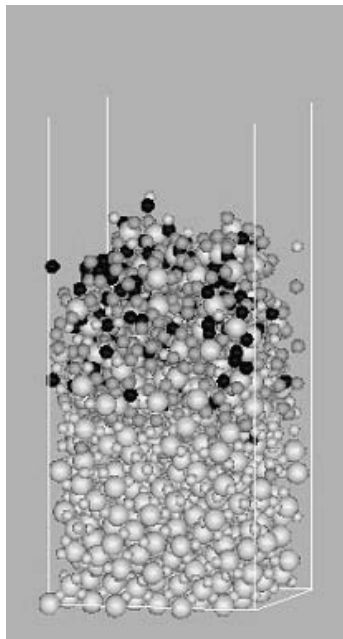


Fig. 3 Typical surface during 300 eV CF₂ beam impact. Big white, small white, gray, and black spheres are Si, O, F, and C atoms, respectively.

Under the conditions given in Fig. 2 (b) (*i.e.*, CF 100 eV), a relatively rich carbon layer is formed. Carbon atoms accumulate gradually as the ions bombard the surface. Under these conditions, sputtering also occurs and the C deposition rate measured in simulations is about 0.7. The main etch products are F and C atoms. When deposition occurs, we have observed that the distribution of F atoms has a peak near the interface between the carbon layer and SiO₂ substrate, which seems consistent with experimental observations [7]. On the other hand, for the 300 eV CF₂ beam, as shown in Fig. 3, a carbon layer is not formed and C atoms remain in the substrate only sparsely. In this case, steady etching was observed. The number of deposited C atoms is saturated at about 3×10^{15} (atoms/cm²). The main etching products in this case are F, CO, C, O, CF, SiF₂, SiF₃, and SiF₄. This is also in agreement with experimental results [6].

In summary, our new potential model for Si/O/F/C systems enables us to perform MD simulations of surface reactions under energetic bombardment by atoms and clusters. In particular, we have observed that deposition processes can be caused by VW interactions. Our simulation results are overall consistent with experimental observations.

Acknowledgements

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