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First-Principles Study on Hydrogen Annealing Effect in Si/SiO_2 Interface by Thermal Oxidation

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Abstract

Why is high-quality Si/SiO_2 interface readily fabricated by simple thermal oxidation? Even though the question is closely related to the great success of silicon technology, the answer has not yet been clarified at the atomic level. In this study, we investigated hydrogen annealing effect in thermally-oxidized Si/SiO_2 interface by the first-principles calculation method to reply the question. According to the Si-emission model of thermal oxidation, Si atoms are spontaneously emitted from the interface, leading to the lattice distortion and dangling bonds at the vacancies. We clarified that the interface states originating from the dangling bonds can be passivated by hydrogen terminations of Si atoms with dangling bonds. This means that the interface-state density can be decreased by hydrogen annealing after thermal oxidation. Our results rationalize the reason why the quality of Si/SiO_2 interface formed by thermal oxidation is higher than that by the other technique such as CVD.

1. Introduction

It's not too much to say that the great success of silicon technology came from the fact that high-quality Si/SiO_2 interface can be readily fabricated by simple thermal oxidation. In general, there exist a lot of defect states at the interface. However, the density of interface states in Si/SiO_2 interface formed by thermal oxidation can be reduced to 10^{10} ($cm^{-2}\cdot eV^{-1}$) by hydrogen annealing [1]. On the other hand, it is well-know that the interface-state density *cannot* be reduced by the other oxidation technique even if hydrogen annealing is done as post-processing. Why does hydrogen annealing after thermal oxidation lead to the high-quality interface? The microscopic picture remains unclear at the atomic level. In this study, hydrogen annealing effect in thermally-oxidized Si/SiO_2 interface was investigated by the first-principles calculations.

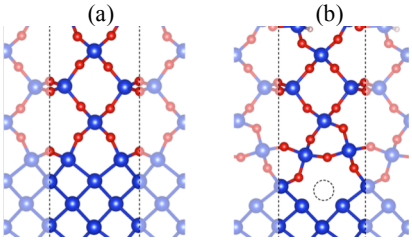

Fig. 1 Slab models of Si/SiO_2 interface (a) without and (b) with a Si vacancy. The larger, medium and the smaller balls are Si, O and H atoms, respectively. The dotted lines indicate the periodic boundary.

2. Methods and Models

In this study, we utilized VASP (Vienna Ab simulation package) code based on the density functional theory [2-4]. The cutoff energy of plane-wave basis set was 500eV and ***k*** points were sampled with a 6×5×1 Monkhorst-Pack grid. VESTA was used to draw atomic configurations and electronic states [5].

We employed the repeated slab models of thermally-oxidized Si/SiO_2 interface to investigate the microscopic picture of hydrogen annealing after thermal oxidation, as shown in Fig. 1. The vacuum thickness (distance between the slabs) was 7Å, and Si atoms at the slab edge were terminated with hydrogen atoms. All atoms except for the edge Si atoms have been relaxed until the Hellmann-Feynman force becomes smaller than 50 meV/Å.

3. Results and Discussions

We revisit the pioneering work on Si thermal oxidation by Kageshima and Shiraishi [6] in order to identify the origin of interface states in thermally-oxidized Si/SiO_2 interface. According to their work, a Si atom is spontaneously emitted from the stable interface without defects once three oxygen atoms come into the interface, and dangling bonds appear at the Si vacancy. Inserting additional three O atoms into the resultant interface, the structure becomes the stable interface again. In general, thermal oxidation is expected not always to be terminated by the stable interface without Si vacancies. Accordingly, we assumed that the interface states mainly come from a Si vacancy at the interface appearing in the middle of the oxidation process.

Figure 1(a) and (b) are the stable interface and the interface with a Si vacancy appearing in the middle of thermal oxidation process, respectively. The corresponding electronic-band structures are given in Fig. 2(a) and (b). Figure 3 shows electronic-density distributions of the interface state appearing in Fig. 2(b). As you can see from Fig. 2(a), the stable interface given in Fig. 1(a) has a weak-

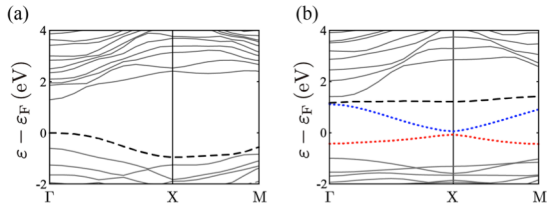

Fig. 2 The electronic-band structures corresponding to Fig. 1(a) and (b), respectively. The broken line in (a) and (b) is the weakly-bounded interface state, and the dotted lines in (b) are the dangling-bond states inherent in the interface with a Si vacancy.

ly-bounded interface state. On the other hand, the interface with a Si vacancy given in Fig. 1(b) possesses two interface states originating from dangling bonds in addition to a weakly-bounded interface state (not shown here), as shown in Fig. 3. The weakly-bounded interface state cannot be removed because it is inherent in the interface. However, the interface state derived from the dangling bonds could be passivated by a termination.

Next, we considered the termination by hydrogen atoms because there would be many H_2 molecules in the interface due to hydrogen annealing. A H_2 molecule is dissociated into two H atoms and each H atom is adsorbed to a Si atom with a dangling bond. It was observed from Fig. 4 that two dangling-bond states disappear but the weakly-bounded interface state remains. The H-terminated interface was 1.31eV more stable than the interface with a Si vacancy in Fig. 1(b). This indicates that the dangling bonds in Fig. 1(b) can be steadily terminated by H atoms if H_2 molecules come into the interface.

Finally, we verified whether H_2 molecules can come into the interface and terminates the dangling bonds. To do this, we used the statistical-mechanical approach by Kangawa et al. [7], in which the formation energy at finite temperature $E_{ad}(p,T)$ was defined by Gibbs free energy. The behavior of $E_{ad}(p,T)$ with respect to hydrogen pressure and temperature is shown by the broken curve in Fig. 5, which means that the dangling-bond states can/cannot be terminated if a condition (p,T) is the lower/upper region. One of the typical fabrication conditions, (0.1atm, 400°C), is depicted by the solid circle. We found from Fig. 5 that the dangling-bond states can be terminated under the typical condition (0.1atm, 400°C).

4. Conclusion

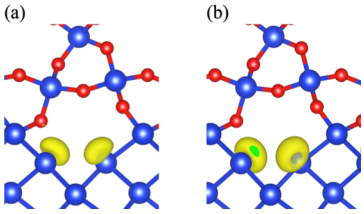

Fig. 3 Electron-density distributions of the dangling-bond states in Fig. 2(b).

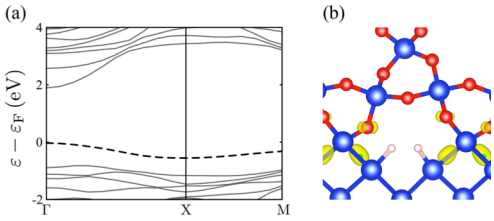

Fig. 4 Electron-band structure of the interface with H termination and the electron-density distribution of the interface state. The state depicted by the broken line is the weakly-bounded interface state.

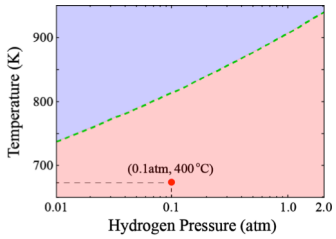

Fig. 5 $p-T$ diagram on hydrogen termination. For the condition in the upper region, hydrogen molecules cannot approach to the interface. On the other hand, for the condition in the lower region, the dangling bond can be terminated by H atoms.

We clarified from the atomic level that hydrogen annealing significantly reduce the interface states formed by thermal oxidation, leading to high quality Si/SiO_2 interface.

Our simulations are based on Si-emission model in thermal oxidation. The oxidation process is step by step and the primary interface defect is the dangling-bond state, as we clarified in this work. Therefore, the size of interface defects by the model would be relatively small. On the other hand, an oxidation process by the other oxidation technique such as CVD is completely different from the Si-emission model and the defect size is expected to be inhomogeneous. Consequently, the quality of Si/SiO_2 interface formed by the other technique is *not* improved compared with thermal oxidation even if hydrogen annealing is done.

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