



Topologically induced surface electron state on Si(1 1 1) surfaces

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ABSTRACT

First-principle electronic structure calculation reveals the appearance of a new class of surface state on hydrogenated and clean Si(1 1 1) surfaces. The states are found to exhibit different characteristics to conventional surface electron states in terms of the peculiar distribution of the wavefunction depending on the wavenumber. In addition, the state results in flat dispersion bands in a part of the surface Brillouin zone having energy of about 8 eV below the top of the valence band. An analytic expression based on the tight-binding approximation corroborates the surface electron state results from the delicate balance of the electron transfer among the atoms situated near the surface. The obtained results give a possible extension and generalization of the edge state in graphite ribbons with zigzag edges.

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1. Introduction

Electron states in condensed matters with translational symmetry generally extend throughout whole systems satisfying the Bloch theorem. The introduction of imperfections in the condensed matters causes mixing of the Bloch states thereby inducing localized electron states: point and line defects (e.g. vacancies, interstitials and dislocations) induce particular electron states whose wavefunctions are localized at or near the defects. Surfaces are also regarded as planer imperfections. Wavefunctions of the surface states are indeed distributed throughout the surface regions. All of these electron states, despite the different characteristics, possess a common feature: The wavefunctions have more or less a character of the atomic orbital of the constituent elements and a localized character throughout the whole Brillouin zone.

A different class of electron state has been found in graphene with imperfections (edges [1–3] and topological defects [4]): in the case of graphene, such imperfections result in peculiar electronic states around the Fermi level whose characteristics are totally different from the conventional defect/surface induced states. When graphene flakes or ribbons have edges with a zigzag shape, this causes the emergence of an electron state located at the Fermi energy that is localized near to but extended along the edges, and lacks dispersion along the edge directions in a part of

the Brillouin zone [1–3]. An early analytical study showed that the flat-band states (i.e. the edge state or border state) result from a delicate balance of electron transfers among the π orbital situated near the edge atoms [1,2]. Thus, the distribution of the edge state strongly depends on the wavenumber in a one-dimensional Brillouin zone: The edge state is exactly distributed on edge C sites at the zone boundary of the Brillouin zone, then, by decreasing the wavenumber, the edge state loses their localized character and penetrates inner region of the ribbon. Finally, at $k = 2\pi/3$, they are smoothly connected to the dispersive bulk π and π^* bands. Thus, the edge state can be classified as a new surface electron state which is induced by the topological conditions imposed on the certain lattice structures. Such edge-localized states near the Fermi level have been observed in a susceptibility measurement experiment and a recent scanning tunneling microscopy experiment [6,7].

The edge state is not peculiar to graphene ribbons with zigzag edges, but occurs at particular edges, interfaces, and surfaces in various lattice structures [8,9]. Indeed, based on the first-principle total energy calculation, it has been demonstrated that the similar edge localized state emerges in the zigzag ribbons consisting of boron and nitrogen atoms with a honeycomb network [8]. In this case, owing to the chemical species difference, the edge state no longer degenerates at the Fermi level but splits into a valence band top and a conduction band bottom localized at the edge N and B atoms, respectively. In addition, within the framework of the tight-binding approximation for the s orbital, it has been predicted that the edge state emerges in several three dimensional networks with particular surfaces [9]. It has been demonstrated that surfaces and edges of the bipartite lattices are essential to the emergence of

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the edge states: In a part of the Brillouin zone, the edge state is distributed on one of two sublattices of the bipartite network exhibiting the localized nature while they possess the nodal point on another sublattice. Furthermore, the edge state are distributed on the whole lattice sites of the network in the rest of the Brillouin zone [9].

However, among the examples studied except the hexagonal-BN ribbons, it is still unclear whether the state emerges or not in the realistic materials, such as Si(111) surfaces and diamond (111) surfaces. Thus, in this work, based on the density functional theory, we performed the first-principle calculation on the surfaces of Si to explore the possibility of the edge states on the (111) surface of the diamond lattice. Our calculations clearly show that this state emerges on both hydrogenated and clean Si(111) surfaces. We also show an analytical solution for the state based on the tight-binding approximation and explicitly show the region where the flat-dispersion band emerges in the two-dimensional Brillouin zone. Furthermore, an expression of the wavefunction clearly shows an origin of the unusual distribution depending on the wavenumber.

2. Calculation methods

All the calculations have been performed on the basis of the density functional theory [10,11]. We use the local density approximation to express the exchange-correlation energy of interacting electrons [12,13]. Norm-conserving pseudopotentials with separable forms are adopted to describe the electron-ion interaction [14,15]. The valence wavefunctions are expanded in terms of plane-wave basis set with the cutoff energy of 10 Ry which gives enough convergence of the relative total energy of Si [16]. The surface is simulated using a repeating slab model in which 6 Si atomic layers and 12 Å-vacuum regions are included. For both hydrogenated and clean Si(111) surfaces, we use 1×1 lateral periodicity to explore the edge states on those surfaces. As for the integration over the surface Brillouin zone, we use 16- k points. Geometry optimization has been performed for all the atoms in the slab. The conjugate-gradient minimization scheme has been used both for the electronic structure calculation and for the geometry optimization [17]. In the optimized geometries, the remaining force acting on the atoms is less than 0.005 Ry/Å.

To obtain the analytic solution of the edge state on the Si(111) surfaces, we use simple tight-binding model in which we take account of the single atomic orbital for each site and the constant transfer integral for all adjacent pair of the sites.

3. Results and discussion

Fig. 1a shows the surface energy band structure of the hydrogenated Si(111) surface. Here, we find peculiar electron states in the Brillouin zone boundary, which are absent in the energy band of bulk silicon (Fig. 1c). These states emerge around 8 eV below the top of the valence band exhibiting the flat band nature in the part of the K- Γ line. Furthermore, by decreasing the wavenumber or approaching the Γ point from the zone boundary K point, these states lose their flat band nature and exhibit a similar character to the other electron states around the Brillouin zone center. The characteristics of the state are similar to the edge state of the graphene ribbons with zigzag edges. Thus, we can regard the states as a generalized class of edge state emerging on Si(111) surfaces.

To corroborate the issues, we analyzed the distribution of the wavefunctions for these states at K, Γ , and M points. Fig. 2 shows the wavefunction of the states denoted by the indexes in Fig. 1a. Obviously, the state is completely localized at the K point of which character is s orbital of the top/bottom-most Si atoms (Fig. 2a). In sharp contrast, the states are distributed throughout the whole Si slab at the Γ point (Fig. 2b and c) and at the M point (Fig. 2d and e). The distribution of wavefunctions of the state completely differs from that of the conventional surface electron states of which the wavefunction is basically distributed at/around the surface atomic sites for the whole Brillouin zone. On the other hand, the characteristics are exactly the same as those of the edge state of the graphite ribbons with zigzag edges. Thus, the obtained surface state associated with the relatively flat dispersion band results from the delicate balance of the electron transfer among the atoms situated around the surfaces in the range of the particular wavenumbers.

It is interesting to note how the hydrogen atoms saturating the surface Si atoms affect the distribution of the surface localized state mentioned above, since distribution of the surface localized state is slightly asymmetric due to the on-site energy difference between hydrogen and silicon atoms. Fig. 1b shows the surface energy band of the clean Si(111) surfaces with 1×1 lateral periodicity. Obviously, flat dispersion bands emerge around the K point some 8 eV below the top of the conduction band. Furthermore, the state loses their flat band nature when they approach the Brillouin zone center. The results corroborate the fact that the new surface state is robust toward the adsorption of hydrogen atoms and only affected by the network topology of the Si-Si covalent bonds. Indeed, the distribution of the states is almost the same as that obtained in the hydrogenated surfaces: The state is completely localized at the top/bottom-most Si atoms at the K point (Fig. 3a), while

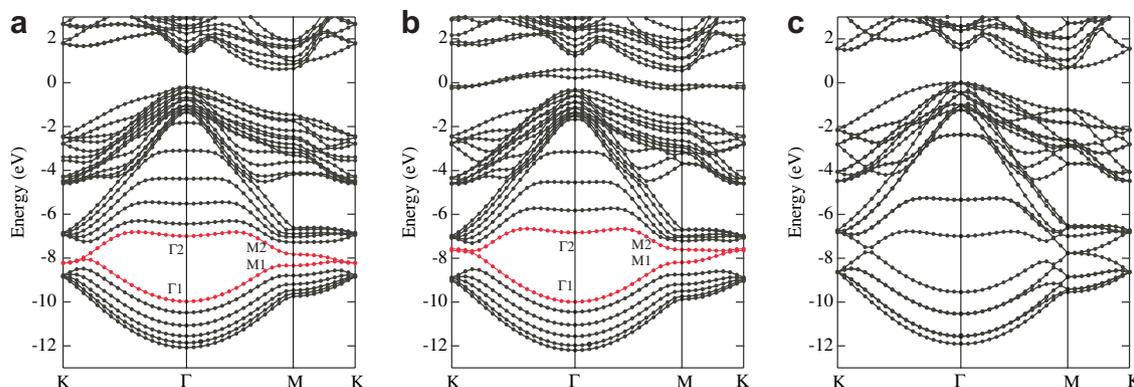


Fig. 1. Surface energy band of: (a) hydrogenated; (b) clean Si(111) surfaces with 1×1 lateral periodicity and (c) Electronic energy band of bulk Si on the surface normal to the (111) axis. In (a) and (b), the red lines denote the electron states exhibiting the localized nature at the K point. Energies are measured from the top of the valence band for the hydrogenated surface and the bulk silicon. In the clean surface, the energy is measured from the Fermi level energy. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

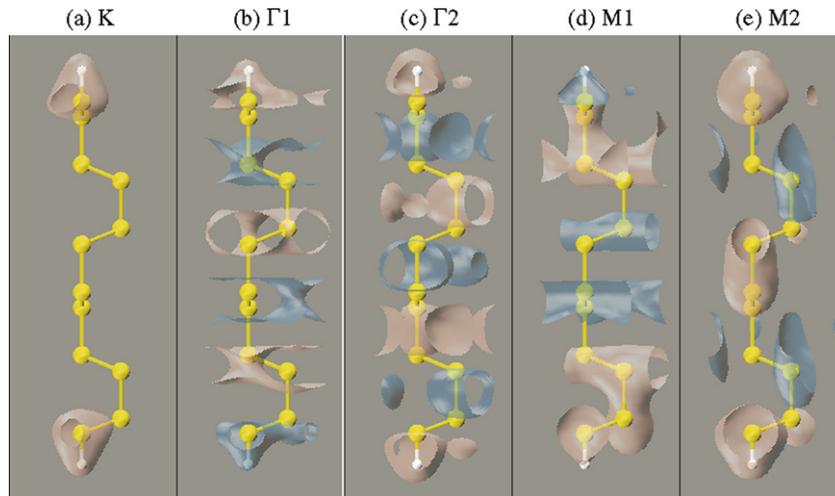


Fig. 2. Distribution of the wavefunctions of the surface states (red lines in Fig. 1a) on hydrogenated Si(111) surfaces at high symmetry points in the two dimensional Brillouin zone. In the case of the Γ and M points, the energy level of the wavefunction is denoted in Fig. 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

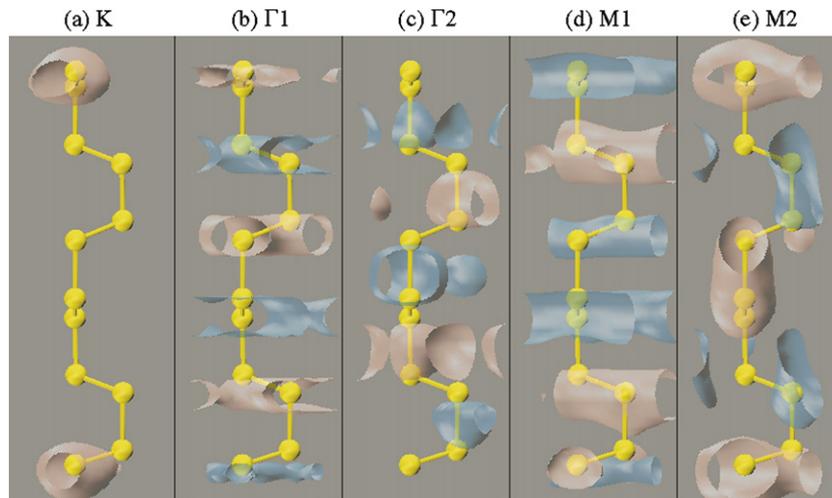


Fig. 3. Distribution of the wavefunctions of the surface states (red lines in Fig. 1b) on clean Si(111) surfaces at high symmetry points in the two dimensional Brillouin zone. In the case of the Γ and M points, the energy level of the wavefunction is denoted in Fig. 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

it extends to the whole atoms in the slab at the other symmetry point in the Brillouin zone (Fig. 3b–e).

It should be noted that the new surface state is totally different from the dangling bond states distributed at the top/bottom-most Si atoms on clean surfaces. Because it emerges not only on clean surfaces but also on hydrogenated surfaces as pointed above. Furthermore, the distribution of the states is unusual: the wavefunction is localized at a particular symmetry point in the surface Brillouin zone.

Our LDA calculations clearly indicate the peculiar properties of the new surface electrons state on a Si(111) surface that emerges some 8 eV below the top of the conduction band. The state exhibits a flat band like nature only in a part of the K- Γ line. However, it is still unclear how the flat band region extends throughout the two-dimensional Brillouin zone and why the state loses its localized nature in the larger part of the Brillouin zone. To answer these questions, we derive an analytical expression for the electronic wavefunctions for the new surface states by considering a semi-infinite Si slab with a (111) surface based on the tight-binding

approximation in which we consider the single atomic orbital for each site and the transfer integral between adjacent sites.

The analytical form of the wavefunctions is shown in Fig. 4a. Since the surface possesses translational symmetry, we can construct analytical solutions for the surface localized state at the top-most atomic layer by applying the Bloch component \dots , $e^{i(k_a n + k_b m)}$, $e^{i[k_a(n+1) + k_b(m+1)]}$, $e^{i[k_a n + k_b(m+1)]}$, \dots to successive surface atomic sites, where n and m denote a site location at the top-most atomic layer. The condition necessary for the wavefunction being $E(\mathbf{k}) = \text{constant}$ is that the total sum of the component of the wavefunction over the adjacent to the Y site should vanish. Then, we get the condition,

$$-e^{i(k_a n + k_b m)} - e^{i[k_a(n+1) + k_b(m+1)]} - e^{i[k_a n + k_b(m+1)]} - X = 0,$$

where X is the wavefunction of the site X in the second sub-surface. By solving the equation, the wavefunction of X is found to be decomposed into

$$X = e^{i[k_a(n+1/3) + k_b(m+2/3)]} [e^{i(-k_a/3 - 2k_b/3)} + e^{i(-k_a/3 + k_b/3)} + e^{i(2k_a/3 + k_b/3)}].$$

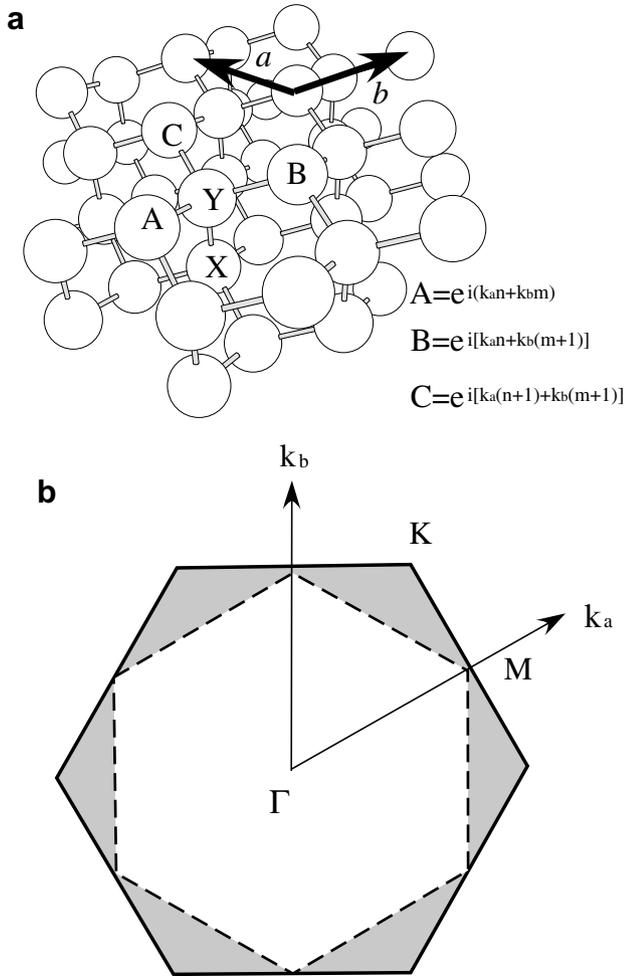


Fig. 4. (a) An analytic form of the surface state for semi-infinite slabs having a diamond lattice with (111) surfaces. Each atomic site is specified by location indexes n and m . The magnitude of the wavefunction at each site, such as X and Y is obtained analytically (see text). (b) The two dimensional Brillouin zone of the (111) surface of diamond lattice. The shaded area denotes the region where the flat dispersion band state exists. Dotted lines denote the boundary that gives the dumping factor of the wavefunction is unity.

Then successive application of the formula to each sub-surface results in a generalized expression of the wavefunction in the l th subsurface X^l .

$$X^l = e^{i[k_a(n+t) + k_b(m+s)]} [e^{i(-k_a/3 - 2k_b/3)} + e^{i(-k_a/3 + k_b/3)} + e^{i(2k_a/3 + k_b/3)}]^{l-1},$$

$$t = 0, s = 0 \quad \text{for } l = 3n,$$

$$t = \frac{1}{3}, s = \frac{2}{3} \quad \text{for } l = 3n + 1,$$

$$t = \frac{2}{3}, s = \frac{1}{3} \quad \text{for } l = 3n + 2,$$

where n is an integer. The convergence condition of $[e^{i(-k_a/3 - 2k_b/3)} + e^{i(-k_a/3 + k_b/3)} + e^{i(2k_a/3 + k_b/3)}] \leq 1$ is required for the physically relevant solution. The convergence condition results in the shaded area in the two-dimensional Brillouin zone (Fig. 4b) where the flat dispersion band emerges.

From further analysis on the analytical solution of the new surface state, it is found that the wavefunction completely localized only at the K point, $\mathbf{k} = (1/3, 1/3)$, at which the dumping factor of the wavefunction, $D = e^{i(-k_a/3 - 2k_b/3)} + e^{i(-k_a/3 + k_b/3)} + e^{i(2k_a/3 + k_b/3)}$, exactly vanishes. In sharp contrast, on the dotted line in Fig. 4b, for example at the M point, $\mathbf{k} = (1/2, 0)$, the dumping factor D is

unity resulting in the extended nature of the wavefunctions. In the other shaded area, the wavefunction is rather localized near the surface region and penetrates inside the slab.

In the case of the graphite ribbon with zigzag edges, due to a large Fermi level density of states, the ribbon exhibits interesting electronic and magnetic properties, such as peculiar transport properties [18] and magnetism [5,19]. Regrettably, the surface state on the Si(111) surfaces emerges at about 8 eV below the Fermi level. Thus, such characteristics properties predicted in the graphite is not expected to take place. However, spectroscopic experiments with higher energy provide evidence of the state which exhibits unusual properties compared with the other bulk-like and conventional surface electron states.

4. Summary

We find that topologically induced surface electron states emerge on hydrogenated and clean Si(111) surfaces. These states exhibit a peculiar distribution depending on the wavenumber: At the K point, the wavefunction of the state completely localized at the top/bottom-most Si atoms in the slab, whereas the same wavefunction is extended throughout the whole slab for those wavenumbers other than the K point. Furthermore, around the zone center, the states possess substantial dispersion in comparison to other bulk energy bands. The analytical solution for a semi-infinite slab of diamond lattice with a (111) surface clearly shows that the delicate balance in the electron transfer between atoms result in the peculiar surface state, and that the state is regarded as the generalized edge state which is inherent in graphite ribbons with zigzag edges.

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