Structural stabilities and electronic properties for planar Si compounds

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We have investigated atomic arrangements and electronic properties of two-dimensional Si compounds having the Si(111) skeletons with H and/or OH-radicals terminators, using first-principles calculations within the density functional theory. A mechanism of the onset of a direct gap for the planar siloxene has been clarified from the chemical bonding points of view. The direct energy gap does not change with increasing thickness of the Si-skeleton of the planar siloxene, but the indirect one decreases: the direct and indirect gaps of the planar siloxene are associated with the surface state and the Si-skeleton states, respectively. If both surfaces of the planar siloxene are terminated with the OH-radicals, the stacking of the Si-skeleton changes from the diamond structure to the Wurtzite one as the Si-skeleton thickness increases. In such artificial compounds, a direct gap appears only at the thinnest Si thickness as well as the case of the planar siloxene. [DOI: 10.1380/ejssnt.2006.528]

Keywords: Density functional calculations; Silicon; Silicon/Oxygen compounds; Surface states

I. INTRODUCTION

Strong light emitting materials are always required for many optical applications. Recently, low dimensional materials such as two-dimensional (2D) silicon oxides have been studied extensively. 2D silicon oxides are categorized by positions of oxygen atoms according to whether oxygen atoms settle out of or in-plane of their Si-skeleton. Of these materials, the graphite-like material having the Si(111)-skeleton terminated by hydrogen and OH is called as the planar siloxene as shown in Fig.1(b). Structural properties of the planar siloxene have been explored with various experimental technique; Raman and infrared transmission spectroscopy [1], X-ray diffraction [2–4].

Takeda and Shiraishi have investigated the electronic properties of various low-dimensional silicon/oxygen compounds using the LCAO calculations [5–7] in comparison with the planar polysilane consisting of Si(111) 1 bi-layer (BL) terminated by H atoms on both surfaces. They have shown that some kinds of materials have direct energy gaps. These results have been confirmed experimentally by Dettlaff-Weglikowska et al. [4]. Such series of materials have been also studied theoretically by Deák et al. [8] and van de Walle and Northrup [9]. For several years later, “siloxene-tube” has also been invented on the basis of the planar siloxene as one of the extended applications [10]. However, precise atomic arrangements and detailed characteristics of band edge states of the planar siloxene, especially a mechanism of the onset of a direct gap, have not been revealed yet.

In this study, we focus on the planar siloxene comparing with the planar polysilane, because the planar siloxene has a direct gap, while the planar polysilane has an indirect gap. We aim to reveal the accurate atomic arrangement and the electronic properties of a series of the planar siloxene. Furthermore, we explore two types of new siloxene-like materials: One has OH-radicals on both surfaces of Si(111)-1BL and the other has a Si-skeleton with a larger Si BL thickness. We show an artificial siloxene-like new material has a direct gap.

II. CALCULATION METHODS AND MODELS

We executed total-energy calculations based on the first-principles pseudopotential method within the density functional theory [11, 12]. As for the pseudopotentials, Troullier-Martins type [13] was chosen for Si, H and ultra-soft Vanderbilt-type [14] for O. The generalized gradient approximation [15] was used for the exchange-correlation potentials. The cutoff energy was set to be 36 Ry for the planewave expansion, k points were sampled with 48 points over the two dimensional Brillouin zone, and the structural relaxation was carried out until forces acting on atoms were below $10^{-3}\text{Ha}/\text{a_B}$. We considered various compounds consisting of the Si-skeleton with surfaces terminated with H atoms or OH-radicals. We prepared models for the planar polysilane

FIG. 1: The most stable atomic arrangements of side (upside) and top (downside) views for (a) the planar polysilane and (b) the planar siloxene. Blue, red, and gray balls indicate Si, O, and H atoms, respectively.
TABLE I: Lattice parameter in an unit of Å.

|                        | bulk silicon | planar polysilane | planar siloxene | OH-terminated siloxene |
|------------------------|--------------|-------------------|-----------------|------------------------|
| in-plane lattice constant, $a_0$ | 3.84         | 3.93              | 3.86            | 3.88                   |
| bi-layer thickness, $d_{BL}$   | 0.786        | 0.695             | 0.746           | 0.764                  |
| Si horizontal distance, $d_{hor}$ | 2.22         | 2.37              | 2.22            | 2.23                   |
| Si-Si bond length        | 2.36         | 2.34              | 2.34 & 2.36     | 2.36 & 2.37            |
| Si-H bond length         | -            | 1.51              | 1.50            | -                      |
| Si-O bond length         | -            | -                 | 1.69            | 1.69                   |
| O-H bond length          | -            | -                 | 0.984           | 0.984                  |

FIG. 2: Band structures (a) for the planar polysilane and (b) for the planar siloxene. The planar polysilane has an indirect gap of 2.25 eV and a direct gap of 2.26 eV, while the planar siloxene has a direct gap of 1.42 eV at $\Gamma$ and a degenerate of the valence band top at $\Gamma$ is lifted by 0.18 eV. An energy window is fixed for $-15 \sim 5$ eV. $2s$ orbital of an O atom lies out of this range.

FIG. 3: Distributions of the probability density at $\Gamma$ of the valence band top for the planar polysilane. (a)∼(c) and (d)∼(f) show two-fold degenerate equivalent orbitals on the valence band top. Three cross sections are shown for the three equivalent skeleton bonds. Distribution functions are divided into twenty equal parts in the range from $4 \times 10^{-3}$ to $4 \times 10^{-2}$ $a_0^{-3}$.

and the planar siloxene having 1∼7 BL Si-skeleton. We also considered artificial compounds based on the Si-skeleton; both surfaces of which are terminated by OH-radicals. Any models employed are placed in the supercell with a vacuum region (15∼25 $a_0$). The planar siloxene must have a spontaneous polarization perpendicular to the surface, but an artificial electric field causing by the periodic boundary condition was negligibly small because of a large vacuum region. In all calculations, we adopted the in-plane 1 × 1 unitcell and in-plane lattice constants were fitted using the quadratic polynomial for the total energy after the structural relaxation.

III. RESULTS AND DISCUSSION

A. Optimized atomic structures

We calculated the most stable atomic structure of the planar siloxene and compared it with the planar polysilane. In the structural relaxation, we started from an initial configuration where O and H atoms were located right above Si atoms of the Si(111)-BL skeleton, i.e., vertical and on-top OH-radical to the Si(111) surface. First, we relaxed only H atoms toward two directions along the skeleton Si bond ([10] in Fig.1) or the hexagonal center.
FIG. 4: Distributions of the probability density at Γ of the valence band (a)∼(c) top and (d)∼(f) 2nd-top for the planar siloxene for three cross sections. O-H and Si-O bonds are on the cross section in (a) and (d). The other cross sections are not on any bond without Si-skeleton bonds. Distribution functions are divided into twenty equal parts in the range from $4 \times 10^{-3}$ to $4 \times 10^{-2} \text{Å}^{-3}$.

FIG. 5: Distributions of probability density of the conduction band minimum at Γ (a)∼(c) for the planar polysilane and (d)∼(f) for the planar siloxene. Cross sections are taken to be the same plane as Fig.4. Contour plots were mapped with twenty equal parts in the range from $4 \times 10^{-3}$ to $4 \times 10^{-2} \text{Å}^{-3}$.

We compared the optimized structure of the planar siloxene with those of the planar polysilane and bulk Si in Table I. It is remarkable that the BL thickness of the Si(111) skeleton for the planar polysilane shrinks by 12% while the Si-Si bond length does not change so much compared to bulk Si. H atoms can remove electrons from the Si-skeleton because the electro-negativity of H is larger than that of Si. Consequently, $sp^3$-orbitals of bulk Si take on the character of $sp^2$-like orbitals, and hence the BL thickness decreases. On the other hand, the lattice parameter of the Si-skeleton for the planar siloxene is in an intermediate extent between bulk Si and the polysilane. Even though the electro-negativity of O is very large, the OH-radicals does not change so much the Si-skeleton structure.

B. Electronic properties

We investigated in detail the band structures shown in Fig.2, for both the planar polysilane and the planar siloxene with their optimized atomic arrangements. The planar polysilane has the conduction band edge in the vicinity of the M point and the second minimum at Γ, and the valence band maximum is constructed by two-fold degenerate states at Γ. The planar polysilane has an indirect gap of 2.25 eV and a direct gap of 2.26 eV at Γ,
FIG. 6: Direct and indirect gaps for the planar siloxene-like materials as a function of the thickness of the skeleton. Direct energy gap is at Γ point and indirect gap measured between the Γ point of the valence band top and at/near the M point of the conduction band. Horizontal broken and solid lines correspond to a direct gap at Γ an indirect gap of bulk silicon, respectively.

FIG. 7: Distributions of the probability density at Γ for (a)∼(c) the conduction band bottom and (d)∼(f) the valence band top for 7 BL model of the planar siloxene-like materials. The probability densities are plotted for three cross sections.

C. Si-skeleton thickness dependence

We studied artificial "siloxene-like" materials which have the Si-skeleton with thicknesses of n BL (n = 1 ~ 7). The planar siloxene corresponds to the case of n = 1. The atomic arrangements for thicker skeleton siloxene models were assumed as follows: one Si(111) surface is terminated with the OH-radicals and the other surface is terminated with the H atoms. The initial atomic arrangement was set to be that of the planar siloxene and all degrees of freedom were optimized. For these models, the stacking of the Si-skeleton was kept to be diamond structure. Even after the relaxation, the atomic arrangements of the Si-skeleton layers hardly change from the bulk structure. As clearly seen in Fig. 6 and Table II, the direct energy gap at Γ does not depend on the Si-skeleton thickness, but the indirect gap energy between the conduction band bottom in the vicinity of M point and the valence band top at Γ depends on the Si-skeleton thicknesses; decreases monotonically as the thickness increases. This suggests that the direct gap at Γ is dominated by the surface-originated states while the indirect gap is influenced by the quantum confinement.

respectively. The band structure is reminiscent of bulk Si, because the M point in 2D BZ corresponds to the X point in the bulk 3D BZ. On the other hand, the planar siloxene has a direct gap of 1.42 eV at Γ. In addition, the two-fold degeneracy of the valence band maximum at Γ is lifted with a splitting of 0.18 eV, which had already mentioned in Ref.[16]. The splitting occurs because in-plane $p_x$ and $p_y$ orbitals of the Si-skeleton become inequivalent by the inclination of the OH-bond and the O-Si bond.

It is shown in Fig.3 that three bonds of the Si atoms in the skeleton have equivalent probability densities for degenerate two states at the valence band maximum of the planar polysilane. On the other hand, the hybridization between Si and O states occurs as shown in Fig.4, resulting in the splitting of the top valence band into two states for the planar siloxene. If we refer the projected direction of the OH bond in the Si(111) surface as the $x$ axis ([10] in Fig.1), the edge state for the planar siloxene does not contain the O 2$p_y$ orbital as shown in Fig.4(a), but consists mainly of two other Si-Si bond-orbitals along the different directions from the $x$ axis and the O 2$p_y$ orbital. On the other hand, the second highest valence band state consists mainly of the Si-Si bond-orbital along the $x$ axis and O 2$p_y$ orbital. These hybridizations with O 2$p$ orbitals push up their energies and the difference in fashion of the hybridization induces the energy splitting of the two-fold degenerate states.

It can be seen in Fig.5(a)∼(c) that the conduction band edge for the planar polysilane at Γ is an antibonding state between two Si-H molecular orbitals. Fig.5(d)∼(f) shows that the conduction band bottom for the planar siloxene at Γ is an antibonding state between Si-H and Si-O-H molecular orbitals. For planar siloxene, the conduction band minimum at Γ point lies at a lower level by mixing with O 2$s$ state than the local minimum in the vicinity of M point. As a result, a direct gap appears in this system.
TABLE II: Dependence of the energy gaps on the thickness in an unit of eV.

| Model          | indirect gap | direct gap at Γ | minimum energy gap |
|---------------|-------------|----------------|-------------------|
| bulk          | 0.727       | 1.78           | indirect         |
| planar polysilane | 2.25       | 2.26           | indirect         |
| planar siloxene  | 1.87       | 1.42           | direct           |
| 2 BL           | 1.20        | 1.48           | indirect         |
| 3 BL           | 0.961       | 1.43           | indirect         |
| 4 BL           | 0.842       | 1.43           | indirect         |
| 5 BL           | 0.802       | 1.44           | indirect         |
| 6 BL           | 0.695       | 1.44           | indirect         |
| 7 BL           | 0.716       | 1.42           | indirect         |

effect. The quantum confinement effect on the conduction band edge near the M point is remarkable for thinner films. Therefore, a direct gap at Γ appears only at the thinnest 1 BL Si-skeleton for the planar siloxene. For the thickest siloxene model employed, the probability density at Γ is shown in Fig.7. It is found that the probability density at Γ is localized near the surface terminated with OH-radicals and it decays toward inside of the skeleton as expected. The top of the valence band is localized near the surface, and hence it does not depend on the thickness of the Si-skeleton.

D. Artificial materials

We study also an artificial two-dimensional Si compound in which both surfaces of the skeleton Si(111) are terminated with OH-radicals. Atomic arrangement of this model shown in Fig.8(a) is nearly equal to that of the planar siloxene, as if OH-radicals on one side were replaced by H atoms. This artificial materials has a direct gap at Γ as shown in Fig.9(a) as well as the planar siloxene, but its value (0.234 eV) is much smaller than that of the planar siloxene. This has already been pointed out by Northrup et al. [9]. However, its mechanism has not been mentioned as yet. The termination of OH-radicals on both surfaces enhances hybridization of the skeleton bond-orbitals with oxygen orbitals; the hybridization with O-2p states pushes up the valence band edge at Γ and the hybridization with O-2s state pushes down the conduction band edge at Γ. Thus, the energy gap is reduced remarkably with compared to the planar siloxene.

In addition, we considered also thicker models of the Si-skeleton as the case of the siloxene-like materials. The layer stacking of the optimized structure was faced to be transformed to the Wurtzite structure from the diamond structure at 2 BL thickness of Si as shown in Fig.8(b). This may be attributed to the dipole-dipole interaction between OH-radicals on two sides. As for the electronic properties, the models with higher Si thicknesses have indirect gaps as is the case with the siloxene-like materials.

IV. CONCLUSION

We obtained a detailed atomic structure for the planar siloxene. We found that OH-radicals and SiO bond incline in the opposite direction. The degeneracy of the top of the valence band is lifted by these inclinations and the induced energy splitting becomes 0.18 eV. From the calculations of the artificial materials having multiple Si-skeleton thicknesses for the planar siloxene, we can conclude that an indirect gap is influenced by the quantum confinement effect but a direct gap at Γ is not. This means the direct gap of these system is dominated by the surface hybridized states with OH-radicals, being the reason why a direct gap of 1.42 eV appears only for the planar siloxene with 1BL Si thickness. The artificial two-dimensional Si compounds terminated with OH-radicals on both surfaces has a direct gap of 0.234 eV at 1BL Si thickness. As the Si-skeleton thickness increases above 1BL, the type of the gap is converted to an indirect gap and the stacking of the Si-skeleton changes from the diamond structure to the Wurtzite one because of the dipole-dipole interaction between the surfaces.

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FIG. 9: Band structures for artificial siloxene-like materials, in which both surfaces of (a) Si(111)-1 BL and (b) -2 BL are terminated with OH-radicals. While the model of 1 BL has a direct gap, the model of multiple BLs have indirect gaps.

[1] H. D. Fuchs, M. Stutzmann, M. S. Brandt, M. Rosenbauer, and J. Weber, Phys. Rev. B 48, 8172 (1993).
[2] J. R. Dahn, B. M. Way, E. Fuller, and J. S. Tse, Phys. Rev. B 48, 17872 (1993).
[3] H. Nakano, M. Ishii, and H. Nakamura, Chem. Commun. 23, 2945 (2005).
[4] U. Dettlaff-Weglikowska, W. Höne, A. Molassioti-Dohms, S. Finkbeiner, and J. Weber, Phys. Rev. B 56, 13132 (1997).
[5] K. Takeda and K. Shiraishi, Phys. Rev. B 39, 11028 (1989).
[6] K. Takeda and K. Shiraishi, Solid State Commun. 85, 301 (1993).
[7] K. Takeda and K. Shiraishi, Cond. Mat. Phys. 18, 91 (1997).
[8] P. Deák, M. Rosenbauer, J. Weber, and M. S. Brandt, Phys. Rev. Lett. 69, 2531 (1992).
[9] C. G. van de Walle and J. E. Northrup, Phys. Rev. Lett. 70, 1116 (1993).
[10] G. Seifert, T. Frauenheim, T. Köhler, and H. M. Urbassek, Phys. Stat. Sol. 225, 393 (2001).
[11] M. Tsukada et al., computer program package TAPP, University of Tokyo, Tokyo, Japan (1983-2006).
[12] J. Yamauchi, M. Tsukada, S. Watanabe, and O. Sugino, Phys. Rev. B 54, 5586 (1996).
[13] N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991).
[14] D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
[15] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[16] H. Kageshima and K. Shiraishi, Phys. Rev. B 56, 14985 (1997).