Chemisorption of H_2O on the H-terminated Si(001) surface

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First-principles molecular dynamics simulations of H-terminated Si(001) surfaces interacting with an H_2O or OH molecule are carried out on the basis of density-functional theory, norm-conserving pseudopotential and plane-wave basis set. Optimized configurations, electronic structures, local density of states, and atomic and bond populations are obtained. It is revealed that the interaction between an H_2O or OH molecule and the surface silicon atom on the step edge decreases the Si-Si backbond strength and initiates the etching or the oxidation process, depending on the chemisorption site and the number of chemisorbed molecules.

1 Introduction

The study of the interaction of H_2O or OH molecules with the H-terminated silicon surface is interesting in terms of important application fields, such as oxidation or etching process. For example, silicon surface atoms can be etched in alkaline solution which consists of H_2O and OH molecules. In particular, it has been reported that water immersion of the H-terminated Si(111) surface induces the structure-selective etching process which produces a homogeneous and atomically flat surface [1]. There have been, however, only a few reliable theoretical studies on these processes based on the first-principles electronic state theory[2].

In the present work, we apply the first- principles molecular dynamics simulation method[3] to the chemisorption of H_2O or OH molecules on the H-terminated Si(001) surfaces with a surface step. We determined the optimized structure for an H_2O or an OH chemisorbed system and clarified the electronic structure relevant to the oxidation and the etching mechanism. The first attempt to simulate the etching process of the H-terminated silicon surface interacting with OH molecules was also carried out in order to reveal the etching mechanism in alkaline solution.

2 Simulation method

The present calculation is based on the Kohn-Sham local-density-functional formalism [4]. A plane-wave basis set is used. The exchange-correlation interaction is approximated by the Ceperley-Alder form.[5]. A norm-conserving pseudopotential was used in the originally developed separable form based on the Bachelet-Hamann-Schlüter form[6].

We adopt the standard molecular dynamics method for the optimization of the ionic system and the preconditioned conjugate-gradient (CG) method for the quenching procedure of the electronic degrees of freedom [7]. In the present simulation the time step is 1.0 or 2.0fs. The criterion for the optimized configuration is that forces exerted on all the ions are lower than 1.0×10^{-3} Hartree/au. The simulations were executed in two steps to reduce computation time. In the first step, rough configurations were determined, and the cut-off energy was 23.9Ry. In the second step it was increased to 73.9Ry, which corresponds to 65000 plane waves.

As a localized basis set for the population analysis[8], the MINI-1 Gaussian basis set which was proposed by Huzinaga[9] was used . We have already proposed and developed the method of population analysis for the plane-wave basis set in a supercell system[10].
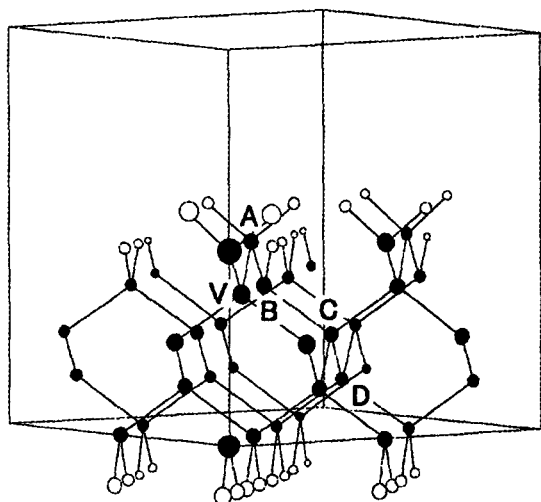
Figure 1 H-terminated Si(001) surface with surface step ($\bigcirc$: silicon, o : Hydrogen)

Table 1 Change of total energy after chemisorption (in eV)

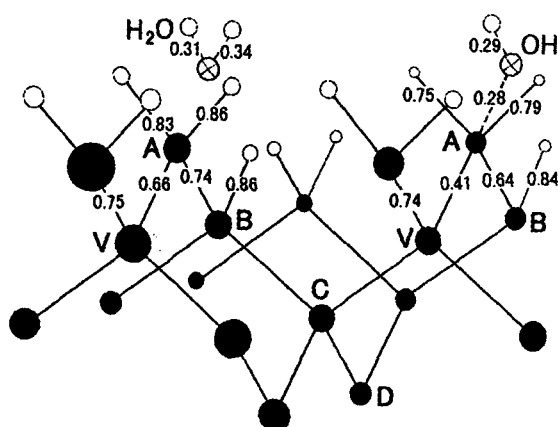| site	A	B	C	D
no step $+H_2O$	3.26	0.51	1.26	1.40
step $+H_2O$	4.40	-0.60	0.92	1.50
no step $+OH$	–	-1.28	–	–
step $+OH$	–	-3.32	–	–

Figure 2 Bond population of H-terminated silicone surface with surface step interacting with H_2O and OH on B sites

The models studied in this work consist of silicon, oxygen and hydrogen atoms. The lengths of the unit lattice vectors of the supercell parallel to the x, y and z axes are $2a, 2a$ and $4a$,respectively, where a denotes the lattice constant of silicon bulk, and the slab consists of five silicon layers and two hydrogen layers terminating the silicon surfaces, as shown in Fig.1. The thickness of the vacuum region is equivalent to nine silicon layers. Four surface silicon atoms were selected as the on-top chemisorption sites of H_2O or OH molecules, and the atoms were called A,B,C and D sites, as in Fig.1.

3 Results and discussion

In the cases of chemisorptions of H_2O molecules on the A,B and C sites , no marked change of the ionic configurations occurred. On the other hand, in the case of D-site chemisorption, reconstruction of the configurations was observed.

Table 1 shows the total energy change after the chemisorption of molecules. This result suggests that the B site is the most stable chemisorption site.

Fig.2 shows the results of the bond population analysis for the case of H_2O and OH chemisorp-

tion on the B site. The backbond population between A and V silicon atoms decreased to 87% in the case of H_2O chemisorption. Since an OH molecule has an unoccupied state lower than the top of the valence band of the silicon surface, the OH molecule is more reactive than the H_2O molecule. Therefore, the backbond population between A and V silicon atoms decreased to 54 %.

Fig.3 shows the calculated local density of states for oxygen atoms and A-silicon atoms. Since the lowest unoccupied orbital of the OH molecule is p-type, there exist orbital hybridizations between the oxygen 2p state and the silicon 3p state. Therefore, the hybridized states form the antibonding states in the backbond of the A silicon atom.

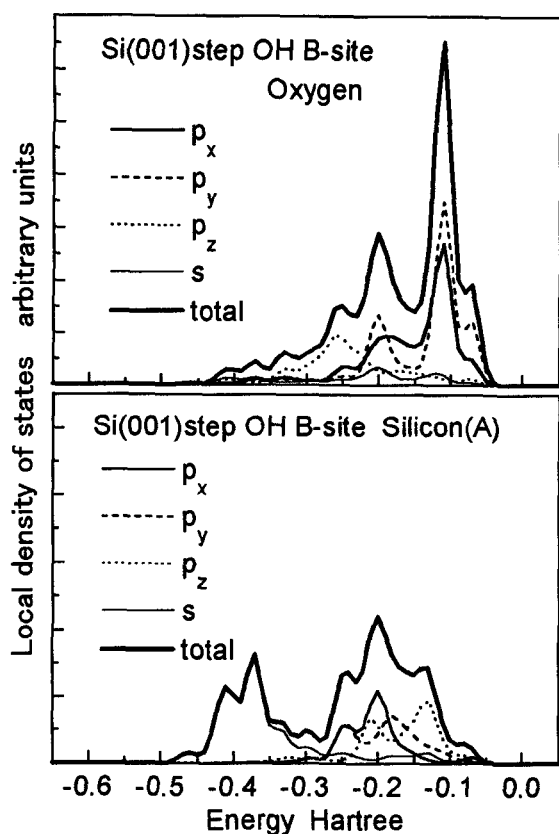Similar orbital hybridization occurred in the

Figure 3 Local density of states for oxygen and A silicon atoms in the case of OH chemisorption on B site

Figure 4 Schematic of the simulated result for the case of H_2O chemisorption on D site: (a) initial configuration, (b) optimized configuration ($\bigcirc$: silicon, o : hydrogen, $\otimes$: oxygen)

case of C and D site chemisorptions, and the Si-Si backbond populations decreased. On the other hand, in the case of the A site, there were no remarkable changes of the backbond population.

Fig.4 shows a schematic of the simulated results for the case of H_2O chemisorption on the D site. The results of the bond population analysis are also shown. The hydrogen atom (H1) which terminates the A silicon atom moves to the on-top site of the oxygen atom and the other hydrogen atom (H2) moves to the on-top site of the A silicon atom. The results of bond population analysis suggest that the Si(A)-H(1) bond was broken and a new chemical bond between the oxygen atom and the A-silicon atom formed. It is thought that this is the initial process of surface
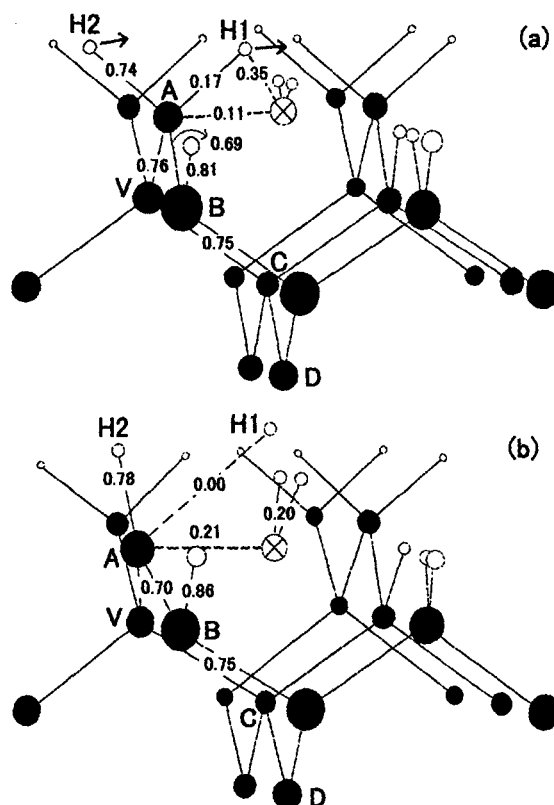
oxidation.

As a first attempt to simulate the etching process in alkaline solution, we carried out the molecular dynamics simulation of the H-terminated Si(001) surface step interacting with four OH molecules. Fig.5 shows the result. The total simulation time is 1ps. The charge density distribution is also shown as isosurfaces whose volumes correspond to the bond population which decreases as the etching process proceeds. This result suggests that the chemisorbed OH molecules break the Si-Si backbond, and induce etching of the silicon surface atoms.
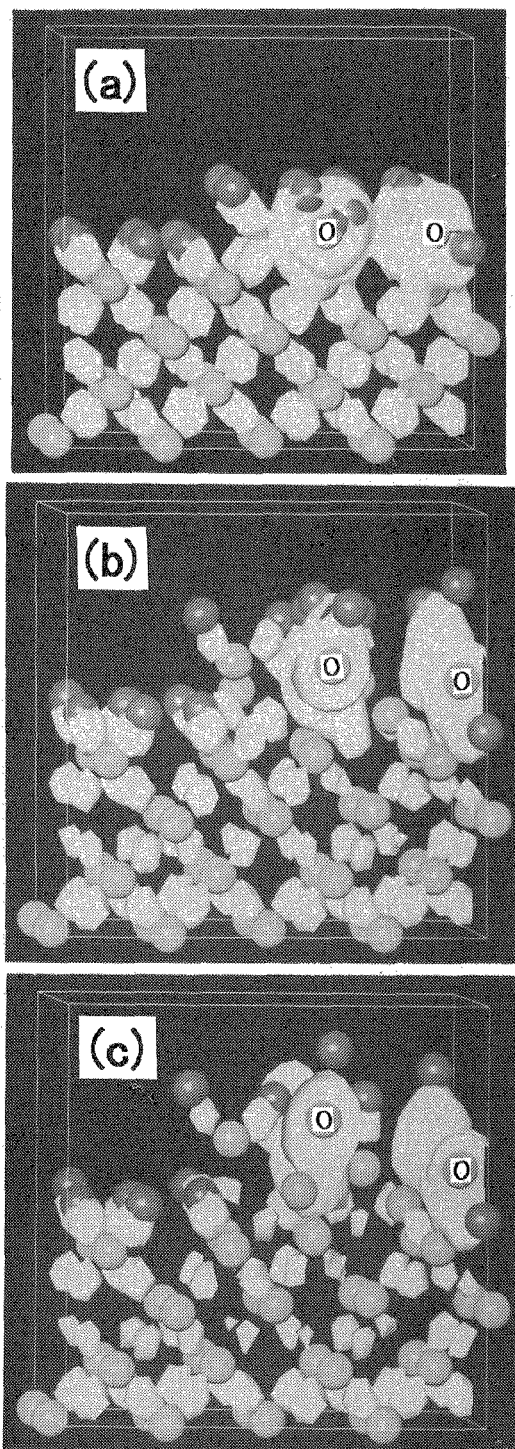
Figure 5 Simulated result of H-terminated Si(001) surface interacting with four OH molecules: (a) initial configuration, (b) 610fs, (c) 1100fs

4 Summary

By applying first-principles molecular dynamics simulation for the H-terminated Si(001) surfaces interacting with H_2O or OH molecules, optimized configurations, electronic structures, local density of states, and atomic and bond populations were obtained. It was revealed that the interaction between an H_2O or OH molecule and the surface silicon atom on the step edge decreases the Si-Si backbond strength and initiates the etching or the oxidation process, depending on the chemisorption site and the number of chemisorbed molecules.

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