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Quantum Chemical Molecular Dynamics Simulation on the Plasma Etching Processes

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1. Introduction

Plasma-etching is one of the most important processes for atomic-scale fabrication of silicon devices. Diminishment of the microelectronic devices in the modern integrated circuits requires atomic-scale control of the semiconductor manufacturing processes. Detailed understanding of the surface chemical reaction dynamics during the plasma-etching process can facilitate the development of such atomic-scale control techniques. However, the surface chemical reaction in the plasma processes cannot be measured experimentally because the dynamic behaviors of various ions and radicals produced in the plasma process are significantly complicated. Hence, the analysis of the plasma etching processes by computer simulation has been expected to play an important role for the advancement of the plasma technologies.

Among a lot of simulation methods, classical molecular dynamics approach has been used to study the surface chemical reaction dynamics in the various processes. However, this method employs empirical inter-atomic potentials and hence it cannot be applied to the unknown system and cannot predict new phenomena. Moreover, it cannot consider the electron transfer during the chemical reactions and hence it cannot accurately simulate the chemical reaction dynamics. In contrast, first-principles molecular dynamics simulation can consider the electronic states of the system and simulate the chemical reaction dynamics accurately, however it requests huge computational costs and can be applied to very small system. Therefore, it cannot be applied to the plasma etching process, which requires a large simulation model.

Hence, recently we have succeeded in the development of an accelerated quantum chemical molecular dynamics program "Colors", based on our original tight-binding theory [1,2]. This program is more than 5,000 times faster than the regular first-principles molecular dynamics approach. Hence, this program enables us to simulate the chemical reaction dynamics considering the electronic states on the large simulation model. Hence, in the present study we applied the above new simulation software to the investigation of the various plasma etching

processes on the SiO₂ surface.

2. Calculation Method

Our accelerated quantum chemical molecular dynamics program "Colors" is employed to simulate various plasma etching processes on the SiO₂ surface. In these simulations, some energetic particles are bombarded to the SiO₂ surface in order to model the etching process.

This program employs some parameters in order to accelerate the quantum chemical molecular dynamics simulations. If these parameters are determined as to fit the experimental results empirically, this program cannot be applied to the unknown system. Hence, we developed a new methodology to determine all the parameters as to fit the first-principles calculation results. This methodology enables us to perform fast and accurate quantum chemical molecular dynamics simulations.

3. Results and Discussion

α -cristobalite(100) surface was used as a SiO₂ substrate and their dangling bonds were terminated by hydroxyl groups. The simulations were performed at 300 K with a time step of 0.1×10^{-15} s. Here, we presented some examples of the etching simulations. CF₂ radical was used as an energetic molecule and was bombarded to the SiO₂ substrate with high kinetic energies of 5 eV and 10 eV. Fig.1 shows the snapshots of the molecular dynamics simulations on the plasma etching processes, when the CF₂ radicals with a high kinetic energy of 5 eV and 10 eV were bombarded to the SiO₂ substrate. In this figure, large circles indicate the incident CF₂ radical. C atoms are expressed by the lighter color, while F atoms are expressed by the darker color. Small circles indicate the substrate atoms. Si atoms are expressed by the lighter color, while O atoms are expressed by the darker color. The smallest circles indicate H atoms.

The incident CF₂ radical with 5 eV energy was reflected by the SiO₂ substrate without the change of the SiO₂ surface structure. On the other hand, the incident CF₂ radical with 10 eV energy intruded into the SiO₂ substrate and the chemical reactions were observed. These results indicate that the high incident

energy lead to the intrusion of the incident radical into the SiO_2 substrate and some chemical reactions.

We analyzed the atomic bond population on some Si and O atoms, obtained by the Mulliken analysis, in order to clarify the bond-breaking and bond-formation process during the chemical reactions, when the incident CF_2 radical with 10 eV energy was bombarded to the SiO_2 substrate. Fig. 2 (a) shows the bond population of one O atom in the SiO_2 substrate. This result indicates that the bombardment of the CF_2 radical led to the Si-O bond-breaking and C-O bond-formation. Fig. 2 (b) shows the bond population of one Si atom in the SiO_2 substrate. This result indicates that the bombardment of the CF_2 radical led to the Si-O bond-breaking and Si-F bond-formation. These results are in good agreement with the experimental observations. Experimentally, the formation of the volatile molecules such as SiF_4 and CO was observed during the SiO_2 etching processes

by the fluorocarbon plasma. It indicates that our new simulation software is very effective tool to simulate the chemical reaction dynamics during the plasma etching process.

The above bond-breaking and bond-formation processes caused by the electron transfer can not be accurately clarified by the classical molecular dynamics approach. Hence, we confirmed that only our accelerated quantum chemical molecular dynamics program can clarify the chemical reaction dynamics during the plasma etching processes.

References

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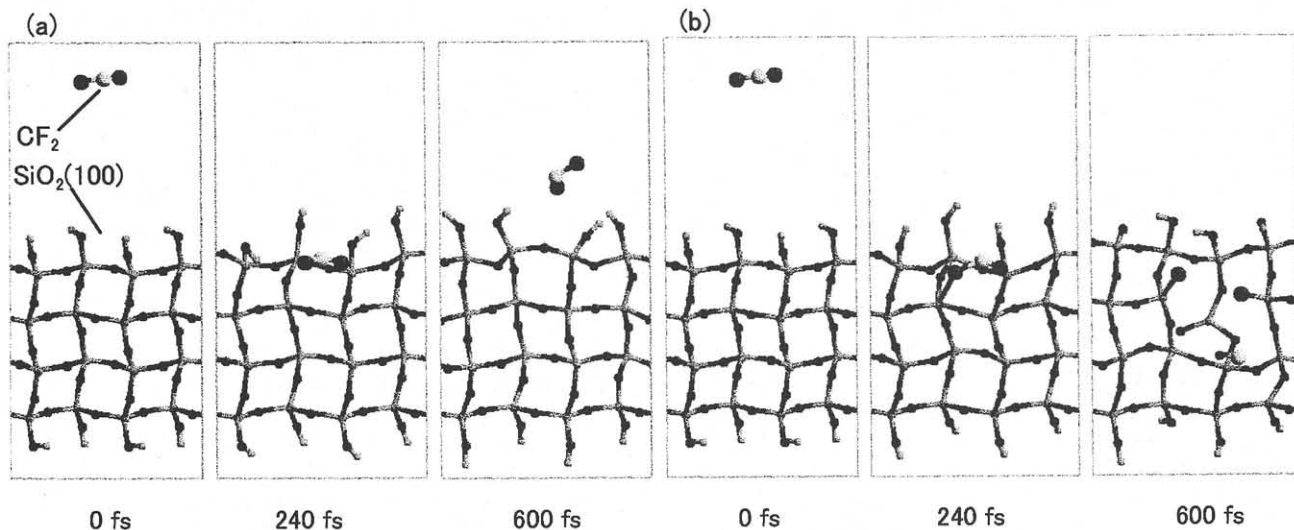


Fig. 1 Dynamic behaviors of the plasma etching process of SiO_2 surface by CF_2 radical
– (a) incident energy of 5 eV and (b) incident energy of 10 eV

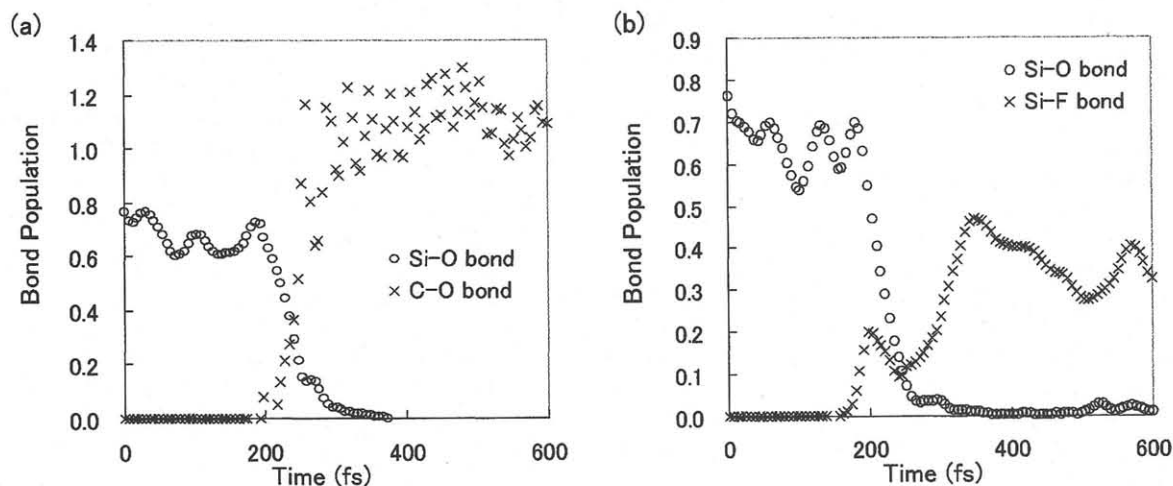


Fig.2 Change in the bond population of O and Si atoms during the plasma etching process by CF_2 radical
– Bond Population of (a) One O atom in the SiO_2 substrate and (b) One Si atom in the SiO_2 substrate