

Electronic structure of an atomic wire on a hydrogen-terminated Si(111) surface: First-principles study

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Using first-principles calculations, we have examined structural stability and electronic states of an atomic wire that consists of a row of dangling bonds formed by extraction of hydrogen atoms from a H-terminated Si(111) surface. This atomic wire is found to be stable. Within the local-density-functional approach, it is electrically conductive due to the appearance of a half-filled state in the energy-gap region of the surface. This wire becomes semiconducting if the Peierls distortion is taken into account, but the total energy gain due to this distortion is estimated to be only 6.5 meV. Silicon atoms with dangling bonds are found not to dimerize as is expected in the usual Peierls distortion condition, but to relax in the direction perpendicular to the wire.

Atomic-scale fabrication on solid surfaces has recently attracted much attention. Several groups have succeeded in manipulating single atoms¹⁻³ and in fabricating atomic-scale structures^{4,5} by using scanning tunneling microscopes. This technique opens the way to atomic-scale devices, which are promising candidates to replace silicon metal-oxide-semiconductor transistors in future integrated circuits. One of the authors and his co-workers have recently proposed a possible atomic-scale device which we call the atom relay transistor (ART).⁶ To realize the ART and other atomic-scale devices, it is necessary to appropriately design device structures and materials as well as to improve the technique of atomic-scale fabrication. However, designing atomic-scale devices is difficult at present because of our limited knowledge of properties of atomic-scale structures. Even if the properties of a particular structure are well known for a size of the order of 10 nm or larger, its properties may be greatly changed if its size is reduced to atomic scale. Concerning this, Bouju *et al.*⁷ have reported an instructive example: According to their molecular-dynamics calculations, a single-atom row of gold on a NaCl substrate was found to be unstable, while a gold wire with much larger width is apparently stable. In view of the above, there is a strong need to examine properties of various atomic-scale structures to obtain guiding principles for designing materials and structures of atomic-scale devices.

In this paper, we report our attempt to examine atomic-scale artificial structures using first-principles calculations. We focus on an atomic-scale wire, which is a simple but indispensable element of atomic-scale devices. One may think that an atomic wire on a solid surface is a good example of the one-dimensional (1D) electronic systems, the characteristics of which have been studied intensively on the basis of theoretical models such as the 1D Hubbard Hamiltonian. However, this is not necessarily true. An atomic wire may lose 1D character due to the interaction with its substrate. In some cases, even 1D atomic arrangement of the wire becomes unstable be-

cause of this interaction, as in the case of Au atoms on NaCl. Therefore, before studying electronic properties of an atomic wire in detail by assuming its 1D atomic arrangement and characteristics, we should examine its structural stability and how much it can preserve its 1D characteristics in electronic properties.

As an example of atomic wires, we choose a hydrogen-terminated Si(111) substrate surface and consider an atomic wire constructed by extracting a row of single H atoms. After the extraction of a H atom from the surface, one dangling bond (DB) is left on a remaining Si atom. A row of these DB's forms a kind of atomic wire, which we call a DB wire. Although this DB wire is chemically too reactive to use in real atomic-scale devices, we expect that it may be an instructive example of an atomic-scale wire on an insulating or semiconducting surface. Further, this wire may play an important role in fabrication of more promising atomic wires. This DB wire has not yet been fabricated experimentally, but we believe that it will be achieved in the near future judging from the recent rapid developments in atomic-scale fabrication. For example, Shen *et al.*⁵ have recently succeeded in fabricating DB lines with a width of less than 1 nm on a H-terminated Si(100) surface.

In our calculation, the H-terminated Si(111) surface was represented by a slab model consisting of six layers of Si atoms and two layers of H atoms, and the periodic boundary condition was imposed. An atomic wire was constructed on one side of the slab by extracting a row of hydrogen atoms in a 1×4 or 2×4 supercell as shown in Fig. 1. In the calculations, the 1×4 cell was mainly used, and the 2×4 cell was used in examining the effect of the Peierls distortion. As we will show later, interaction between neighboring DB wires can be neglected if this size of supercell is used in the calculations. The length of the cell in the direction normal to the H-terminated Si(111) surface is six times as long as the Si-Si atomic distance in a bulk Si crystal.

On the basis of this model, optimized atomic geom-

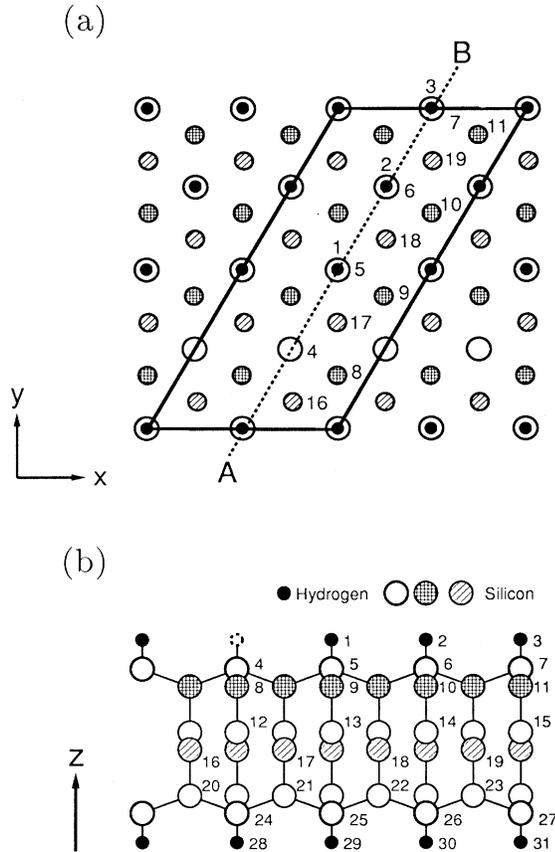


FIG. 1. Slab model of an atomic wire on the H-terminated Si(111) surface. (a) Top view. A 2×4 supercell is shown with thick solid lines. (b) Side view along A - B line in (a). Atoms within plane A - B are shown by circles with thick solid lines. An extracted hydrogen atom is shown by a dashed circle. Atom numbers and coordinate axes correspond to those in Table II.

etry and electronic structures were calculated within the local-density-functional approach. The exchange-correlation term used in the calculation was the Ceperley-Alder form⁸ parametrized by Perdew and Zunger.⁹ For electron-nuclei interaction, an ultrasoft pseudopotential¹⁰ was employed. The pseudopotential for H is generated in the electron configuration of $(1s)^{0.5}$, and only the s component was taken for the nonlocal part with one reference energy at the eigenvalue. The cutoff radii for the valence wave function (r_c^{WF}) and for the local potential (r_c^{Pot}) were 0.8 and 0.7 a.u., respectively. For Si, the pseudopotential was generated in $(3s)^{1.25}(3p)^{1.75}$ configuration with $r_c^{\text{WF}} = 1.8$ a.u. and $r_c^{\text{Pot}} = 1.6$ a.u., and s and p components were included with two and one reference energies, respectively. The second reference energy

for the s component was 1.0 Ry above the eigenenergy. The charge augmentation functions were constructed using the method of Laasonen *et al.*¹¹ with cutoff radii of 0.7 a.u. for H and 1.6 a.u. for Si. Wave functions were expanded in a plane-wave basis set with an energy cutoff of 16 Ry. Two special k points were used for the integration in k space, which corresponds to a total of four k points in the whole first Brillouin zone. Both electronic and ionic degrees of freedom were optimized using the conjugate gradient method.¹²⁻¹⁴

Before examining the DB wire, we calculated electronic structures and optimized geometries of H_2 and SiH_4 molecules and bulk Si to check the reliability of our calculations. Calculated atomic distances of H-H in H_2 , Si-H in SiH_4 , and Si-Si in bulk Si are 0.768, 1.472, and 2.329 Å, respectively, which agree well with the observed values of 0.741, 1.480, and 2.352 Å, respectively. We also calculated the optimized geometry of the Si(111) 1×1 -H surface without DB wires. In doing so, the atomic positions of the two innermost Si layers were fixed. In Table I, the calculated Si-H atomic distance and layer distance between the outermost two Si layers are shown together with results of previous first-principles calculations.¹⁵⁻¹⁷ The present results are in good agreement with those of Li and Vanderbilt¹⁶ and Li *et al.*,¹⁷ which are expected to be more reliable than those of Kaxiras and Joannopoulos¹⁵ considering the computational conditions.

In geometry optimization of the H-terminated Si surface with a DB wire, we started from the calculated optimized geometry of the Si(111) 1×1 -H surface without DB wires. Position changes after optimization from the initial geometry are summarized in Table II. As can be seen from this table, the position of the Si atom with a DB (atom 4 in the table) becomes lower than others in the same layer (atoms 5-7) by 0.110 Å, while one of the Si atoms in the next layer (atom 8) is shifted upward by 0.037 Å. This result suggests that the character of chemical bonds between the Si atom with the DB and its neighbors changes from the pure sp^3 to somewhat sp^2 -like to stabilize the electronic states of the DB wire. Other atoms remain at nearly the same positions; they move at most 0.01 Å. Therefore the DB wire structure on this surface can be considered to be structurally stable.

The calculated energy band structure of the H-terminated Si(111) surface with a DB wire is shown in Fig. 2 together with that of the surface without a DB wire. This shows that introduction of a DB wire creates another state in the energy-gap region of the H-terminated Si(111) surface. This midgap state has an energy-dispersion width of 0.36 eV along the DB-wire direction (the Γ - M line), while the dispersion width

TABLE I. Calculated optimized geometry of H-terminated Si(111) 1×1 surface. (Units: Å.)

	Ref. 15	Ref. 16	Ref. 17	Present calc.
Si-H distance	1.54	1.524	1.506	1.510
Si-Si layer distance (outermost layers)	0.72	0.755		0.757

TABLE II. Difference in calculated atomic positions between the H-terminated Si(111) surface with a DB wire and those of the surface without DB wires. (Units: Å.)

Atom	Δx	Δy	Δz	Atom	Δx	Δy	Δz
1	-0.002	0.007	0.002	12	-0.001	-0.014	0.013
2	-0.001	0.002	0.003	13	0.000	0.016	0.006
3	-0.003	-0.004	0.012	14	0.000	0.003	0.002
4	-0.001	-0.020	-0.110	15	-0.002	-0.003	0.005
5	-0.003	-0.004	-0.002	16	0.001	-0.002	0.013
6	-0.001	0.001	0.001	17	0.002	0.010	0.013
7	-0.001	-0.012	0.012	18	0.004	0.010	-0.009
8	0.003	-0.013	0.037	19	0.001	0.000	-0.003
9	-0.002	-0.011	0.004	20	-0.002	0.004	0.010
10	0.001	-0.003	-0.001	21	-0.002	0.001	0.006
11	0.001	0.000	0.001	22	-0.002	0.002	-0.003
				23	-0.002	0.002	-0.003

along the direction across the wire (the Γ - J' line) is only 0.02 eV. This shows that the midgap state has one-dimensional character. It also shows that the interaction between neighboring wires is weak enough to regard each wire as isolated from the others.

To examine the characteristics of the midgap state in detail, charge density profiles of the midgap state at the Γ point were calculated. The results are shown in Fig. 3. Figure 3(a) is the charge density contour map along the AB line in the plane including the DB wire. This shows that the charge density of the midgap state is localized around the dangling bond in this plane. The contour map along the CD line in a plane including a row of H atoms across the DB wire is shown in Fig. 3(b), which indicates that the wave function of the state is rather localized around the DB. From these charge density distributions in Figs. 3(a) and 3(b), we can understand the relatively large energy dispersion along the bond wire direction. It also confirms that each DB wire can be regarded as being isolated from neighboring wires as mentioned previously. These charge density distributions also lead to the following characteristic of the DB: There is much smaller asymmetry than expected for the sp^3 orbital, indicating that the character of the DB changes from sp^3 to

somewhat p -like. This is consistent with the fact that the bonding character between the Si atom with DB and neighboring atoms changes from sp^3 to sp^2 .

In fact, the spread of the wave function of the midgap state is a little larger than expected from Figs. 3(a) and 3(b). Figure 3(c) shows the contour map along the EF line in a plane including both the Si atom with a DB and its nearest neighbor. Here we can see that the charge density spreads over the Si with a DB, its nearest neighbor, and the second nearest neighbor in the third Si layer. Thus the character of the midgap state is much more complicated than it appears to be at first sight. Nevertheless, we can still say that the charge density of this state is localized around the DB wire on the atomic scale.

Since only one electron occupies the midgap state, we expect that the DB wire is electrically conductive within the local-density-functional approach. However, this wire may become semiconducting because of the following effects which are significant in purely 1D systems. First, the effects of electron correlation and spin are known to cause purely 1D systems with a half-filled energy band to be always insulating within the 1D Hubbard model.

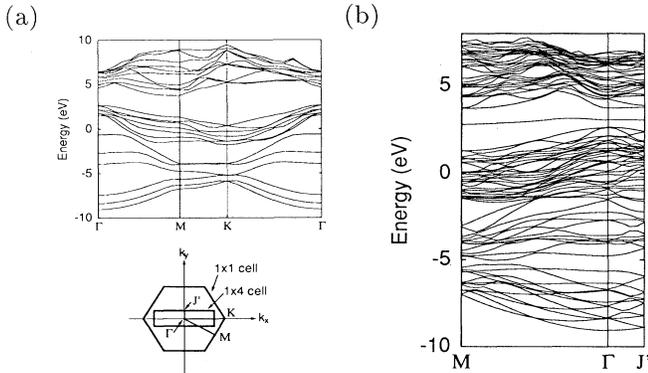


FIG. 2. Calculated energy band structure of the H-terminated Si(111) surface: (a) without a DB wire and (b) with a DB wire. The surface Brillouin zones for 1×1 and 1×4 cells are also shown.

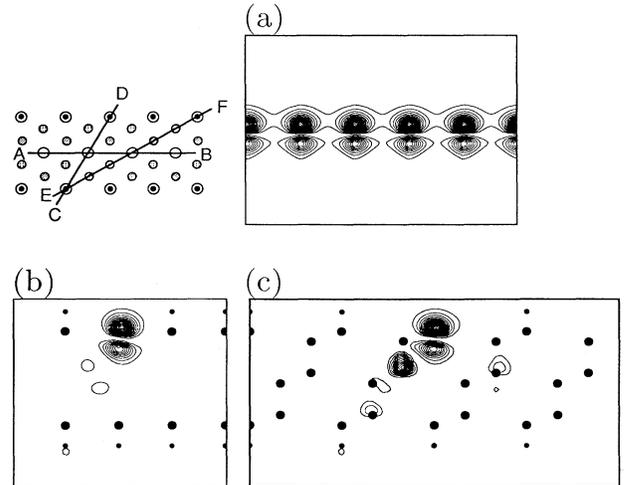


FIG. 3. Charge density contour maps of the midgap state at the Γ point: (a) along line A - B , (b) along line C - D , and (c) along line E - F .

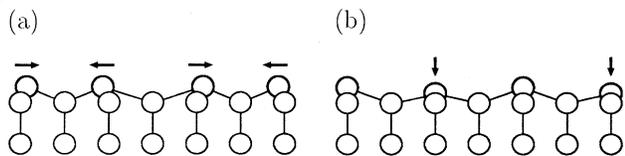


FIG. 4. Schematic view of the Peierls distortion of the DB wire: (a) distortion based on a purely one-dimensional system and (b) results of the present calculation.

However, examining these effects in the present DB wire might be difficult, since the character of the half-filled midgap state is rather complicated as mentioned above and thus simple models such as the 1D Hubbard model are not applicable. Therefore to examine these effects remains a future problem. Another important effect is the polaronic one. This effect causes the Peierls distortion, which is also significant in 1D systems. Since it is not certain how this effect is important in the present case, we evaluated the effect of the Peierls distortion by calculating a stable structure with the 2×4 supercell shown in Fig. 1.

In general, the Peierls distortion causes the atomic distortion shown in Fig. 4(a), that is, dimerization of wire atoms. However, we have found that this kind of distortion does not occur in the present system even if slight distortion in this direction is assumed in the initial geometry. Instead, our calculation leads to a different stable geometry shown in Fig. 4(b): No dimerization occurs, but there is a height difference of 0.023 \AA between the Si atom with a DB and the neighboring Si atoms. Since the period of this distortion is twice as large as the atomic distance, it is thought to be a kind of Peierls distortion.

Because of this distortion, the midgap state in Fig. 2 splits into two bands and the DB wire becomes semiconducting. According to our calculation, the value of this

energy gap is only 38 meV , and the total energy gain due to this distortion is only 6.5 meV , which corresponds to a thermal energy of about 75 K . Therefore at room temperature this Peierls distortion does not occur.

In summary, we have investigated the structural stability and electronic state of an atomic-scale wire constructed by extracting a row of H atoms from a $\text{Si}(111)1 \times 1\text{-H}$ surface using first-principles calculations within the local-density-functional approach. This atomic wire was found to be energetically stable with a slight inward shift of Si atoms with dangling bonds by 0.1 \AA compared with a fully H-terminated surface. A half-filled surface state due to the dangling-bond wire appears in the energy-gap region, and has one-dimensional character with the energy-dispersion width of 0.36 eV along the wire direction. This state contains not only components of dangling bonds but also those of neighboring Si bonds. However, we can still say that this state is localized on the atomic scale around the dangling-bond row. The effect of the Peierls distortion was examined using a first-principles calculation, and the total energy gain due to this distortion was evaluated to be only 6.5 meV . The wire was found to be distorted in the direction perpendicular to the wire, in contrast to the case of purely one-dimensional systems. Within the present study, we can say that this structure behaves as an electrically conductive atomic-size wire at room temperature. The effects of electron correlation and spin may increase the transition temperature between semiconducting and metallic states from that predicted in this study, about 75 K . Examining these effects in more detail remains a future problem.

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¹ D. M. Eigler and E. K. Schweizer, *Nature* **344**, 524 (1990).

² I.-W. Lyo and Ph. Avouris, *Science* **253**, 173 (1991).

³ S. Hosoki, S. Hosaka, and T. Hasegawa, *Appl. Surf. Sci.* **60/61**, 643 (1992).

⁴ D.-H. Huang, H. Uchida, and M. Aono, *J. Vac. Sci. Technol. B* **12**, 2429 (1994).

⁵ T.-C. Shen, C. Wang, G. C. Abeln, J. R. Tucker, and J. W. Lyding, *Science* **268**, 1590 (1995).

⁶ Y. Wada, T. Uda, M. Lutwyche, S. Kondo, and S. Heike, *J. Appl. Phys.* **74**, 7321 (1993).

⁷ X. Bouju, C. Joachim, and C. Girard, *Phys. Rev. B* **50**, 7893 (1994).

⁸ D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).

⁹ J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).

¹⁰ D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).

¹¹ K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, *Phys. Rev. B* **47**, 10 142 (1993).

¹² D. M. Bylander, L. Kleinman, and S. Lee, *Phys. Rev. B* **42**, 1394 (1990).

¹³ M. P. Teter, M. C. Payne, and D. C. Allan, *Phys. Rev. B* **40**, 12 255 (1989).

¹⁴ O. Sugino and A. Oshiyama, *Phys. Rev. Lett.* **68**, 1858 (1992).

¹⁵ E. Kaxiras and J. D. Joannopoulos, *Phys. Rev. B* **37**, 8842 (1988).

¹⁶ X.-P. Li and D. Vanderbilt, *Phys. Rev. Lett.* **69**, 2543 (1992).

¹⁷ X.-P. Li, D. Vanderbilt, and R. D. King-Smith, *Phys. Rev. B* **50**, 4637 (1994).