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Adsorption States of an Oxygen Molecule on Si(001) Surfaces

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Abstract

We investigated adsorption state of an oxygen molecule on Si(001) surfaces using first principles calculation. Evaluating adsorption energies of several models, we found that an oxygen molecule could adsorb on an oxidized Si atom without breaking the O-O bond, i.e. a molecularly chemisorbed oxygen. This result explains well the recent experimental report.

1. Introduction

Fabrication of Si based field effect transistor devices are approaching its fundamental limits. In this situation, the fabrication of the devices needs atomically controlled interface between Si and its oxide. Therefore, it is important to understand the oxidation process on Si surfaces in more detail.

In general, molecular oxygens have been recognized as the precursor for oxidation process and thought to be dissociatively adsorbed onto Si(001) surfaces. Namely, it has been considered that there is no molecular oxygen on Si(001) surface during oxidation. Recently, Yoshigoe et. al. observed XPS spectra that suggests the presence of a molecular oxygen on Si (001) surfaces during oxidation process [1]. Figure 1 shows several adsorption structure models suggested in the paper. "*ins*" represents a structure in which an O adatom is inserted between Si-Si bond. There are two possible structures of oxygen molecule adsorbed on a top-layer Si atom, *paul* and *grif* (see Fig. 2). In the former, one O atom of a molecule is bonded to a surface Si atom, while in the latter, both O atoms are bonded to a surface Si atom. In both structures, the O-O bond is kept, as shown in the figure.

Among these models, Yoshigoe concluded that the most plausible structure for the adsorbed molecular oxygen is the *ins*×2-*paul* structure based on the experimental data for the oxidation states of Si and the surface coverage of O. In the very initial oxidation stage, the molecular oxygen is known to adsorb dissociatively [2]. Then, molecularly adsorbed oxygen is considered to exist only with the existence of oxidized Si atoms. However, detailed adsorption states have not been cleared yet. Especially, it is difficult with experimental results to distinguish the *paul* and *grif* structures [3]. The purpose of this study is to investigate adsorption states of the oxygen molecule on Si(001) surfaces using first principles calculation based on the density functional theory.

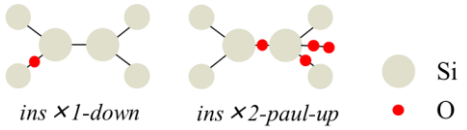

Fig. 1 Possible oxide structures during room-temperature oxidation of Si(001) surface (top view)

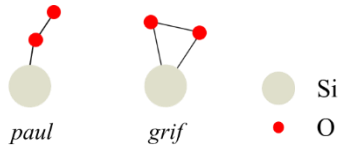

Fig. 2 Side view of the *paul* and the *grif* structures

2. Theory and calculation model

To investigate the adsorption states of oxygen molecules, we adopt a five-layer 4×4 Si(001) slab model for substrate. Then, we construct several oxidation models and calculate adsorption energy of a molecular oxygen by comparing *ins*×*n* with *ins*×*n*-*paul(grif)* (n = 1, 2, 3). The adsorption energy of a molecular oxygen E_{ad} is calculated by the following equation.

$$E_{ad} = E_{ins\times n\text{-}paul(grif)} - E_{ins\times n} - E_{O_2}\,, \qquad (1)$$

where, $E_{ins\times n\text{-}paul(grif)}$ is the total energy of *ins*×*n*-*paul(grif)* structure and $E_{ins\times n}$ is the total energy of *ins*×*n* structure, and E_{O_2} is the total energy of an oxygen molecule in a vacuum. By this definition, negative E_{ad} indicates that such adsorption would be realized. On the contrary, positive E_{ad} indicates that such adsorption is unlikely to cause thermodynamically.

To calculate total energies and evaluate adsorption state theoretically, we used the PHASE/0 code, which is a package program for performing first-principles calculation based on the density functional

theory (DFT) [4, 5]. The generalized gradient approximation was used as the exchange-correlation term [6]. The cutoff energies for the wavefunction and for charge density were 25 and 225 Ry, respectively. The spin polarization is considered.

3. Results and discussions

Table I shows calculated values of E_{ad} for *ins×n-paul* structures. We will discuss about calculated values of E_{ad} for *ins×n-grif* structures in the presentation. Here, up (down) means an upper (lower) dimer Si atom as an O_2 adsorption site.

Table I Calculated values of E_{ad} (in eV)

Adsorption Structure	*up*	*down*
ins×1-paul	-1.88	-1.49
ins×2-paul	-2.42	-2.17
ins×3-paul	-2.64	-2.52

All adsorption structures have negative E_{ad}. These results indicate that all constructed structures are preferable for adsorption. We find that the most stable adsorption state of a molecular oxygen is the *ins*×3-*paul-up* with E_{ad} = -2.69 eV. This result is different from the expectation by experiments that *ins×2-paul* is the most stable structure.

Figure 3 illustrates the optimized structure of *ins×3-paul-up*. The distance between molecular oxygen atoms is 1.41 Å. Figure 4 illustrates the optimized structure of *ins×2-paul-up*, which is expected as the most plausible structure from the experiment. The distance between molecular oxygen atoms is 1.40 Å. These bond lengths are larger than the calculated one for an oxygen molecule in a vacuum (1.24 Å). This change in the bond length originates from the partial breaking of the double bond of an oxygen molecule and the charge transfer from the Si atom into the oxygen atom. As for a bond angle, the O-O-Si angle in the former structure, 110.5 degree is almost the same as that in the latter 111.7 degree.

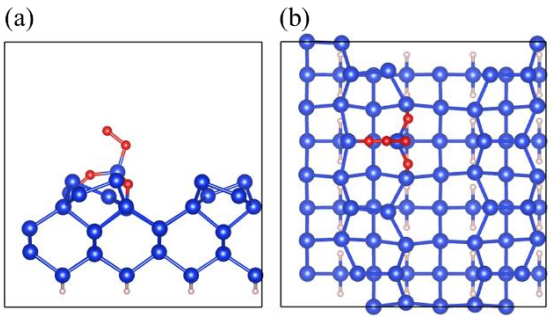

Fig. 3 Schematic drawings of optimized *ins×3-paul-up* structure (blue: Si atom, red: O atom, white: H atom). (a) and (b) are side view and top view, respectively.

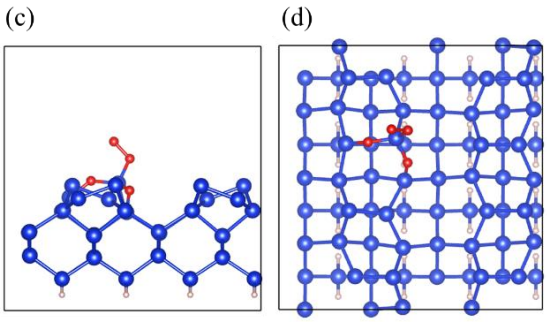

Fig. 4 Schematic drawings of optimized *ins×2-paul-up* structure (blue: Si atom, red: O atom, white: H atom). (c) and (d) are side view and top view, respectively.

In both structures, E_{ad} is large and the O-O bond is elongated without breaking the bond, meaning that these structures are a molecularly chemisorbed oxygen. Considering the fact that an oxygen molecule dissociateively adsorbs on a non-oxidized Si surface [2], our result explains well the experimental report [1].

The number of *ins* O atoms would mean the oxidation state of the Si atom. The change in the oxidation state might result in the change in the resultant adsorption structure of a molecular oxygen, but our calculation does not show such a structure difference. This may mean that the charge transfer in the two structures are almost the same and it is difficult to distinguish those structures in experiments.

4. Conclusions

On the basis of first principles calculation based on DFT, we investigated adsorption state of an oxygen molecule on Si(001) surfaces in the initial oxidation stage. Our calculations reveal that an oxygen molecule chemisorbs on an oxidized Si atom keeping the O-O bond. This result explains well the recent experimental report.

Acknowledgements

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