First-principles studies on the adsorative properties of hydrogenated Si cluster

Q. Wang, Q. Sun*, J.Z. Yu, M. Ishihara, Y. Kawazoe

Kawazoe Laboratory, Institute for Materials Research, Tohoku University, Sendai 980-77, Japan

Received 25 January 1999; accepted 24 February 1999

Abstract

The adsorption of Si, O and Al adatoms on the most stable hydrogenated Si cluster (Si₆H₁₂) has been explored by using first principles. A special attention is paid to the comparisons of the similarity in adsorptions between the hydrogenated Si cluster and H-terminated Si surface: substitutional adsorption configuration is found for Si atom on Si₆H₁₂ cluster, similar to that on H-terminated Si surface; Si–O–Si adsorption configuration is found for O atom on Si₆H₁₂ cluster, similar to the case on H-terminated Si surface; nonadsorption of Al atom on Si₆H₁₂ cluster is found, similar to the very weak adsorption of Al atom on H-terminated Si surface. This similarity in adsorption between hydrogenated Si₆H₁₂ cluster and hydrogenated Si surface would be attributed to the fact: in hydrogenated Si₆H₁₂ cluster, H atoms have terminated the dangling bonds, and the Si atoms favor the bulk-like sp³ bonding even in this small cluster. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption; Cluster; Hydrogenated Si cluster

1. Introduction

Recent development of Si surface cleaning technique employing buffered HF treatment enables us to provide atomically flat H-terminated Si surface [1,2], which has following properties: Surface states resulted from the dangling bonds are passivated by hydrogen adsorption, the chemical reactivity is reduced. Therefore, the adsorptive properties of H-terminated Si surface attract a great attention nowadays [3–8], and it has been found that the H-terminated Si surface is a promising substrate for fabricating atomic-scale structure and nanoscaled device.

On the other hand, with the new advent of flexible and precise experimental techniques, the hydrogenated Si clusters are produced [9–13]. Especially, the stable structures of hydrogenated Si clusters are determined recently [9], it is found that for neutral hydrogenated Si clusters Si₆H₁₂ is most stable. Because hydrogenation would help the recovery of the tetrahedral bonding network by saturating the dangling bond [9], as a result, the similarity in adsorptions between hydrogenated Si cluster and H-terminated Si surface would be intuitively expected. In this paper, the adsorptive properties of Si, O and Al adatoms on Si₆H₁₂ cluster are studied, a special attention is paid to the comparisons of the similarity in adsorptions between the hydrogenated Si cluster and H-terminated Si surface. Because clusters can be used to understand
how physical properties and structures evolve from atom to molecule to cluster, and in the end to the bulk phase. We wish that this study would provide more comprehensive understandings on adsorption for adatoms in different environments.

2. Theoretical method

Ab initio methods based on density-functional theory (DFT) are well established tools for studying structural properties of materials. Especially, the plane-wave basis and pseudopotential method combined with DFT has provided a simple framework whose accuracy and predictive power have been convincingly demonstrated in large variety of systems, because this method has following advantages: (1) the treatment of nonspherical charge densities and potentials is straightforward (no shape approximations); (2) the calculation of Helmann–Feynman forces is greatly simplified so that extensive geometry optimization is possible; (3) the basis is spatially unbiased with no preference for a particular arrangement of atoms.

Our calculations are based on density functional theory, the exchange-correlation energy of valence electrons is adopted the form of Ceperly and Alder [14] as parameterized by Perdew and Zunger [15]. The ion–electron interactions are described by pseudopotentials, the silicon potential is generated in the norm-conserving pseudopotential scheme of Troullier and Martins [16], the reference configuration is chosen as $3s^23p^1$, the cutoff radius for both s and p orbital is taken to be 1.6 a.u., and s and p orbitals are treated as nonlocal components. This potential gives a lattice constant of 5.37 Å for the bulk diamond silicon, and for Si$_3$ cluster, this potential produces isosceles triangle configuration with bond length 2.172 Å and bond angle 77.65°, which are in agreement with ab initio molecular orbital calculations [17]. For Al, the reference configuration is chosen as $3s^23p^1$, the cutoff radius for both s and p orbital is taken to be 1.7 a.u., and s and p orbitals are treated as nonlocal components. This potential gives the bond length of 2.47 Å for Al$_2$.

However, for oxygen, due to the lack of corresponding core states for cancellation, the tightly bound 2p valence wave functions are sharply peaked. As a result, in the conventional norm-conserving pseudopotential scheme, a relatively hard pseudopotential has to be generated and a relatively large number of plane-wave basis functions are required in calculations. Therefore, in our calculations, the potential of oxygen is generated in the ultrasoft pseudopotential scheme introduced by Vanderbilt [18], 2s$^2$2p$^4$ configuration is used as the reference state to construct the oxygen potential, for both s and p orbital, the cutoff radius is 1.28 a.u.

In order to improve the transferability, two reference energies are set to be the eigenvalues of orbitals, the other parameters are referred to in Liu et al. [19]. In this way, for O$_2$ molecule, the bond length of 1.205 Å, which are in good agreement with experiment. For H$_2$O molecule, this potential gives H–O bond length 0.961 Å and $\angle$HOH bonding angle of 104.9°, also in agreement with experimental results. 40 Ry has been used as cut-off energy in the plane-wave expansion of the pseudowave functions, which is large enough to obtain convergence. The minimization of the total energy over the degrees of freedom of electron densities and atomic positions is performed using the conjugate-gradient iterative minimization technique [20]. In the optimizations, the cluster is placed in a cubic cell with edge length of 16 Å, this size is sufficiently large to make dispersion effects negligible. The structure optimization was symmetry unrestricted, and the optimization was terminated when the forces acting on the atoms are less than 0.03 eV/Å.

3. Results and discussions

It has been found that the most stable structure for Si$_6$H$_{12}$ cluster is cyclohexasilane [9,21], we have also got this structure as shown in Fig. 1(a), where the Si–Si bond length is about 2.325 Å, the Si–H bond length is 1.50 Å. The density of states (DOS) and pair correlation function (PC) are shown in Fig. 1(b) and (c), respectively. We have searched the possible adsorption sites in the whole range over the hydrogenated Si$_6$H$_{12}$ cluster, we place an adatom at one site and then perform geometry optimization according to the calculated force acting on atoms, then we next choose another.
site and repeat this procedure. In this way, we can find the most stable adsorption configuration.

3.1. The adsorption of Si atom

The stable adsorption configuration is shown in Fig. 2(a), a striking feature is the substitutional adsorption: the Si adatom forms a bond with a Si atom in substrate cluster, which releases a H atom, and the H atom is in turn bonded to the adatom. This kind of substitutional adsorption has also been found for Si adatom on hydrogenated Si(1 0 0) surface recently [3]. This similarity in adsorption between hydrogenated Si$_6$H$_{12}$ cluster and hydrogenated Si(100) surface would be attributed to the fact: in hydrogenated Si$_6$H$_{12}$ cluster, H atoms have terminated the dangling bonds, and the Si atoms favor the bulklike sp$^3$ bonding even in this small cluster [9]. The adsorption energy for Si is 3.90 eV, which is greater than that for Si adatom on H-terminated Si(100) surface (3.2 eV) [3]. The bond length between the adsorbed Si atom and the nearest substrate Si atom is 2.28 Å, similar to that on H-terminated Si(001) surface (2.26 Å) [3]. The bond length between Si adatom and H is 1.52 Å. Fig. 2(b) and (c) show the density of states (DOS) and pair correlation function (PC).
3.2. The adsorption of O atom

Two interesting adsorption configurations are found: In configuration I, the substitutional adsorption is also found: the O adatom forms a bond with a Si atom in substrate cluster, which releases a H atom, and the H atom is in turn bonded to the adatom, forming Si–O–H configuration. The adsorption energy for O in this configuration is 8.57 eV. The Si–O bond length is 1.648 Å, The bond length between O and H is 0.961 Å, closed to that in H₂O. In configuration II, as shown in Fig. 3(a), the O adatom breaks the Si–Si bond and the O adatom is bridge bonded to two Si atoms. The adsorption energy is 9.238 eV, greater than that in type-I configuration, so it is more stable. The Si–O bond length is 1.633 Å, and the Si–O–Si angle is 137°. In Fig. 3(b) and (c), the density of states (DOS) and pair correlation function (PC) for the type-II configuration are given.

Recently, the initial oxidation process of H-terminated Si(001) surfaces have been investigated by means of high-resolution electron energy loss spectroscopy [22], it has been found that the adsorption of atomic oxygen on H-terminated Si(001) surfaces occurs even at room temperature, there are two adsorption configurations: Si–O–H configuration and Si–O–Si configuration, however, the coverage of Si–O–H species is less than 0.15, and oxygen atom preferentially adsorb on one of the two back-bond site of a surface Si atom, forming Si–O–Si bond, which is similar to the case in Si₆H₁₂ cluster.

3.3. The adsorption of Al atom

We have found that Al atom cannot be adsorbed on Si₆H₁₂ cluster, similar to that on H-terminated Si surface. It has been demonstrated [7,8] that Al atom just only resides on the H-terminated Si(111) surface without making any chemical bond, the energy required for Al atom migration on this surface is very small (2 meV), and the diffusion length is quite large, which has been confirmed by scanning tunneling microscopy (STM) studies on H-terminated Si(001) (2×1) surface [4]. Shimizu et al. [23] also studied Al adsorption on the hydrogenated Si(100) surface by using scanning tunneling microscopy (STM), although the Al adatoms grown on the clean Si(100) surface initially make a long chain perpendicular to the Si dimmer row and form a 2×2 reconstructed geometry at 0.5 ML, however this kind of ordered structure cannot be observed on the hydrogenated surface.

Similar case has also been found experimentally with Ga (isoelectronic to Al), Ga atoms on H-terminated Si(001) (2×1) surface are mobile and a stable adsorption site is preferentially on the H-missing dangling bonds [5]. Comparing the density of states (DOS) and the pair correlation functions (PC) as shown above, we can see that the adsorption changes the electronic structure as well as geometry structure.
In summary, the adsorption of Si, O and Al adatoms on the most stable hydrogenated Si cluster (Si$_6$H$_{12}$) has been explored by using ab initio method, and the similarity between the hydrogenated Si cluster and H-terminated Si surface is found. On the H-terminated Si surface, the hydrogen atoms can be desorbed by using the tunneling current of the STM and nanoscaled dangling bond patterning can be formed [5], which makes it to be a promising substrate for fabricating atomic-scale structure and nanoscaled device [4-8], the similarity in adsorption between the hydrogenate Si cluster and H-termination Si surface would suggest that some new potential uses could be existed for the hydrogenated Si clusters in the nano-materials.

Acknowledgements

The authors would like to express thanks to the Materials Information Science Group of the Institute for Materials Research, Tohoku University, for their continuous support of the HITAC S-3800/380 supercomputing facility.

References