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# Stacking sequence preference of pristine and hydrogen-terminated Si nanowires on Si(111) substrates

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The hexagonal versus cubic structural preference in vertically grown silicon nanowires on Si(111) substrates is systemized by using first-principles pseudopotential calculations. The calculated formation energy for pristine and H-terminated silicon nanowires with both hexagonal and cubic stacking sequences demonstrates that the stability depends on hydrogen chemical potential and the hexagonal-type nanowires are energetically favorable over a wide range of hydrogen chemical potential. This preference offers a possible origin for little detection of the [111]-oriented silicon nanowires with small diameters, qualitatively consistent with experimental findings.

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One-dimensional semiconductor nanostructures are expected to play a key role in future nanotechnology as well as to provide model systems to demonstrate quantum size effects.[1] Silicon nanowires (Si NWs) are in particular attracting great interest for their compatibility with conventional Si-based technology. So far, Si NWs of diameters below 10 nm have been synthesized by solution techniques,[2] an oxide-assisted catalyst-free method,[3–5] and a metal-catalytic vapor-liquid-solid (VLS) method.[6–9] In spite of considerable attention experimentally, the growth control of single crystal Si NWs with diameters approaching molecular dimension has been difficult because they usually have large diameter distribution and contain bulk defects and a thick surface oxide layer.

Recently, Si NWs fabricated by using an Au nanocluster-catalyzed VLS method have been shown to be the controlled growth of molecular-scale Si NWs: High-resolution transmission electron microscopy shows that Si NWs are single crystal with little or no visible amorphous oxide down to diameters as small as 3 nm.[8] Furthermore, it has been shown that, importantly, the smallest-diameter NWs are grown primarily along the [110] direction while the NWs with large diameters are grown along the [111] direction, implying that the nanowire formation along the [111] direction is suppressed for small diameters less than 10 nm. Since the crystal structure of these Si NWs is characterized by the cubic (diamond) structure (an *ABCABCABC*… sequence along the [111] direction) as seen in the bulk, the suppression of single-crystal Si NWs along the [111] direction seems to be due to the incorporation of Si NWs with different stacking sequences. Actually, the formation of the hexagonal-type sequence (an *ABABAB*… sequence) has been observed in the cubic-type sequence as stacking faults.[5] It is thus expected that the relative stability between hexagonal and cubic stacking sequences in Si NWs is different from that of the bulk case.

From a theoretical viewpoint, the electronic and optical properties of H-terminated Si NWs grown along the [100], [110], and [111] directions have been extensively investigated by using the *ab initio* calculations.[12–19] Yet most of these calculations have been performed by assuming the stacking sequence of atomic layers of Si NWs has been identical to that of the bulk. There are few studies for the structural stability taking account of stacking sequences. Furthermore, effects of H atoms that terminate surface dangling bonds (DBs) on the facets of NWs on the stability still remain unclear. Therefore, precise investigations with first-principles quantum mechanics are desirable to clarify the structural characteristics of Si NWs.

Here, we report structural stability of vertically grown Si NWs on Si(111) substrates based on total-energy electronic-structure calculations. Our calculations for Si NWs with diameters ranging from 8 to 28 Å demonstrate that the stability of Si NWs depends on hydrogen chemical potential. Although the hydrogen passivation stabilizes the cubic-type nanowires, the hexagonal-type nanowires are energetically favorable over a wide range of hydrogen chemical potential. This prediction is a possible explanation for experimental absence of small-sized single-crystal Si NWs along the [111] direction.

Figure 1 depicts the schematic of Si NWs considered in this study. In addition to NWs with cubic stacking sequence (*c*-NWs) [Figs. 1(a) and 1(b)], we adopt NWs with hexagonal stacking sequence (*h*-NWs), as shown in Figs. 1(c) and 1(d). Effects of different ordered stacking sequences are clarified for diameters between 8 and 28 Å. We consider both pristine and H-terminated Si NWs with hexagonal shape which is assumed from the crystal symmetry consideration: The structure consisting of hexagonal rings can minimize the number of surface DBs for a certain diameter; i.e., *c*-NWs and *h*-NWs are surrounded by six {110} and $\{\bar{1}100\}$ side wall facets normal to (111) and (0001) planes, respectively. We here denote the NWs by the number of Si and H atoms in the unit cell. In addition to these hexagonal-shaped NWs, the *h*-NWs in a triangle shape, $Si_{26}$ and $Si_{26}H_{18}$, are also considered in order to determine the relative stability between *c*-NWs and *h*-NWs at diameter $d_{NW}$ $\approx 9.0$ Å.

The calculations have been performed within the generalized gradient approximation[20] (GGA) in density functional theory.[21,22] To describe electron-ion interaction, we use norm-conserving pseudopotentials.[23] The conjugate-gradient technique[24,25] is utilized both for the electronic structure calculation and for the geometry optimization. In the optimized

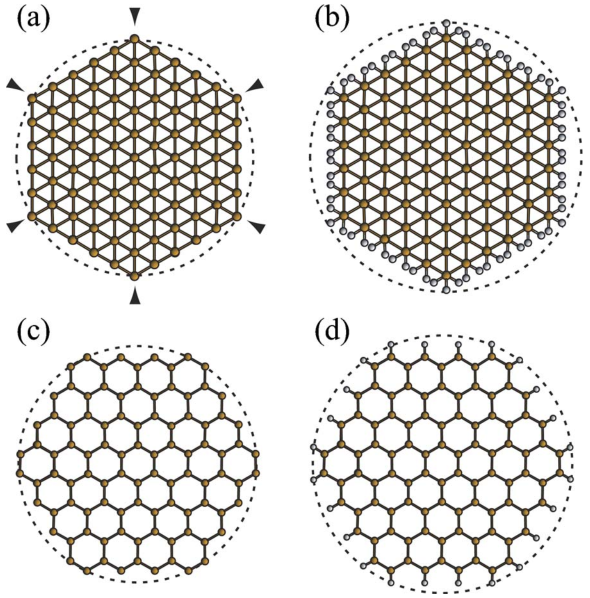


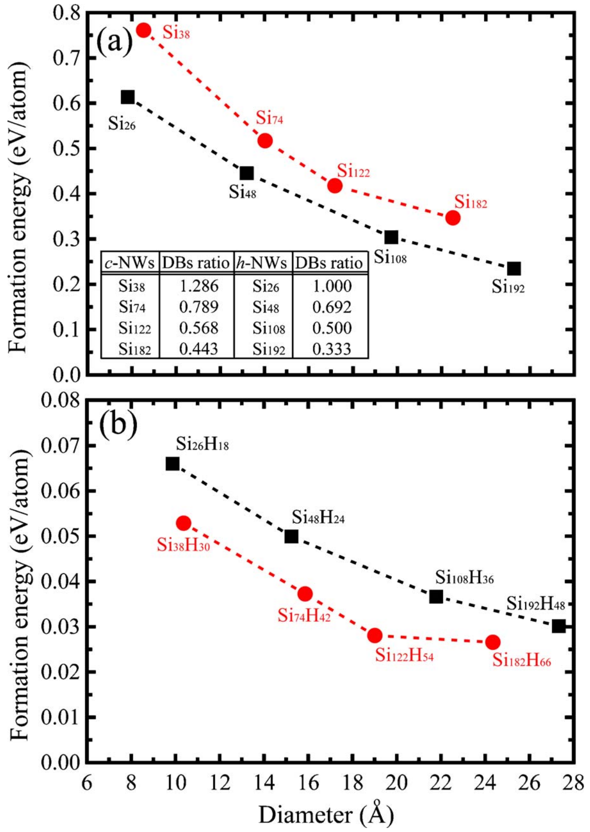
FIG. 1. (Color online) Cross-sectional view of (a) pristine *c*-NW ($Si_{182}$), (b) H-terminated *c*-NW ($Si_{182}H_{66}$), (c) pristine *h*-NW ($Si_{192}$), and (d) H-terminated *h*-NW ($Si_{182}H_{48}$). Brown (large) and white (small) circles denote Si and H atoms, respectively. Diameter of nanowire is defined as that of a circle precisely enclosing a hexagonal wire. Arrowheads indicate two-coordinated atoms located at the corners of NW facets.

geometries the remaining forces acting on the atoms are less than $7.0\times10^{-3}$ Ry/Å. The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 10 Ry which gives enough convergence of total energy to discuss the relative stability. We employ a supercell in which a nanowire is placed with its facets being separated by ~7 Å from those of adjacent NWs. The number of periodic double layers along the nanowire is two (three) for nanowires with hexagonal (cubic) stacking sequence. The four *k*-points for cubic structure and the six *k*-points for hexagonal structure, both of which are folded into the two *k*-points sampling in the least common multiplied supercell with six double layers, are used in the integration over the one-dimensional Brillouin zone. The present *k*-points sampling is found to provide sufficient accuracy in the total energies.[26]

In order to determine the stability of Si NWs, we calculate the formation energy $\Omega$ (Ref. 27) written as

$$\Omega = E_{\mathrm{tot}} - n_{\mathrm{Si}}\mu_{\mathrm{Si}} - n_{\mathrm{H}}\mu_{\mathrm{H}} + n_{\mathrm{H}}e_z, \quad (1)$$

where $E_{tot}$ is the total energy of Si NWs in the supercell, $\mu_{\mathrm{Si}}$ ($\mu_{\mathrm{H}}$) the chemical potential of an Si (H) atom, $n_{\mathrm{Si}}$ ($n_{\mathrm{H}}$) the number of Si (H) atoms, and $e_z$ the zero-point energy of Si-H vibrations. The value of $\mu_{\mathrm{Si}}$ is equal to that in bulk Si and the zero of $\mu_{\mathrm{H}}$ is taken to be the chemical potential at which the formation energy of $SiH_4$ is equal to zero. The value of $e_z$ is taken to be 0.21 eV which corresponds to the zero-point energy per H atom in $SiH_4$. Since the number of Si atoms per unit length is almost the same among Si NWs with close diameter, the Si-Si vibrational contribution to the formation energy are assumed to be equal and therefore cancel out of



| *c*-NWs | DBs ratio | *h*-NWs | DBs ratio |
|---|---|---|---|
| $Si_{38}$ | 1.286 | $Si_{26}$ | 1.000 |
| $Si_{74}$ | 0.789 | $Si_{48}$ | 0.692 |
| $Si_{122}$ | 0.568 | $Si_{108}$ | 0.500 |
| $Si_{182}$ | 0.443 | $Si_{192}$ | 0.333 |

FIG. 2. (Color online) Formation energy (in eV/atom) of (a) pristine and (b) H-terminated Si NWs with cubic and hexagonal stacking sequences as a function of nanowire diameter $d_{\mathrm{NW}}$. Squares and circles denote the formation energies of cubic and hexagonal structure, respectively. The zero of the formation energy corresponds to the energy bulk Si. The energy of $\mu_{\mathrm{H}}$ corresponds to the energy of $SiH_4$ molecule at zero temperature.

the relative stability. Thus, we neglect the zero-point energy of Si-Si vibration in Eq. (1).

Figure 2(a) shows the calculated $\Omega$ of pristine Si NWs as a function of the nanowire diameter. For both *c*-NWs and *h*-NWs, $\Omega$ per Si atom converges into that of bulk Si. This is because the ratio of corner and facet atoms to the total number of atoms decreases with increasing the diameter. The figure also shows that $\Omega$ of *h*-NW is ~0.1 eV/atom lower than that of *c*-NW with close diameter, indicating that the hexagonal stacking sequence is more preferable than the cubic one. Our analysis of structural characteristics shows that for pristine NWs the relative stability between *c*-NWs and *h*-NWs can be explained by the contribution of surface atoms on the NW facets to the total energy. In addition to three-coordinated atoms formed on {110} facets of *c*-NWs, two-coordinated corner atoms [arrowheads in Fig. 1(a)] each of which is bonded with three-coordinated atoms are inevitably formed in the optimized pristine *c*-NWs. Six dimers consisting of two- and three-coordinated atoms are totally formed in the unit cell of *c*-NWs. On the other hand, all of $\{\bar{1}100\}$ facet atoms in the optimized pristine *h*-NWs are three-coordinated. As a result, the ratio of DBs to the total number of atoms in *c*-NWs listed in Fig. 2(a) takes a large value compared with

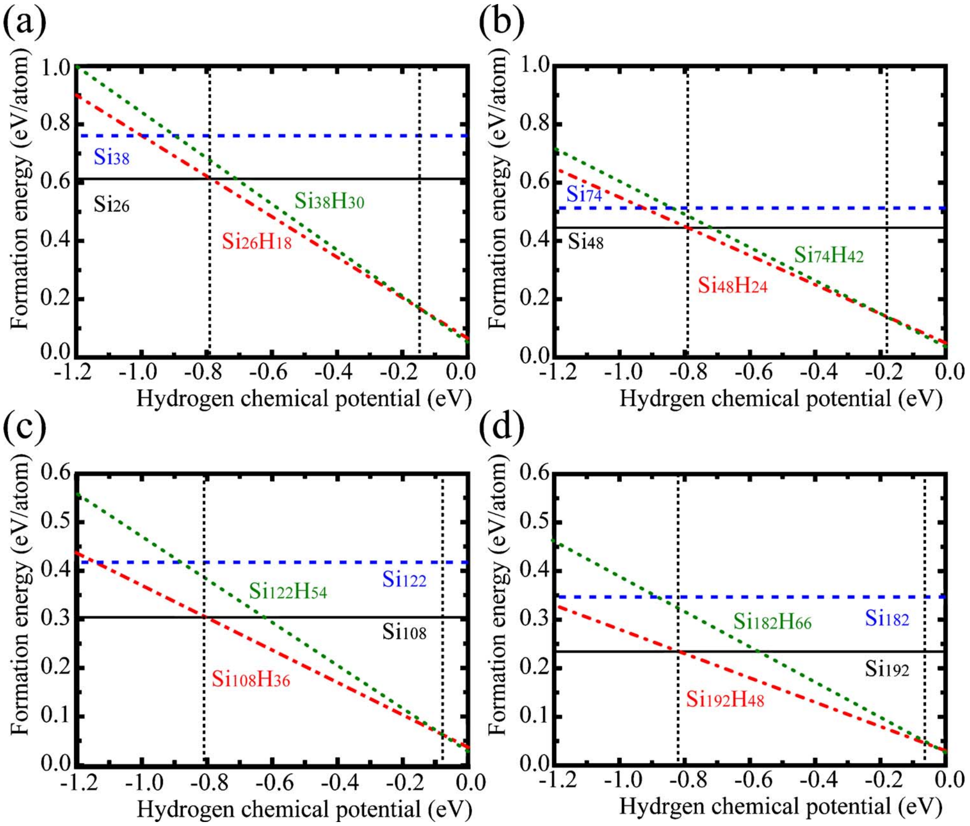


FIG. 3. (Color online) Formation energy (eV/atom) of (a) $Si_{26}$, $Si_{26}H_{18}$, $Si_{38}$, and $Si_{38}H_{30}$; (b) $Si_{48}$, $Si_{48}H_{24}$, $Si_{74}$, and $Si_{74}H_{42}$; (c) $Si_{108}$, $Si_{108}H_{36}$, $Si_{122}$, and $Si_{122}H_{54}$; and (d) $Si_{192}$, $Si_{192}H_{48}$, $Si_{182}$, and $Si_{182}H_{66}$ as a function of hydrogen chemical potential $\mu_H$. The origin of $\mu_H$ is the value at which the formation energy of $SiH_4$ is zero.

that in *h*-NWs with close diameter, leading to the higher formation energy in *c*-NWs.

Figure 2(b) shows $\Omega$ of H-terminated NWs as a function of the nanowire diameter. Here, we assume that the energy of $\mu_H$ is the energy of $SiH_4$ molecule at zero temperature. The $\Omega$ per Si atom for H-terminated *c*-NWs is found to be lower than that of *h*-NWs with close diameter. Since the ratio of Si-H bonds in H-terminated *c*-NWs is larger than that of H-terminated *h*-NWs, the adsorption energy of hydrogen with the Si-H bond form ($\sim$0.84 eV) results in the stabilization of *c*-NWs. In spite of this stabilization, the energy differences between *c*-NWs and *h*-NWs are less than 0.01 eV/atom. The small energy difference thus implies the bistability forming both *c*-NWs and *h*-NWs at zero temperature.

Structural trends of Si NWs are found from the formation energy diagrams as a function of hydrogen chemical potential. Figure 3 shows $\Omega(\mu_H)$ of pristine and H-terminated NWs with close diameter as a function of $\mu_H$. When $\mu_H$ is larger than $\sim -0.1$ eV, H-terminated *c*-NWs are energetically favorable. H-terminated *h*-NWs are stabilized for $-0.8 < \mu_H < -0.2$ eV, while pristine *h*-NWs are stable if $\mu_H < -0.8$ eV. Therefore, *h*-NWs is shown to be energetically favorable over a wide range of $\mu_H$. Since $\mu_H$ is expected to take considerably lower value during nanowire synthesis in an $H_2$ environment, it is likely that pristine or H-terminated *h*-NWs are stable structures. Our estimation of $H_2$ gas temperature using partition function including both rotational and zero-point vibration energies[28] actually shows that $\mu_H = -0.8$ eV corresponds to the temperature of 390 °C. Since Si NWs employing the VLS method are fabricated at temperatures ranging from 365 to 495 °C,[6–9] the estimated temperature indicates that pristine or H-terminated *h*-NWs are preferentially synthesized during the nanowire growth.

Furthermore, our extrapolation of the formation energy can explain the experimental fact that single-crystal Si NWs grown along the [111] direction are hardly observed for diameters below 10 nm. The estimated formation energy difference between *c*-NWs and *h*-NWs at $\mu_H = -0.8$ eV obtained from a simple formula,[30] which is expressed by the energy loss due to DBs (0.87 eV per dangling bond) and the energy difference in the bulk phase (12 meV/atom), is found to be less than ±5 meV/atom for $d_{NW} \approx 10$ nm. The small energy difference indicates the bistability, leading to the exhibition of polytypes. Therefore, the synthesis of single-crystal Si NWs along the [111] direction is expected to be difficult, qualitatively consistent with experimental findings.[8]

Finally, we comment on the electronic structures of Si NWs.[29] For pristine NWs the calculated gap energy, which is defined by the energy difference between the highest occupied (HO) and lowest unoccupied (LU) states, is smaller than that of bulk Si (0.6 eV) and there is no size dependence in the gap energy. This is because both the HO and LU states correspond to the electronic states induced by DBs. In contrast, the gap energy of H-terminated NWs is $\sim$1.9 eV larger than that of bulk Si and decreases with increasing the nanowire diameter, qualitatively consistent with previous calculations.[10–18] The increase of the gap energy in H-terminated NWs, therefore, should be due to quantum confinement effects. We note that the gap energy of Si NWs for $d_{NW} \leqslant 10$ Å deviates from the $1/d_{NW}^2$ relation, indicating that the contribution from nanowire facets to the electronic structure might not be negligible.

In summary, the relative stability between hexagonal and cubic stacking sequences of vertically grown Si NWs on Si(111) substrates is systematically investigated based on first-principles calculations. We have found that the structural trends in Si NWs are due to the contribution of surface dangling bonds on the nanowire facets to the formation energy. The energy difference between cubic and hexagonal structures for pristine NWs has shown that the *h*-NWs are energetically favorable over the *c*-NWs. We have also found that the stability of H-terminated Si NWs depends on hydrogen chemical potential and *h*-NWs are stable over a wide range of hydrogen chemical potential. Although the relative stability between different growth directions including *h*-NWs should be investigated in subsequent calculations, the results imply that little detection of Si NWs grown along the [111] direction for small diameter could be attributed to the structural preference in Si NWs being different from that in the bulk phase.

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