Stability and Mechanical Properties of Silicon Nanowires

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This work focuses on the structure, stability, and mechanical properties of silicon nanowires (SiNWs) oriented along the ⟨111⟩ direction. A total energy calculation and a quenching-technique based on a non-orthogonal tight-binding molecular dynamics (MD) is used to study the equilibrium structure and relative stability of SiNWs of different diameters (d) ranging from 2 nm to 17 nm. Our study of the structural relaxation of wires of different diameters reveal the following two key findings: (i) A SiNW is composed of a crystalline core surrounded by a bond distortion-dominated surface region, and (ii) the width of the surface region is found to be ~1 nm and is independent of the diameter of the wire. These findings suggest that there exists a critical diameter (~2 nm) below which a crystalline nanowire becomes unstable due to surface–surface interaction. We have also calculated the surface energy (E_s) for wires of different diameters (d), where the E_s versus d curve exhibits several local minima. A more careful study of the local minimum at d ~ 6 nm finds this minimum to be very sharp. The existence of local minima in the surface energy curve is indicative of the existence of magic diameters for SiNWs, while the sharpness of the minima is related to the existence of uniform-diameter wires. A study of the Young’s modulus of the ~6 nm-SiNW suggests that surface effects are critically important in determining the mechanical properties of nanowires with the value of the Young’s modulus reduced from its bulk value by about 40%.

Keywords: Silicon, Nanowire, Axial Orientation, Mechanical Properties, Surface Reconstruction.

1. INTRODUCTION

In recent years, there have been intensive efforts devoted to the study of synthesis and characterization of silicon nanowires (SiNW). Silicon nanowires with high aspect ratio, namely diameters with nm-sizes and lengths with µm-sizes, are expected to endow the SiNWs with unusual electrical, optical, mechanical, and chemical properties. The research activities on SiNWs are closely linked to the effort of exploring the potential of these interesting electrical and optical properties for device applications. For example, in addition to the possibility of improving the optical properties of the bulk silicon which is an indirect gap material, SiNWs may also have the potential for other device applications from probe microscope tip to interconnects and functional components in nanoelectronics.

Large quantities of SiNWs have been grown by the metal nano-particle-mediated vapor–liquid–solid (VLS) method and the oxide-assisted growth (OAG) method. Properties of SiNWs are expected to be strongly orientation- and size-dependent. The growth direction for SiNWs synthesized by the VLS method is along ⟨111⟩. On the other hand, the growth direction for SiNWs produced by the OAG method has been mainly along ⟨112⟩, with some along the ⟨111⟩. In addition, SiNWs grown by the VLS method exhibit narrow diameter-distributions while those grown by the OAG method show broad diameter-distributions. These observations suggest that the method of synthesis plays an important role on the growth of stable SiNWs. It has been discovered recently that the growth direction of a SiNW also depends on its diameter. It is suggested that the interplay of the liquid–solid interfacial energy with the silicon surface energy is responsible for the diameter dependence of the growth direction.

In this work, we report our study on the energetics, the stability, and the mechanical properties of SiNWs with its long axis along the ⟨111⟩ direction. We chose to first study this system because SiNWs grown along the ⟨111⟩ direction have narrow diameter distributions and hence could be diameter-selective. It is known that there are no magic numbers in the stability for Si nanoclusters. But, with its unique shape
(i.e., a quasi-one dimensional structure with a high aspect ratio), could there be magic diameters for a SiNW? Specifically, is the observed 6 nm-diameter for SiNWs grown along the (111) direction a critical size for the growth of "straight" SiNW? Because SiNWs are quasi-one dimensional nanostructures, their properties cannot be predicted simply by scaling down bulk properties due to quantum size effects. The issue here is then what is the critical size for the nanowire (NW) when quantum effects start to emerge and how the properties of the NW depend on the diameter. This paper provides the novel reasoning behind the stability of nanowires by performing a total energy calculation of wires of different diameters using the non-orthogonal tight-binding Hamiltonian.

2. METHOD

To examine how the stability of a NW with its axis oriented in the (111) direction depends on its diameter, we must carry out the energy optimization calculation for that NW as a function of its diameter. Because of our interest in understanding the underlying physics governing the stability of a NW of a given diameter, we choose to use quantum mechanics-based molecular dynamics (MD) simulations to carry out the energy optimization. To cover the range of distribution of diameters of the experimentally grown NWs, we will model the NWs with diameters ranging from 2 nm to about 17 nm. The implementation of quantum mechanical MD simulations for the energy optimization calculations for systems of these sizes will require considering MD cells with the number of atoms N from about 100 to over 10,000. Such simulations are not currently feasible for methods based on density functional theory (DFT). It is even computationally excessive for methods based on tight-binding approaches. The bottleneck in both cases is the scaling of the computational cost with N and the atomic forces where N is the size of the system under consideration. Recently, we have developed an Order-N non-orthogonal tight-binding molecular dynamics (O(N)/NOTB-MD) scheme to circumvent the bottleneck of N^3 scaling. In this scheme, the calculation of the total energy as well as the atomic forces scales linearly with the size of the system. The unique feature of this scheme is that both the total energy and the atomic forces are determined by the same O(N) procedure so that there is no additional overhead in the calculation of the atomic forces. In addition, the O(N) procedure is readily amenable to parallel programming. Therefore, this O(N)/NOTB-MD scheme provides an excellent means to investigate systems of realistic sizes that are currently outside the scope of first principles MD simulations.

We have successfully applied the above-mentioned O(N)/NOTB-MD scheme to obtain the equilibrium configuration of a Si_{1000} cluster and to study the initial stage of growth of Si/Si(001). In these studies, we have used the NOTB Hamiltonian developed by Menon and Subbaswamy to model the interactions between Si atoms. This Hamiltonian has been shown to correctly predict the structural properties and the energetics for Si clusters of small and intermediate sizes. In our study of the initial stage of growth of Si/Si(001), we have carefully tested the Hamiltonian by calculating the energetics and the reconstruction Si(001) surface. Our results are in excellent agreement with DFT-based calculations as well as experimental results. We therefore will use this Hamiltonian to model Si nanowires in our study.

3. THE STRUCTURAL STABILITY AND MAGIC DIAMETERS FOR SILICON NANOWIRES

To study the stability of a SiNW with its long axis along the (111) direction as a function of its diameter, we have carried out the energy optimization for a series of NWs along (111) with diameters ranging from 2 to 17 nm, using our O(N)/NOTB-MD scheme. To start the MD simulations for the NW of a given diameter, the initial configuration is obtained by cutting a cylinder of that diameter out of the bulk silicon with its axis aligned along the (111) direction. In the simulations, the MD cell is composed of six layers of atoms and the periodicity is imposed along the (111) direction. Thus, L the length of the cell along the (111) direction, is equal to \( \sqrt{3} d \) with \( a \) being the length of the cube edge of the cubic cell defining the diamond lattice. The relationship between the number of atoms in the cell and the diameter \( d \) is given by \( N = (1/4) \pi d^2 L_{bulk} \rho_{bulk} \) with \( L_{bulk} = \sqrt{3} a_{bulk} \), \( a_{bulk} \) being the length of the cube edge for the bulk silicon, and \( \rho_{bulk} = 8/a_{bulk}^3 \). The energy of the system decreases (at a decreasing rate) from that of the initial configuration as a function of time of the MD simulation. This MD quenching process continues until the energy fluctuation is less than 10^{-2} eV and the energy has reached its minimum. We have also repeated the simulation for a case corresponding to a periodicity of twelve atomic layers in the MD cell. We found no appreciable difference between the results of the equilibrium structure of the 12-layer cell and the corresponding structure of the 6-layer cell. Therefore, in the subsequent simulations, we have only used the 6-layer cell.

Figure 1 shows the cross-sectional view of the relaxed and reconstructed SiNW oriented along the (111) direction with a diameter of 5.88 nm (corresponding to 1262 atoms in the 6-layer MD cell). Within the resolution of the scale of the figure, the interior of the cross-section exhibits the hexagonal structure of the perfect (111) planes. This pattern is only disturbed in the vicinity of the surface where most of the relaxation and reconstruction occur. The relaxation and reconstruction of other SiNWs considered in this work show a similar pattern, namely, a core region exhibiting bulk crystal-like features and a surface region dominated by features associated with reconstruction and relaxation.
Fig. 1. A cross-sectional view of the six layers of the relaxed nanowire with 1262 atoms (~6 nm) along the (111) direction.

The symmetry pattern of the reconstruction shown in Figure 1 is a result of energy minimization and it is found to be a general feature of the nanowires under our investigation. The reconstruction is still symmetric even a small random distortion is introduced to the initial positions of the atoms cut from the bulk structure. Since the NWs are quasi-one dimensional systems with unusually large aspect ratio, they will have large surface to volume ratio. Therefore, surface properties such as surface reconstruction and relaxation are the key issues which determine the stability for NWs. While the surface reconstruction is the mechanism for the NW to eliminate or at least reduce the dangling bonds associated with the surface atoms, the reduction or elimination of the dangling bonds often comes at a price of creating distorted bonds. Thus, the approach to stability is a delicate balance between the lowering of the energy due to the reduction of the dangling bonds and increasing in energy due to the distortion of the bonding configurations. We have examined the issues related to the elimination of the dangling bonds and bond distortions by determining the number of bonds associated with each atom and the bond lengths in nanowires before and after relaxation, using a recipe given in Ref. [35]. Figure 2 shows the comparison of the number of bonds of each atom before and after relaxation for the SiNW with 1262 atoms in the MD cell. It can be seen that most of the exterior atoms of the unrelaxed NW have 3 bonds while some have 2 bonds as expected. After relaxation and reconstruction, the number of atoms with 4-fold coordinates has dramatically increased, the number of 3-fold coordinated atoms has decreased and there is no longer any atom with just 2 bonds. Figure 3 shows the results of bond-length before and after relaxation of the same nanowire. The small deviation of the bond length from the bulk value for outer atoms before relaxation is due to the fact that the formula used in Ref. [33] calculates the effective bond-length when an atom is not fully coordinated. It is seen that in the interior region (up to about 1 nm from the surface), there is a very small but uniform decrease in the bond length, while this is a substantial stretching of the bond length in the outer region (i.e., within about 1 nm from the surface boundary), after relaxation. This result indicates that, while the relaxation yields a very slightly more packed interior core for the NW, the majority of the bond distortions occur in the vicinity of the surface boundary. We believe this occurs as a result of reconstruction of surface atoms in an effort to lower the energy through reduction of dangling bonds. The newly formed bonds, and to a less degree the existing bonds close to the surface, show a variation of bond length due to geometrical constraints, as shown in Figure 3. Such variations of bond length have been documented in case of small Si clusters. To further

Fig. 2. A comparison of the number of bonds for atoms in the nanowire with 1262 atoms (~6 nm) before and after relaxation. Please note there is no atom with just two bonds after relaxation.

Fig. 3. A comparison of the bond lengths of in the nanowire with 1262 atoms (~6 nm) before and after relaxation.
delineate the concept of the NW as composed of a crystal-like core surrounded by a bond distortion-dominated surface region, we present in Figure 4 the plots of the change of the distance of atoms from the central axis of the NW before and after relaxation as a function of the distance from the axis for three SiNWs of diameter about 6 nm, 14 nm, and 17 nm, respectively. A comparison of the three plots gives a clear indication that the extent of the surface region where the majority of the displacements and thus the bond distortions occurs as a consequence of the relaxation and reconstruction is independent of the size (diameter) of the wire. Specifically, it appears that the surface region extends to about 1 nm (one may make a case for the width to be about 1–2 nm) from the surface boundary for all three cases. This then suggests that there exists a lower limit of about 2 nm for the diameter of the crystalline NW that can be fabricated. For NWs of smaller diameters, the two surface regions opposite to each other would overlap and there would be no core region left. In a sense, the width of the surface region, or more precisely, twice of such width, can be used to define the critical diameter for the nanowire below which crystalline structures would become unstable due to surface–surface interaction. The precise value of the width of the surface region and thus the critical diameter is expected to be dependent on the type of material and for a given material the orientation of the wire. Surface modification such as impurities may also change the width of the surface region. But the concept of the existence of such a critical dimension and its value being about twice the width of the surface region is expected to be applicable to any nanostructures. For example, for a nanoslab, the critical thickness can be expected to be about twice the width of the surface region. Recent studies indeed suggest cage-like structures for SiNWs for very small diameters, in agreement with the concept presented above.

In Figure 5, the surface energy of the NW is plotted as a function of the diameter. The surface energy $E_s$ in our calculation is defined by

$$E_s = \frac{E_{rod}(N) - E_{bulk}(N)}{A}$$

where $A = \pi d L$. $E_{rod}(N)$ is the total energy of the wire with $N$ atoms in the MD cell, and $E_{bulk}(N)$ the energy of $N$ Si atoms in the bulk. From Figure 5, it can be seen that the $E_s$ versus $d$ curve shows a general downward trend as the diameter increases as expected. There are varying degrees of fluctuations in the curve, with some local dips (minima) which might qualify as the “magic” diameters. Since our calculations have revealed that there might be a substantial dip in the surface energy in the vicinity of $d = 6$ nm and it is least expensive computationally to conduct a detailed study of the energetics in the vicinity of the local minima at $d \approx 6$ nm, we have, in addition to calculating the surface energy for a series of diameters from 2 to 17 nm at more coarse intervals, computed $E_s$ at five diameters in the vicinity of and very close to 6 nm. At these five diameters, there are 1250, 1262, 1274, 1298, and 1322 Si atoms in the respective MD cells. The outstanding feature of the surface energy curve in the vicinity of $d = 6$ nm is the extraordinarily sharp dip at $N = 1262$. It indicates that SiNWs with $N$ just slightly greater or smaller than 1262 are unstable with respect to the nanowire with $N = 1262$. This result is also an indication that it is energetically favorable to grow a straight nanowire of diameter close to 6 nm, since change of diameter in either direction at any point along the length of the wire would cost much more energy. We have not carried out an extensive search of other sharp minima at different diameters. It is difficult, if not impossible, to map out all the local minima of the surface energy as a function of the diameter of

Fig. 4. The change of the distance of atoms from the central axis of the nanowire before and after relaxation as a function of the distance from the central axis: (a) For the nanowire with a diameter of 6 nm; (b) for the nanowire with a diameter of 14 nm; (c) for the nanowire with a diameter of 17 nm.

Fig. 5. Surface energy of nanowires of various diameters. The solid circles are the results of our total energy calculations. The solid line, which simply connects all the data points, is to guide the eyes. The series of local minima suggests the possibility of existence of magic diameters.
the nanowire. For example, while Figure 5 seems to suggest a dip of surface energy at \( d = 14 \) nm, one can only be sure that there is at least one local minimum between \( d = 12 \) nm and \( d = 17 \) nm. The position of an actual minimum can be anywhere in-between and the sharpness of the minimum can only be mapped out by a series of very extended (and expensive) simulations. Nevertheless, Figure 5 shows clearly that the surface energy is not a monotonic function of the diameter (The sizes of the dips on the surface energy curve, as seen in Fig. 5, are much larger than the noise levels in the energy fluctuations during the quenching processes). It is quite likely that there are many minima. We propose that the existence of such minima explains that while nanowires of different diameters may be grown in a single experiment, the diameter of each nanowire is uniform because it corresponds to a local minimum. For example, uniform 6 nm Si nanowires have been grown experimentally.\(^3\)

It should be noted that in cases where metal nanoclusters are used as catalysts to mediate the growth of nanowires, sizes of the nanoclusters are known to play a very important role in determining the diameters of the nanowires.\(^3\)

4. MECHANICAL PROPERTIES OF SI NANOWIRES

In this section, we study the effect of reduced dimensionality and the quantum-size effect on the mechanical properties of silicon nanowires. The mechanical properties of a nanostructure are closely related to its stability. Since NWs are nanostructures with unusually large aspect ratio, this close relationship between the stability and mechanical properties is amplified. Therefore, we choose to use the calculation of the Young’s modulus of a NW to highlight this close relationship. The procedure for calculating the force constant of a NW with \( N \) atoms in the MD cell (with a given diameter and a given cross-section) is as follows. For a NW of a given diameter corresponding to a certain \( N \), its initial configuration is constructed for a cell length along the \( \langle 111 \rangle \) direction \( L = \sqrt{3}a \) as given in Section 3. The stable configuration corresponding to that \( L \) is obtained via the energy optimization process using the \( O(N) \)/NOTB-MD scheme. This process also yields \( E_{\text{eq}}(N, L) \), the total energy corresponding to the stable configuration for that \( L \). The total energy of the NW for a fixed \( N \) (with a given diameter) is then calculated for a series \( L \) to determine the equilibrium cell length \( L_0 \) (also the equilibrium “lattice constant” \( a_0 \)) by identifying the minimum of \( E_{\text{eq}}(N, L) \) which should occur at \( L = L_0 \). Figure 6 shows the plot of \( E_{\text{eq}}(N, L)/N \) versus \( a = L/\sqrt{3} \) for the NW with \( N = 1262 \) (\( d \approx 6 \) nm). It can be seen that the equilibrium “lattice constant” for the 6-nm SiNW is \( a_0 = 5.45 \) Å, very close to the equilibrium lattice constant of the bulk silicon (\( a_{\text{bulk}} = 5.46 \) Å) as determined from NOTB Hamiltonian used in this work.\(^3\) This result suggests that, even down to the size level of 6 nm-diameter, the “bulk” structure along the \( \langle 111 \rangle \) axial direction of the long cylinder is still approximately maintained (see also Fig. 1). What is even more interesting is that, in the range from \( a = 5.00 \) Å to \( 6.00 \) Å, the curve is symmetric with respect to \( a_0 \) and it can be fitted very nicely by a quadratic equation of \( a \). Thus the “force constant” for this NW is well defined and can be simply calculated in terms of the second derivative of \( E_{\text{eq}}(N, L) \) with respect to \( a \), which is \( N \) times the coefficient of \( a^2 \) of the fitted quadratic curve (\( \gamma \)). In this way, the Young’s modulus of the NW can be expressed as

\[
\gamma = \frac{F/A}{\Delta L/L} = 16 \gamma L_0^2
\]

The procedure outlined above for the calculation of the coefficient \( \gamma \) is undertaken by allowing the nanowire to fully relax at each step of stretching or compression. In the experimental determination of Young’s modulus by static loading, the time scale for measurements is much greater than the time scale for the system under consideration to relax. Therefore, the above procedure is a theoretical replica of the experimental determination of the Young’s modulus by static loading and its prediction should be compared with the experimental result obtained by static loading. The quadratic fitting of the curve in Figure 6 yields a value of \( \gamma = 0.27 \) eV/Å\(^2\). Substituting this value of \( \gamma \) into Eq. (2) leads to a Young’s modulus of \( 1.27 \times 10^{12} \) dyne/cm\(^2\) for a NW with a 6 nm-diameter.

The Young’s modulus of the bulk silicon crystal along the \( \langle 111 \rangle \) direction can be calculated in terms of bulk elastic stiffness constants \( c_{11} \), \( c_{12} \), and \( c_{44} \), using the following expression derived from the formulation given
in Ref. [41]:

\[
\frac{1}{Y_{111}} = S_{12} - 2[S_{11} - S_{12} - (1/2)S_{44}](l_1^2l_2^2 + l_2^2 + l_3^2 + l_3^2)\]

(3)

where \(S_{11} = (c_{11} + c_{12})/\Delta\), \(S_{12} = -c_{12}/\Delta\), \(S_{44} = 1/\Delta\), \(\Delta = (c_{11} - c_{12})/(c_{11} + 2c_{12})\), and \(l_i's\) are the direction cosines along the axial direction. The bulk elastic stiffness constants calculated with the NOTB Hamiltonian used in this work are: \(c_{11} = 218\) dyne/cm\(^2\), \(c_{12} = 121\) dyne/cm\(^2\), and \(c_{44} = 81.6\) dyne/cm\(^2\). When substituted into Eq. (3), they lead to a value of \(2.10 \times 10^{12}\) dyne/cm\(^2\) for the bulk Young’s modulus. The fact that the Young’s modulus of the 6-nm nanowire is about 40% smaller than that of a bulk rod indicates unambiguously the importance of the surface effects on the mechanical properties of nanostructures of high aspect ratio. As the strain along the axis increases, the surface region of the wire undergoes a series of reconstruction, which led to the softening of the wire. The reduction of the Young’s modulus has also been found in a recent study of Si nanowire whose axis is along the \(\langle 100 \rangle\) direction. In this case, the Young’s modulus of a \(\langle 100 \rangle\) wire is about 30% less than the bulk value. It should not be a surprise that the Young’s modulus of a nanowire depends on the orientation and diameter of the wire as the reconstruction of the surface atoms itself depend on these geometrical factors. Such softening of the elastic response of a nanowire may also have implications to applications of nanowires as microscopes and interconnects, etc. As the surface reconstruction can be greatly affected by the adsorption of foreign atoms on the surface of a nanowire (for example, hydrogen atoms on a Si surface can un-reconstruct the surface), one can speculate that the mechanical properties of a nanowire can be adjusted by the presence of such foreign atoms (or the wire can be used as a sensor). As a final note, we have also calculated \(\gamma\) for the NW of about 6-nm-diameter without any relaxation as the NW is being stretched or compressed from its equilibrium configuration. We obtained a value of 0.489 eV/A\(^2\) for \(\gamma\), leading to a hypothetical Young’s modulus of \(2.34 \times 10^{12}\) dyne/cm\(^2\) for this nanowire. This result is a further demonstration of the role played by the surface reconstruction and relaxation in determining the mechanical properties of nanowires.

5. SUMMARY

Using the \(O(N)\)/NOTB-MD scheme, we studied the stability of Si nanowires grown along the \(\langle 111 \rangle\) direction. The structural analysis suggests that a stable crystalline nanowire can be viewed as composed of a crystal-like core surrounded by a bond distortion-dominated surface region. The width of the surface region is found to be about 1 nm and it is independent of the diameter of the wire. Therefore, a nanowire of \(\sim 2\) nm diameter will be unstable due to surface-surface interaction. This result suggests that the width of the surface region can be used to define the critical size below which the crystalline structure of a nanomaterial can become unstable. Additional studies on the surface energy as a function of the diameter of SiNW shows a series of local minima, indicating the possibility of the existence of several magic diameters. In particular, our study reveals that it is energetically favorable to grow a Si nanowire of uniform cross-section with a diameter of about 6 nm. The calculation of the Young’s modulus of such a nanowire (\(\sim 6\) nm) reveals that its value is reduced compared to that of the bulk by about 40%, underscoring the importance of the surface effects on the mechanical properties of nanostructures.

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