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Peierls Instability in One-Dimensional Borine Wire on Si(001)

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Low-dimensional systems provide many exotic physical phenomena such as Peierls instability,[1] Jahn−Teller distortion,[2] or the formation of non-Fermi-liquid ground states.[3] A simple example of one-dimensional (1D) materials is polyacetylene, which shows the Peierls instability that causes dimerization in pristine polyacetylene, $(-CH)_n$, accompanied by a band-gap opening at the Fermi level.[4,5] Consequently, the bond-alternated structure of polyacetylene, $(-CH{=}CH)_n$, becomes a semiconductor. In recent years, self-assembled 1D molecular wires on the Si(001) surface have attracted much attention from both fundamental and applied points of view.[6−9] Even though such molecular wires involving the covalent-bond formation between adsorbate and substrate are geometrically 1D, they need to have a 1D band structure of chemisorbed molecular adsorbates in order to exhibit a Peierls instability. In this Communication, we introduce a self-assembled borine wire on Si(001), which undergoes a Peierls instability, giving rise to a periodic structural distortion, a band-gap opening, and the formation of a charge-density wave (CDW).

Using the scanning tunneling microscope (STM) nanolithography technique, the dangling bond (DB) wire is generated by the selective removal of H atoms from an H-passivated Si(001) surface along the edge of a Si dimer row.[10] This DB wire can be utilized as a template for the fabrication of a 1D molecular wire.[9] Here, we theoretically predict that such a fabricated borine wire on the DB wire is unstable with respect to a periodic structural distortion which opens an energy gap at the Fermi level, thereby resulting in a semiconductor. Before the structural distortion, there is a half-filled metallic state which is delocalized along the 1D borine wire. The corresponding band is divided into two subbands, accompanying a double periodicity along the borine wire mainly by the pairing of boron atoms. We find that the ground state is characterized by a CDW coupled to the periodic structural distortion. There are two degenerate ground states because of two possibilities of the pairing directions of adsorbed borines. Since the potential-energy barrier between the two ground states is only 0.24 eV, the 1D borine wire is expected to oscillate between the two energy minima with increasing temperature, leading to an order−disorder transition.

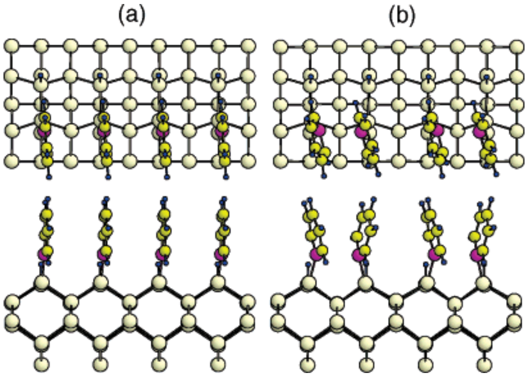

Figure 1. Top and side views of the optimized structures of the borine wire on Si(001): (a) the 4 × 1 structure and (b) the 4 × 2 structure. The circles represent Si, B, C, and H atoms with decreasing size.

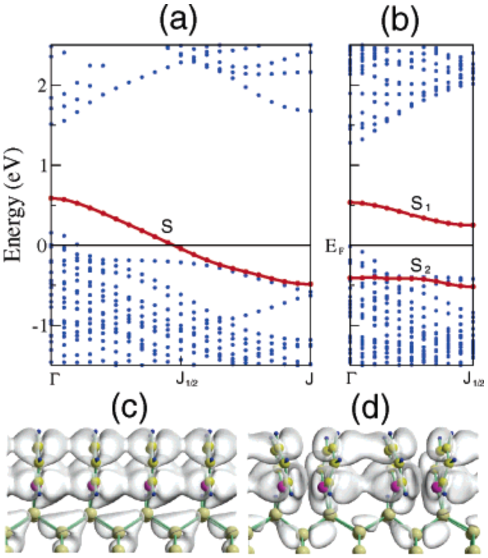

Figure 2. Surface band structure of the borine wire on Si(001): (a) the 4× 1 structure and (b) the 4 × 2 structure. The red circles and line represent the surface state S (S_1 and S_2) of the 4 × 1 (4 × 2) structure. The energy zero represents the Fermi level. The direction of the ΓJ line is along the borine wire. Charge characters of the surface states (c) S and (d) S_1 at the $J_{1/2}$ point are shown. The charge density in 4 × 1 (4 × 2) is displayed with an isosurface of 0.4 (0.2) millielectron/bohr^3.

We first determine the atomic structure of the 1D borine wire adsorbed on the DB wire by using first-principles density-functional[11] theory calculations within the generalized gradient approximation.[12] Here, we consider an infinite-length borine wire by employing the 4 × 1 unit cell where the borine wires are separated, perpendicular to the Si dimer row, by an additional H-passivated Si dimer row. The details of our calculational scheme are given in the Supporting Information (SI). The optimized structure, shown in Figure 1a, has an adsorption energy of 1.68 eV. Similar to the adsorption of other hydrocarbons on a partially H-passivated Si(001) surface,[6,7] borine molecules easily diffuse on the H-passivated area while keeping the Si−H bonds intact (see the SI), leading to formation of the 1D borine wire. Our band-structure calculation for the 4 × 1 borine wire shows that the surface-state band *S* crosses the Fermi level at almost the midpoint of the symmetry line of ΓJ (see Figure 2a). Thus, it is expected that a CDW coupled to a lattice vibration of wavelength $2a_0$ (a_0 is the lattice parameter) along the borine wire might lead to a Peierls instability.[1] Note that the substrate of the 4 × 1 borine wire has a single dangling bond per the 4 × 1 unit cell. The corresponding half-filled surface state (see the SI) is expected to hybridize with the borine π state. As a matter of fact, the charge character of the

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S state, shown in Figure 2c, represents such hybridization between the two states.

To examine the possibility of Peierls instability, we perform an optimization of the symmetry-unrestricted geometry with a doubled periodicity using the 4 × 2 unit cell. Our optimized structure for the 4 × 2 borine wire is shown in Figure 1b. We see that the B atoms of two borine molecules are displaced alternatively to form pairs. The distance of the paired B atoms is reduced to 2.76 Å, compared to the corresponding distance of 3.87 Å in the 4 × 1 structure. We find that the 4 × 2 structure is more stable than the 4 × 1 structure by 0.12 eV per 4 × 1 unit cell. This total energy gain results from the electronic contribution owing to a band-gap opening at the Fermi level (see Figure 2b). Note that in the 4 × 2 structure the structural distortions lead to the split of the S band into the two subbands S_1 (π-antibonding) and S_2 (π-bonding). Here, the direct band gap between S_1 and S_2 is 0.76 eV at the $J_{1/2}$ point. As shown in Figure 2d, the charge character of the S_1 state reveals the π-antibonding state which has nodes between paired borine molecules. It is noticeable that there are two ground states with respect to the pairing directions of borine molecules.

Since the potential-energy barrier between the two ground states is 0.24 eV per paired borines (see the SI), we expect that, as temperature increases, adsorbed borine molecules oscillate between the two energy minima. Assuming an Arrhenius-type activation process with the usual attempt frequency of $\sim 10^{13}$ Hz, this oscillating rate is estimated as $\sim 10^9$ sec^{-1} at room temperature, the average positions of borine molecules yielding the 4 × 1 structure. Such an order−disorder transition is similar to the case of the clean Si(001) surface, where STM experiments[13] observed symmetric dimer images at room temperature owing to the flip-flop motion of buckled dimers between their two ground states. In this way, the order−disorder transition in the present borine wire may be observed by STM at above ~110 K, because it takes about 10^{-2} sec to obtain the STM image of an adsorbed molecule.

For future STM experiments, we simulate the STM images for the filled and empty states of the 4 × 1 and 4 × 2 structures. The results are displayed in Figure 3. For the 4 × 1 structure, the filled-state image (Figure 3a) shows a single bright spot on top of an adsorbed molecule, whereas the empty-state image (Figure 3b) has two bright spots per each molecule at both sides of the molecular plane. Note that the two bright spots in the latter are almost attached to those of neighboring borines. For the 4 × 2 structure, the filled-state (Figure 3c) and empty-state (Figure 3d) images show bright spots with a double periodicity compared to those of the 4 × 1 structure. In Figure 3d, two bright spots (in the 4 × 1 structure) between two adjacent borines alternatively merge to be a single bright spot (marked by arrows).

Our simulated STM images for the 4 × 2 structure clearly show an occurrence of charge ordering with a double periodicity along the borine wire. This periodic charge modulation coupled to a periodic structural distortion manifests that the 4 × 2 structure is characterized by a 1D-CDW formation or, equivalently, a Peierls instability along the borine wire. We have to notice that most of the Peierls or CDW systems are found in 3D materials such as conducting organic molecular crystal[14] and transition metal dichalcogenides.[15] In contrast with these 3D materials, the present borine wire formed on a 2D substrate provides a surface CDW system to allow a real-space observation of CDWs, their fluctuations or critical behaviors at the atomic scale.

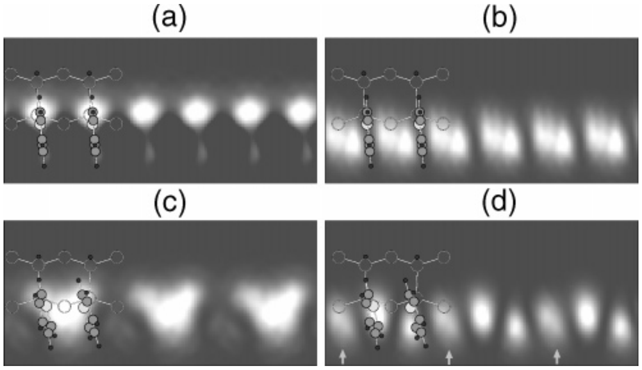

Figure 3. Simulated STM images of the borine wire on Si(001): (a) the filled-state image for 4 × 1, (b) the empty-state image for 4 × 1, (c) the filled-state image for 4 × 2, and (d) the empty-state image for 4 × 2. The filled-state (empty-state) image is obtained by integrating the charge from Fermi level E_F to $E_F + 1.0$ (-1.0) eV. The images were obtained at 2 Å above the outermost H atom.

In summary, we have introduced the 1D borine wire formed on the Si(001) surface, which exhibits a Peierls instability. Our first-principles density-functional theory calculations showed that this molecular wire is stabilized by formation of a 1D-CDW, accompanying a structural distortion with a double periodicity and a band-gap opening at the Fermi level. We hope our predictions will stimulate STM and scanning tunneling spectroscopy experiments for identification of the 1D-CDW ground state as well as its order−disorder transition occurring with increasing temperature.

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Supporting Information Available: Computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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