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# Molecular Dynamics Study of Oxidation Process with SiO emission and incorporation into the $Si/SiO_2$ System

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## 1. Introduction

The oxidation process in the $Si/SiO_2$ interface is very important in fabrication of semiconductor devices and as a reference in basic researches of various oxidations. As the oxidation proceeds, stress is accumulated in the $Si/SiO_2$ interface region due to the expansion of the volume per Si atom in the $SiO_2$. This stress should be released in order to advance further oxidation. Several mechanisms of releasing the stress have been suggested such as emission of Si into substrate as self-interstitials [1] and into $SiO_2$ region to be absorbed there [1-3]. Emission of SiO from the interface and its incorporation into $SiO_2$ region have been also suggested [4]. For detailed discussion of the stress releasing mechanisms, atomic level simulations with dynamical effect are required. However, few studies have been done with taking account of dynamics of the stress relaxation [5] due to difficulty in considering the effect of charge transfer.

In this study, we focus on the SiO emission in the $Si/SiO_2$ interface region [6] and the following SiO incorporation into the $SiO_2$ network. Classical molecular dynamics (MD) simulations with variable charge interatomic potentials [7] have been performed to investigate the stress relaxation during the oxidation process.

## 2. Calculation method

Classical MD methods with fixed charge have difficulty in describing the oxidation process accompanied by atomic diffusion between the Si and the $SiO_2$ regions. In the bulk Si, a Si-Si bond is covalent. While in the $SiO_2$, a Si-O bond has both covalency and ionicity because of difference in electronegativity between Si and O. These effects can be included by first-principles method, which is, however, very time-consuming for large-time-scale dynamics calculations.

Kumagai et al. [8] have developed a variable charge interatomic potential for $Si/SiO_2$ systems, which can describe covalent-ionic mixed bond nature by adding the electrostatic and charge transfer terms to the Tersoff type bondorder potential function [9]. In this study, we use this approach for the $Si/SiO_2$ system.

## 3. Results and Discussions

*SiO emission in the $Si/SiO_2$ interface* :

To investigate the oxidation process in the $Si/SiO_2$ interface region, we prepared the crystal $SiO_2$ (tridymite type) on Si(100) with a (4x4) surface-unit-cell containing 448 atoms as the initial structure [10]. In order to advance further oxidation process in the interface region, we introduced two O atoms (O(1) and O(2)) in the Si-Si bridging sites and eight O atoms in the Si-Si bond center sites (indicated by arrows in Fig.1(a)) and performed the MD simulation under constant NTP conditions (N=458, T=25°C, P=1atm) (Fig.1(a)).

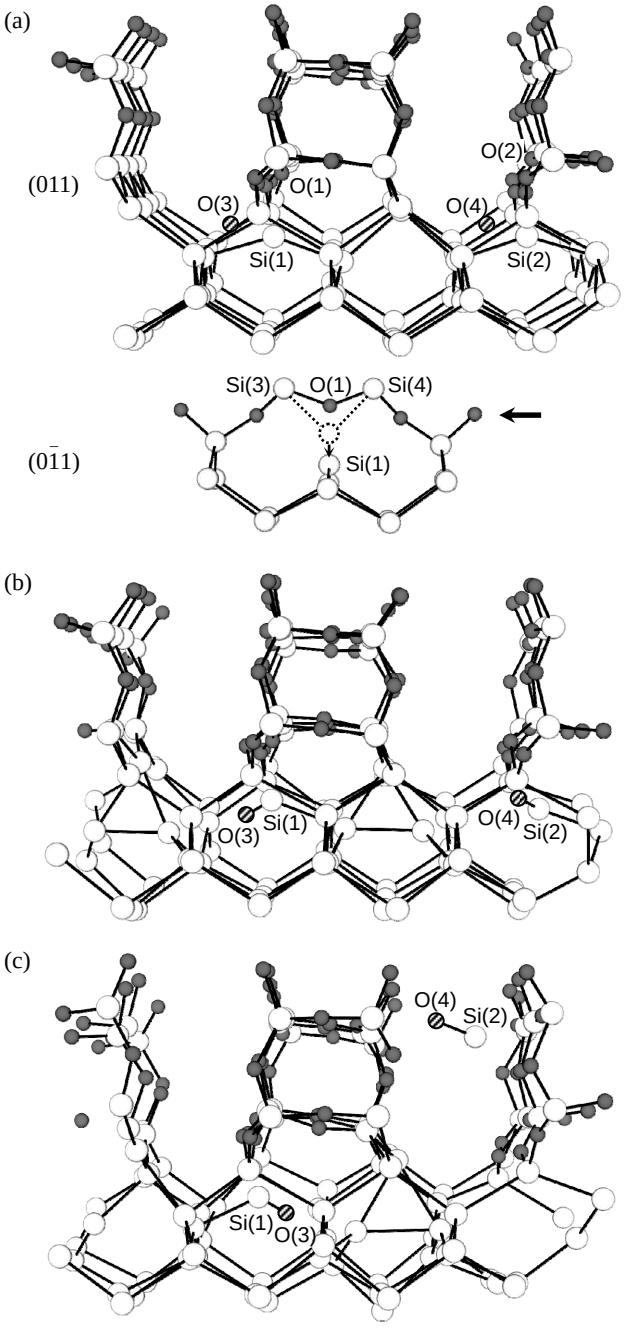


Fig.1 (a) Snapshot of Si/SiO2 after two Si atoms (Si1 and Si2) became two-folded. Cross sections cut by both (011) and (0$\bar{1}$1) planes are shown. (b) Snapshot at 1.4 ps. (c) Snapshot at 31 ps. Open and closed circles denote Si and O atoms, respectively.

In Fig.1(a), each of Si(1) and Si(2) has only two Si-Si bonds because other two Si-Si bonds have been broken to make new Si-O bonds (Si(3)-O(1) and Si(4)-O(1)). Then, we introduced other two O atoms (O(3) and O(4)) in the vicinity of these two-folded Si atoms and performed the MD simulations under constant NTP conditions (N=460, T=1800°C, P=1atm).

The snapshot at 1.4 ps is shown in Fig.1(b). It is noted that one of the two Si-Si bonds of the two-folded Si atoms has been broken and an Si-O bond has been made by this step (Si(1)-O(3) and Si(2)-O(4)). During this process, Si trimers were made in the interface region, which was predicted by first-principles calculations [11]. After 28 ps, a SiO molecule (Si(2)-O(4)) was emitted to the $SiO_2$ region to release the stress accumulated in the interface (Fig.1(c)).

*SiO incorporation into the $SiO_2$ network* :

A SiO molecule emitted from the $Si/SiO_2$ interface region diffuses interstitially in the $SiO_2$ network. If the SiO molecule is incorporated into the $SiO_2$ network during the diffusion, growth of the $SiO_2$ advances. We, then, investigated the mechanism of the SiO molecule incorporation into the $SiO_2$ network. In this study, we consider a stoichiometrically perfect $SiO_2$ unit cell containing 432 network atoms and one SiO molecule and one oxygen atom in interstitial sites. MD simulations are performed under constant NTP conditions (N=435, T=1400°C, P=1atm).

Schematic views of the SiO molecule incorporation into the $SiO_2$ network are shown in Fig.2. In the first step, a Si-O bond (Si(1)-O(1)) of the $SiO_2$ network is broken due to charge transfer from the diffusing SiO molecule (Fig.2(a)). In the second step, the SiO molecule is inserted to be bonded with the Si(1) and O(1) atoms (Fig.2(b)). The Si(3) atom of the SiO molecule is two-folded in this configuration. In the third step, another Si-O bond (Si(2)-O(2)) is broken and the O(2) atom is rebonded with the Si(3) atom (Fig.2(c)). The SiO molecule has almost been incorporated into the $SiO_2$ network by this step, though the Si(2) and Si(3) atoms are three-folded and there is an oxygen vacancy site. In the final step, the SiO molecule will completely be incorporated into the $SiO_2$ network after oxygen vacancy diffusion (Fig.2(d)).

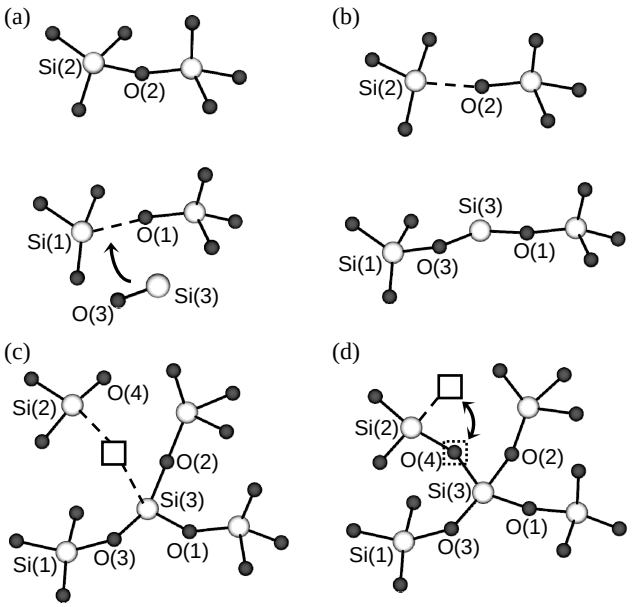


Fig.2 Schematic views of the SiO molecule incorporation into the $SiO_2$ network. (a) 5 ps, (b) 10 ps, (c) 11 ps, and (d) predicted complete incorporation after oxygen vacancy diffusion. An open square denotes the oxygen vacancy site.

Another simulation (constant NTP condition of N=431, T=1400°C, P=1atm) has revealed that this oxygen vacancy diffusion occurs in the $SiO_2$ network (Fig.3). An oxygen atom has diffused into a neighboring oxygen vacancy site between three-folded Si atoms, i.e., the oxygen vacancy has diffused into the neighboring site between two Si atoms.

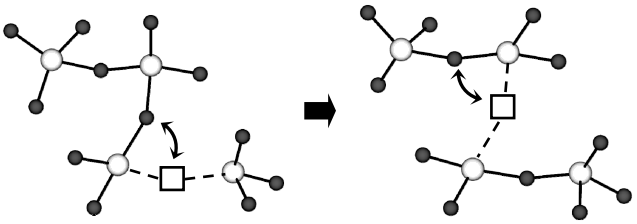

Fig.3 Oxygen vacancy diffusion in the $SiO_2$ network.

**4. Summary**

We investigated the dynamics of oxidation with stress relaxation in the $Si/SiO_2$ interface by using variable charge MD methods. The results are as follows:

(1) As the oxidation proceeds, stress is accumulated in the $Si/SiO_2$ interface. In order to release this stress, a SiO molecule formed in the interface is emitted into the $SiO_2$ region.

(2) The emitted SiO molecule is inserted between network Si and O due to charge transfer and is almost incorporated into the $SiO_2$ network through rebonding processes.

(3) The SiO molecule is completely incorporated into the $SiO_2$ network after oxygen vacancy diffusion.

We have shown that our variable charge MD approach has a great advantage for studying the dynamics of oxidation and stress relaxation of $Si/SiO_2$ interface.

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