Sharp Corners in the Cross Section of Ultrathin Si Nanowires

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We have determined stable geometries for pristine Si nanowires grown along their ⟨100⟩ axis through systematic density functional studies. Strikingly, Si nanowires with diameters smaller than 1.7 nm prefer a shape that has a square cross section. This stems from dimerization between corner atoms and also from benign reconstruction patterns that maximally saturate Si dangling bonds.

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One-dimensional nanostructures are essential building blocks for potentially innovative electronic and photonic applications such as nanoswitches, single electron transistors, optoelectronic units, and chemical sensors [1–7]. Because of their compatibility with existing Si-based technologies, thin Si nanowires (SiNWs) a few nanometers in diameter are particularly important and have attracted extensive attention [7–19]. To tailor their physical properties, it is essential to determine the energetic preference of different atomic structures as the wires shrink to nanometer or subnanometer wide. As was well established through studies for nanoclusters [20], geometries that produce local energy minima correspond to high abundance in fabrication and hence are of the foremost importance in physical responses. According to the Wulff plot constructed with tabulated surface energies, thick SiNWs adopt a cylindrical or prism shape with a core that preserves the diamond structure [21–23]. Therefore, sharp corners are often replaced by mini-facets in most theoretical studies for SiNWs [22–27]. Nevertheless, this conjecture is dubious for SiNWs thinner than 1–2 nm in diameter since the environment is drastically changed for almost all atoms [21] and, furthermore, the surface energies are no longer well defined for small facets a few atoms wide. To the best of our knowledge, the instability of the corner atoms in nanowires has never been directly established. The Wulff plot allows sharp corners in the continuum limit. For nanoscale systems, especially for semiconductor nanowires and clusters, it is also possible that the presence of corner atoms enhances the formation energy by facilitating the formation of benign reconstruction patterns. Theoretical assessments for the most probable shapes of small nanowires, including the “extraordinary” ones, are highly desirable.

In this Letter, we present results of systematic *ab initio* calculations for pristine SiNWs grown along their ⟨100⟩ axis. Strikingly, we found for the first time that structures with sharp corners in the cross section are strongly preferred for ultrathin SiNWs and our studies reveal why this happens. Our findings demonstrate that, although certain geometries for small nanowires might appear to be unfavorable according to the Wulff plots, they should not be immediately excluded from further studies.

The calculations were performed in the framework of density functional theory with the generalized-gradient approximation and ultrasoft pseudopotentials as implemented in the Vienna *ab initio* simulation package (VASP) [28]. We used an energy cutoff of 300 eV for the plane-wave basis functions. The size of the supercells in the lateral plane was adjusted to maintain a sufficiently large separation between adjacent wires (>15 Å from surface to surface). We used 8 k points in the essentially one-dimensional Brillouin zone. Test calculations with more k points and larger energy cutoffs indicated that total energies converge to better than 10 meV/cell with these parameters. Atomic positions were optimized for all configurations with a criterion that requires the maximum force on all atoms to be smaller than 0.01 eV/Å.

As shown in the inset of Fig. 1, the initial nanowire geometries were taken from the diamond structure. Three different atomic arrangements in the cross section were investigated: the complete square (A type), removal of the single corner atom (B type), and removal of four corner atoms (C type). We also extended the periodicities by 2 and 4 times along the axis to examine possible complex reconstruction patterns. Superstructures along the axis, including the semimetallic $2c$ structure reported recently by Rurali and Lorente [27], are unstable in our total energy calculations [29]; therefore we focused only on results obtained from a single cubic cell along the axis. The sizes of wires are characterized by either the number of atoms per cell, N, or the number of two-dimensional primitive cells across the edges in the cross section, N_L (e.g., $N_L = 5$ in the inset of Fig. 1). To identify stable structures of SiNWs under different conditions, we define formation energy per atom:

$$E_{b,\mathrm{SiNW}} = E_{\mathrm{total}}/N - E_{\mathrm{atom}}. \qquad (1)$$

Here E_{total} is the total energy of SiNWs and E_{atom} is the total energy of an isolated Si atom. As is now standard with

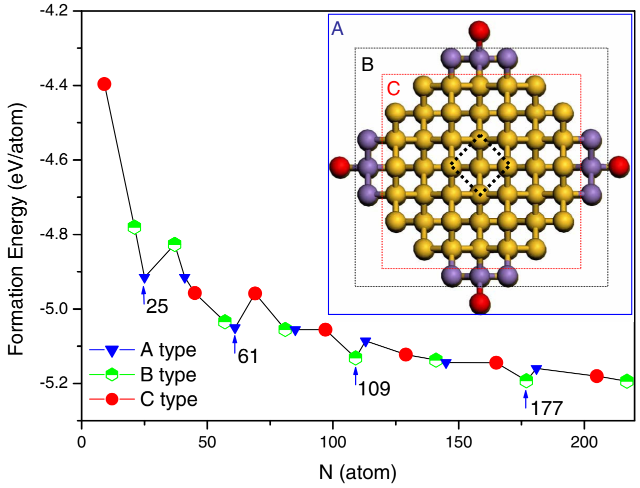

FIG. 1 (color online). The calculated formation energies of different SiNWs. Arrows show the positions of magic structures. The inset shows A-, B-, and C-type geometries before relaxation with $N_L = 5$.

studies for nanoclusters, local minima in the $E_{b,\mathrm{SiNW}}(N)$ curve imply high abundance and the corresponding values of N are called "magic numbers." Several obvious dips can be found in the $E_b(N)$ curve in Fig. 1, indicating the existence of highly probable sizes and shapes for SiNWs. Note that these "magic" structures correspond to cases with odd N_L, a phenomenon which stems from the fact that all surface atoms can be dimerized so that the dangling bonds are maximally saturated. For SiNWs with even N_L, at least one surface atom has to be left alone in the cross section, an obviously unfavorable choice for Si.

The C-type structure remains higher in energy compared to the A- and B-type structures. For large wires, this can be explained by noting that the surface energy of Si(110) is larger than that of Si(100) (1.43 $\mathrm{J\,m^{-2}}$ vs 1.36 $\mathrm{J\,m^{-2}}$) [30] and hence the exposure of large Si(110) surface areas in the C-type structure is unfavorable. Although surface energies become strictly meaningless for small SiNWs, it appears that Si atoms prefer reconstructed (001) facets but have difficulties arranging dangling bonds on the (110) facets where Si atoms are threefold coordinated already. As a result, Si atoms in the middle of the (110) facet in the unfavorable C-type structure are unpaired in Fig. 2(c). Interestingly, the fourfold symmetry is preserved with high stability after atomic relaxation procedures, even starting from asymmetrically distorted geometries. Although the facets reconstruct very differently, the Si-Si bond lengths in the three-type SiNWs differ only slightly (within a range of 0.08 Å), and the reconstructions are mainly accomplished by twisting bond angles.

One fascinating finding here is that SiNWs with $N_L \leq 5$ adopt the A-type arrangement, i.e., with the presence of corner atoms. This is significant for tailoring properties of SiNWs since the corner atoms are expected to behave very differently from other surface atoms. To address why the "corners" are preferred in small SiNWs, it is instructive to analyze the corner energy, defined as

$$E_{\mathrm{corner}} = \tfrac{1}{4}(E_{A,\mathrm{total}} - E_{B,\mathrm{total}}) - E_{\mathrm{atom}}, \tag{2}$$

where $E_{A,\mathrm{total}}$ and $E_{B,\mathrm{total}}$ are the total energies of SiNWs in A-type and B-type structures with the same N_L. For direct comparison, we also define formation energies for each surface and bulk Si atoms based on total energies from separate calculations for a clean reconstructed 12-layer Si(001) slab [using a $p(2 \times 2)$ supercell in the lateral plane], $E_{\mathrm{slab,total}}$, and for the cubic bulk Si, $E_{\mathrm{bulk,total}}$ (for each atom):

$$E_{b,\mathrm{Si(001)}} = [E_{\mathrm{slab,total}} - (N_{\mathrm{slab}} - N_{\mathrm{surface}})E_{\mathrm{bulk,total}}]/N_{\mathrm{surface}} - E_{\mathrm{atom}}, \qquad E_{b,\mathrm{bulk}} = E_{\mathrm{bulk,total}} - E_{\mathrm{atom}}. \tag{3}$$

Here N_{slab} and N_{surface} stand for the number of total atoms and the number of surface atoms in the supercell of Si(001), respectively. As a general rule, the corner atoms are stable as long as E_{corner} is lower than $E_{b,\mathrm{SiNW}}$ (the lowest among A-, B-, and C-type structures for a given N_L), since they gain more energy by taking the corner sites than by drifting away to other SiNW sites nearby. As shown in Fig. 3, this criterion is satisfied for cases with $N_L \leq 5$. On the two extremes, the asymptote of E_{corner} for large N_L is about 0.5 eV higher than $E_{b,\mathrm{Si(001)}}$ and hence sharp corners are unfavorable and Si atoms would rather drift away to a flat surface or to other SiNWs. At the other end, E_{corner} becomes even more negative than $E_{b,\mathrm{bulk}}$ for $N_L = 3, 4$, indicating the high stability of the corner atoms on small SiNWs.

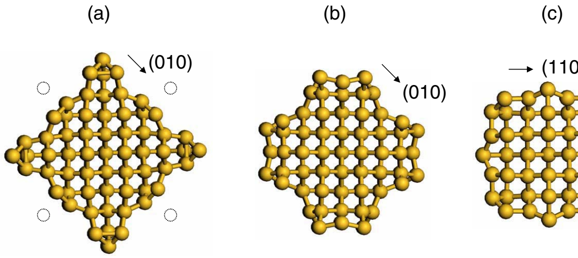

FIG. 2 (color online). Cross-section view of relaxed atomic configurations of SiNWs in three initial geometries with $N_L = 5$.

To further confirm the stability of the symmetric A-type structure against asymmetric distortions, we performed calculations for various alternative structures for SiNWs with $N_L = 5$. These structures were constructed by moving the corner atoms from the A-type structure to different positions as monomers, dimers, and trimers as well as corner-dimer and corner-trimer pairs. Structural relaxa-

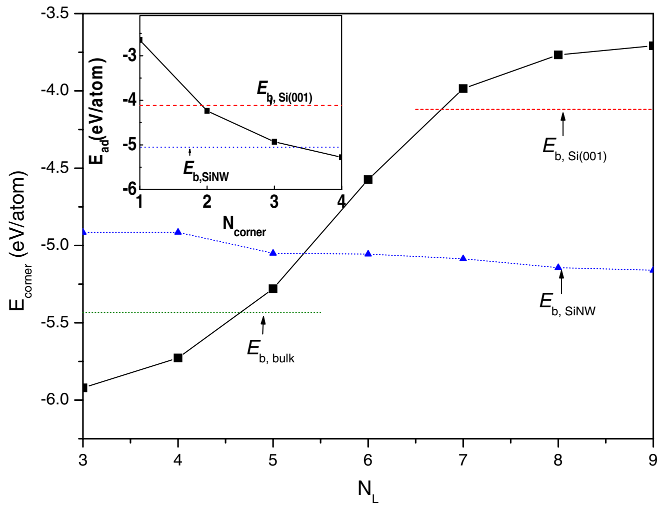

FIG. 3 (color online). The corner energies extracted from data in Fig. 1 for SiNWs of different sizes, along with the formation energies per Si atom in different environments. The adsorption energies of the corner atoms are shown in the inset.

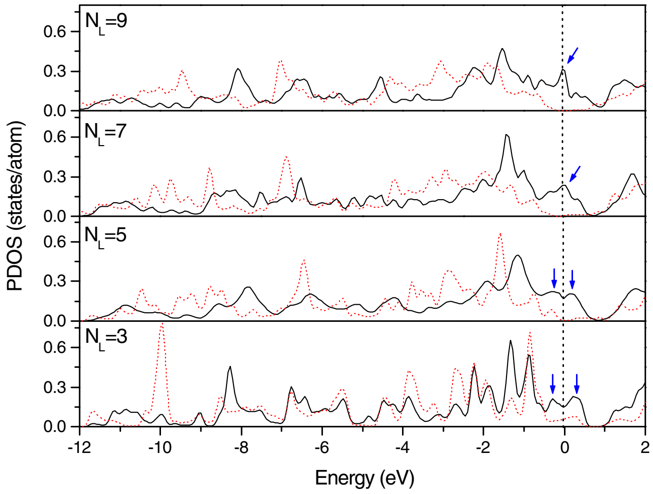

FIG. 4 (color online). Results of the projected density of states (PDOS) of the central (dotted lines) and corner (solid lines) Si atoms in the A-type SiNWs with different N_L. Arrows highlight the corner states.

tions were performed with different initial conditions, including the relaxed A- and B-type geometries as well as unrelaxed geometries. It was found that all these asymmetric operations increase the total energy of SiNWs by at least 0.98 eV from the symmetric A-type structure. Note that the energy comparisons are done between systems with the same number of atoms. These results clearly indicate the strong preference of the A-type structure for small SiNWs.

The enhancement in E_{corner} for thin SiNWs can be attributed to two factors: intercorner interaction and the formation of benign reconstruction patterns. The first factor can be appreciated from the energy splitting in the projected density of states (PDOS) around the Fermi level, displayed in Fig. 4 for both central (dashed lines) and corner (solid lines) Si atoms. For thick SiNWs the PDOS for the central atom is very close to that of the bulk Si and a sizable gap can be found around E_F. In contrast, the PDOS for the corner Si atom displays a sharp peak at the Fermi level. When N_L decreases to 3–5, this peak eventually splits in two, assigned to superbonding and superantibonding states, with an energy separation of 0.5 eV. The deep ditches in PDOS at E_F enhance the formation energy and thereby help stabilize the A-type structures for small SiNWs. The long range intercorner interaction across a distance of 13.08 Å is understandable since the screening lengths in semiconductors are typically large.

Finally, we performed calculations for SiNWs ($N_L = 5$) with different numbers of corner atoms and defined the energy difference from the B-type structure as the adsorption energy:

$$E_{\mathrm{ad}} = \frac{1}{N_{\mathrm{corner}}}(E_{\mathrm{total}} - E_{B,\mathrm{total}}) - E_{\mathrm{atom}}, \tag{4}$$

where N_{corner} is the number of corner atoms. As shown in the inset of Fig. 3, E_{ad} increases monotonically with N_{corner}. This again indicates that strong interaction amongst corner atoms, both structurally and electronically, promotes the stability of the A-type structure. Note that E_{ad} is lower than $E_{b,\mathrm{Si}(001)}$ from $N_{\mathrm{corner}} \geq 2$, but is higher than $E_{b,\mathrm{SiNW}}$ till $N_{\mathrm{corner}} = 4$. Only the simultaneous presence of four corner atoms makes the A-type structure more stable for the 5-layer SiNWs. If one corner atom is added to the B-type structure, it is more likely to stay on a flat surface or drift to other SiNWs nearby, according to the energy argument outlined above. This explains the existence of magic numbers for SiNWs, since "coherence" amongst several atoms is important in small structures. For cases with $N_{\mathrm{corner}} = 2$, the two corner atoms can be placed either on the same surface or across the diagonal. We found that the former is lower in energy by about 1.05 eV because of (i) the formation of a better reconstruction pattern in one facet and (ii) the stronger intercorner interactions across a shorter distance.

In conclusion, we have conducted extensive *ab initio* studies to search for stable geometries of $\langle 100 \rangle$ SiNWs. One of our main findings is the existence of magic numbers for nanowires, a topic that deserves much attention in the future. Furthermore, SiNWs with $N_L \leq 5$ were found to adopt sharp structures with corners, driven by the combination of surface reconstruction and strong intercorner interaction. These findings are important for guiding the syntheses of Si nanowires and also Si nanoclusters in a controlled manner and for tailoring their physical properties for different exploitations.

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