

## Atomistic Simulation of Si Oxidation

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### 1. Introduction

Since the advent of silicon device technologies, the scaling-down of device sizes has proceeded to within ready of atomic scale lengths. Consequently, it is necessary in some cases to reconsider device fabrication processes in the light of an understanding atomic scale phenomena. Since gate insulating films have been made thinner to such an extent that they are approaching nanometer thickness, a fabrication process for the thin insulating films can be one of good candidates for those considerations among others [1]. We have been conducting theoretical analyses of Si oxidation to understand the mechanism of the early stages of oxygen molecule chemisorption and Si-O bond network formation [2]. Those theoretical analyses require atomic-scale simulations, including electronic structure calculations. We have been, therefore, concentrating on the theoretical study to deal with this problem and to find some new principles inherent in oxidation processes. Then, by applying some of our calculated results, the findings have led to a new idea for the realization of atomically more uniform Si oxidation processes [3].

### 2. Calculations and Methods

It is well known that the ground state of an oxygen molecule is a spin-triplet state. The first and second row elements in the periodic table require a more rigorous theory that goes beyond the local density approximation (LDA) [4]. Calculations have been, therefore, performed with a generalized gradient approximation including spin polarization (SPGGA) [5]. In particular, an oxygen molecule has to undergo dissociation processes upon chemisorption before forming a Si-O bond network. Oxygen molecules are first put above the Si surfaces as shown in Fig. 1. Then, they are moved toward the Si surfaces by the forces acting on each atom in order to find basic atomic reaction processes and electronic structure changes upon chemisorption [6]. The careful analyses of these reaction processes and the deepening the knowledge about Si oxidation provide some clues to a new physics underlying Si oxidation [2], which leads directly to some new

ideas for new Si oxidation processes

### 3. Results and Analyses

#### (1) Spin-conversion in chemisorption

As an oxygen molecule is moved first with conserving the initial spin-triplet state, the oxygen molecule shows a weak adsorption on the Si(100) surface with maximum adsorption energy of 0.39 eV, but shows no sign of bond-elongation or further more of dissociation. This indicates that the oxygen molecule cannot be dissociatively chemisorbed on the Si surface in so far as the initial spin-state is maintained and that oxygen chemisorption can only be caused by changing its spin state. Those considerations lead to the idea that the spin-flip transition can be initiated through a spin-orbit interaction because of no magnetic field in actual cases. This very weak perturbation, however, only works when the duration time of a molecular collision with Si surfaces is sufficiently long [7], implying that the chemical reaction probability is in itself small as compared with reactions on ordinary metallic surfaces and that it can be well controlled by regulating the incident energy of an oxygen molecule. No activation energy is needed for the first layer oxidation, as will be shown later, but the reaction rate is very small. This spin-state dependent small reaction rate features the molecular oxygen reactions on the clean Si surfaces.

#### (2) Layer-changing energy barrier

As the spin-state is treated as one of the degrees of freedom, we found that chemisorption on the topmost layer occurs with no energy barrier in cases (b) and (c) as shown in Fig. 2. The molecule is totally dissociated in the case (b) while the oxygen molecular bond is almost broken in the case (c). For cases from (d) to (e)' (Fig. 2) corresponding to direct chemisorption to sub-surface layers, they cost energy barriers of 0.29 to 1.08 eV. The chemisorbed structures in the cases (b) and (c) in Fig. 2 are not, however, the final configurations for the dissociative chemisorption processes in this reaction scenario, as was implied in the experiment [3]. Figure 3 shows the calculated migration process for the case (b) after the chemisorption. The dissociative chemisorption of an oxygen molecule generates an energy gain of 5.99 eV because of electronic orbital rehybridization between O and Si atoms. An energy barrier of 1.27 eV and another small barrier of 0.50 eV appearing later on a midway in the migration process can be overcome by the initial kinetic energy gain of almost 3 eV by the dissociated O atom after the initial dissociative chemisorption. Thus, both dissociated O atoms can migrate deeper into a back-bond center with almost the same manner as in the cases (b) and (c). If another oxygen molecule comes in between two parallel dimers or on a dimer, the same process can occur and the dissociated O atoms finally occupy the rest of the unoxidized back-bonds or dimer-bonds. Those processes occur without any activation energy. Hence, the first sub-surface layers are fully oxidized from the topmost layer with low oxygen gas pressures even at low temperatures. For

the case of direct oxidation to the second sub-surface oxidation as shown in Fig. 1(f) and 2(f) the reaction costs surprisingly a high energy barrier of 2.4 eV.

### (3) Application to oxidation process

As we look back our calculated results on the dissociative chemisorption of an oxygen molecule from the topmost first layer to the second sub-surface layer, we can say that the activation energy for the reaction increases layer-by-layer from the topmost layer to deeper sub-surface layers with 0 eV to 2.4 eV. Since the first sub-surface layer oxidation occurs at low oxygen gas pressures and low temperatures, the oxidation processes can be saturated at each sub-surface layer with appropriate low oxygen gas pressures and low temperatures. The most advantageous usage of the activation energy difference among each sub-surface layer is to select appropriate lowest oxygen gas pressures and lowest temperature conditions for each sub-surface layer oxidation, leading to the step-by-step partial gas pressure or temperature increase. Then, the oxidation thickness can be controlled with an atomic layer accuracy from the very beginning of oxidation. In fact, the layer-by-layer oxidation is found to occur as we have expected from our calculated results [3,8].

### 4. Summary

We have presented theoretical simulations for the early stage of oxidation on Si(100) surfaces. Although the usage of these theoretical simulations is still limited to a small-size system and to a small time period even in the case of using the latest supercomputer technology. The calculated results, however, can open up a new physics underlying atomic scale phenomena and provide a new guideline for designing far more integrated silicon processes.

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### References

- [1]T. Engl, Surf. Sci. Rep. 18, 91(1993).
- [2]K. Kato, T. Uda, and K. Terakura, Phys. Rev. Lett. 80, 2000(1998).
- [3]H. Watanabe, K. Kato, T. Uda, K. Fujita, M. Ichikawa, T. Kawamura, and K. Terakura, Phys. Rev. Lett. 80, 345(1998).
- [4]P. A. Serena, A. Baratoff, and J. M. Soler, Phys. Rev. B 48, 2046(1993).
- [5]J. P. Perdew, in Electronic Structures of Solids '91(Akademie Verlag, Berlin); J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244(1992).
- [6]K. Kato, Phys. Rev. B 54, 2210(1996).
- [7]M. S. Child, Molec. Phys. 28, 495(1974).
- [8]N. Miyata, H. Watanabe, and M. Ichikawa, Phys. Rev. B 58, 13670(1998).

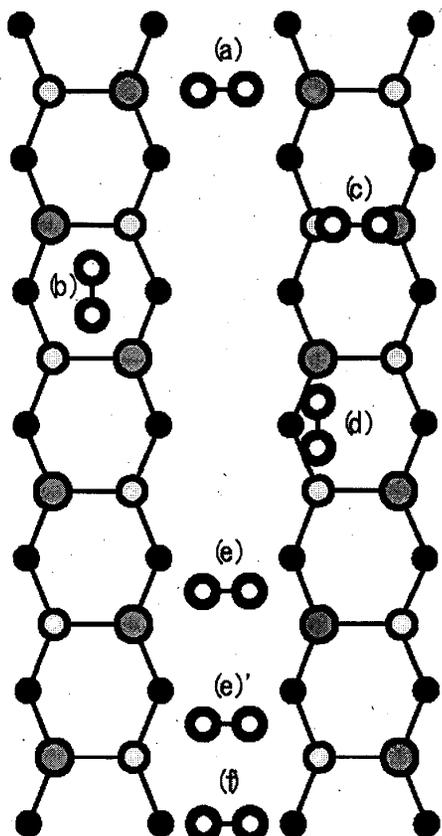


Fig. 1. Initial O molecule configurations on Si(100) surface

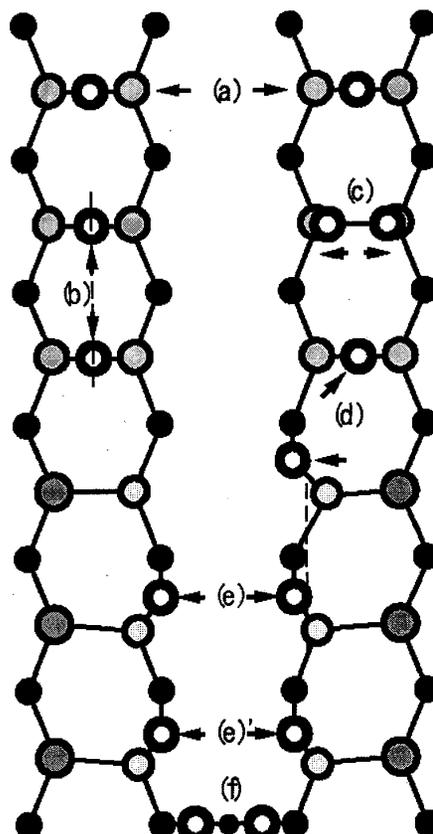


Fig. 2. Final O atom configurations on Si(100) surface

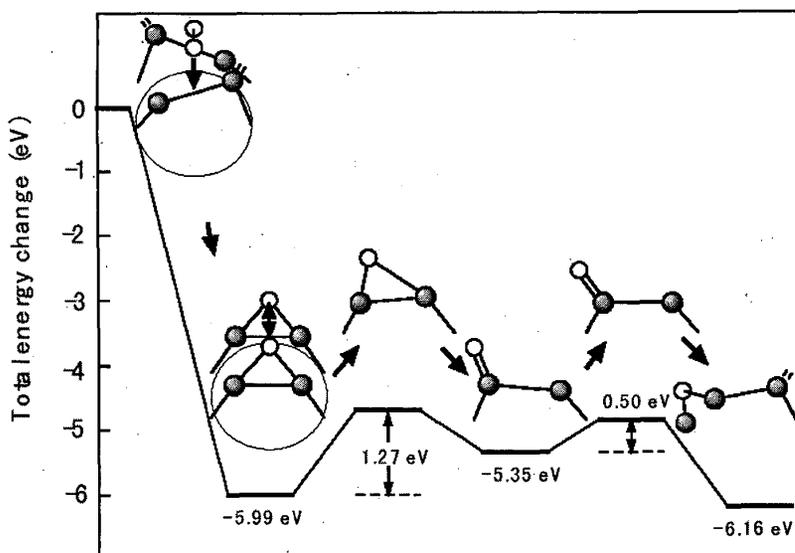


Fig. 3. Energy and geometry changes when an oxygen molecule is dissociatively chemisorbed and the oxygen atom migrates into a back-bond.