Size-sensitive Young’s modulus of kinked silicon nanowires

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Abstract
We perform both classical molecular dynamics simulations and beam model calculations to investigate the Young’s modulus of kinked silicon nanowires (KSiNWs). The Young’s modulus is found to be highly sensitive to the arm length of the kink and is essentially inversely proportional to the arm length. The mechanism underlying the size dependence is found to be the interplay between the kink angle potential and the arm length potential, where we obtain an analytic relationship between the Young’s modulus and the arm length of the KSiNW. Our results provide insight into the application of this novel building block in nanomechanical devices.

1. Introduction

In 2009, a new type of building block—kinked silicon nanowire (KSiNW)—was synthesized by Tian et al in Lieber’s group at Harvard University [1]. The growth direction of the KSiNW changes from ⟨112⟩arm to ⟨110⟩joint to ⟨112⟩arm at the kink. In particular, the researchers are able to manipulate the arm length of the kink by controlling the growth time. Great experimental efforts have been devoted to investigating the growth mechanism of the kinks in silicon nanowires since then [2–7]. Besides these experimental works, Schwarz and Tersoff have proposed a theoretical model to interpret the growth mechanism of the KSiNW. In their model, the kink formation is due to the interplay of three basic processes: facet growth, droplet statics, and the introduction of new facets [8, 9]. Stimulated by KSiNWs, several groups have synthesized kinks in other nanowires, such as In2O3 multikinked nanowires [10], kinked germanium nanowires [11], germanium–silicon axial heterostructures with kinks [12], and kinked ZnO nanowires [13]. While existing works for KSiNW mainly concentrate on its growth mechanism, the study of elastic properties such as Young’s modulus is also important for its application in nanomechanical devices.

Bulk silicon is an anisotropic mechanical material with a value of Young’s modulus distributed roughly between 110 and 180 GPa, depending on the lattice direction [14–16]. Hopcroft et al have shown that the Young’s modulus in bulk silicon along the ⟨110⟩ direction is about 45% higher than that in the ⟨100⟩ lattice direction [17]. In nanomaterials, due to large surface to volume ratio, size effects [18] and nanodefects [19] have been found to be important for mechanical properties such as the Young’s modulus. For example, the AFM-measured Young’s modulus ranged from 93 to 250 GPa depending on the nanowire diameter [20].

In this paper, we apply both molecular dynamics (MD) simulations and finite element methods to study the size dependence of the Young’s modulus in KSiNW. We find that the Young’s modulus is sensitive to its arm length; specifically, it decreases fast with increasing arm length. The underlying mechanism for this size dependence is disclosed to be the competition between kink angle potential and the arm length potential.

2. Lattice constraint on the diameter of the KSiNW

Figure 1 displays the configuration of a KSiNW. Figure 1(a) shows the growth axis of the KSiNW in a cubic lattice. \( \vec{a}_1, \vec{a}_2, \) and \( \vec{a}_3 \) are the three primitive vectors in the cubic lattice, with lattice constant \( a = 5.43 \) Å. Lattice vectors \( \vec{R}_{12} = (2, 1, 1) \) and \( \vec{R}_{34} = (1, 2, \bar{1}) \) form two arms of the kink, while...
Figure 1. The configuration of a KSiNW. (a) shows the growth axis from (112)arm to (110)joint to (112)arm. (b) A schematic geometry, disclosing a lattice constraint on the diameter $d$, i.e. $d/2 = r_{23}$. (c) Configuration of a real KSiNW with structure parameters $(n_{\text{arm}}, n_{\text{joint}}) = (2, 1)$. The rectangular box (blue) highlights a unit cell of the KSiNW.

$R_{23} = (1, 1, 0)$ forms the joint of the kink. Geometrically, the KSiNW is denoted by a pair of integers $(n_{\text{arm}}, n_{\text{joint}})$. The arm length is $b_0 = n_{\text{arm}}R_{12}$ and the joint length is $n_{\text{joint}}R_{23}$.

From the schematic view shown in Figure 1(b), the diameter of a KSiNW is restricted to some discrete values as determined by the lattice vector $R_{23}$, i.e. $d = 2r_{23} = 2n_{\text{joint}}R_{23} = 1.54n_{\text{joint}}$ nm. This lattice constraint will have a direct result on the configuration of the kink. In the experiment, the diameter $d$ is pre-defined during the growth of the KSiNW [1], and will likely deviate from the above discrete values. There are two possible consequences for the KSiNW to accommodate the pre-defined diameter. Firstly, the diameter of the joint part may become more difficult to control in the experiment if the diameter of the arm deviates from the discrete values. As a result, there will be a discontinuity at the kink between the (112)arm and (110)joint growth directions. This discontinuity helps to break the lattice constraint. The obvious discontinuity in [1] may relate to this consequence. Another possible way to break the lattice constraint is that the axial length of the joint becomes more difficult to control when the diameter of the arm deviates from the discrete values. As a result, the joint is no longer a perfect regular triangle. Instead, the joint turns into a echelon-like structure, which is clearly shown in figure 2(c) of [1]. In KSiNW samples with diameters down to a few nanometers, the lattice constraint will play a more important role. Figure 1(c) shows four unit cells of a KSiNW of 1.54 nm in diameter and 2.66 nm in arm length, i.e. $(n_{\text{arm}}, n_{\text{joint}}) = (2, 1)$. The unit cell is highlighted by a rectangular box.

3. Results and discussion

3.1. Results from MD simulation and finite element method

In our MD simulation, the interaction between Si atoms is modeled by the widely used Stillinger–Weber empirical potential [21]. The structure of the KSiNW is first relaxed without applying strain, yielding the minimum total energy $E_0$. After applying strain $\epsilon$ to the system, the tensile structure is optimized with left and right ends fixed, which results in a total energy $E(\epsilon)$. The axial Young’s modulus is then calculated from the second derivative of the strain energy density $(E(\epsilon) − E_0)/V$ with respect to the strain $\epsilon$ in $[0, 0.01]$; $V$ is the volume. It should be noted that the obtained Young’s modulus is that of the overall kinked system (i.e. parallel to the unit cell in figure 1(c)), and not the Young’s modulus in the axial direction in each part of the nanowire.

A sensitive size dependence is observed for the Young’s modulus, as shown in figure 2 for three sets of KSiNWs with diameters 1.54, 3.07, and 4.61 nm. Only one unit cell is considered here, and we found that the Young’s modulus does not depend on the number of unit cells in the KSiNW. The Young’s modulus decreases with increasing arm length and can be fitted to an analytic function (solid lines) $y = c_1/(b_0 + c_2/b_0)$, which can be explained well by the valence force field model, as will be shown later. The two coefficients $(c_1, c_2)$ are $(216.5, 0.23)$, $(591.1, 1.45)$, and $(881.7, 2.12)$ for these three sets of KSiNWs. It shows that the Young’s modulus can be very small for KSiNW with a very long arm length. This prediction can be readily verified experimentally, considering the arm length of KSiNW samples can be successfully controlled in the laboratory [1].

The inset of figure 2 shows the diameter dependence for the Young’s modulus in KSiNWs with arm length 13.3 nm. The Young’s modulus increases exponentially and saturates to a constant value of 151.0 GPa. A similar diameter dependence was observed in straight silicon nanowires [22]. Using the Stillinger–Weber potential, we have calculated the Young’s modulus in bulk silicon to be 159.0 GPa in the (110) direction and 132.0 GPa in the (112) direction. Both values fall in the experimental range of the Young’s modulus in bulk silicon [14–16]. The saturation value of 151.0 GPa in the large
The size effect on the axial Young’s modulus. The MD simulation results for the Young’s modulus versus arm length in KSiNW with diameters 1.54 nm (black points), 3.07 nm (blue triangles), and 4.61 nm (red squares). Simulation results are compared with the valence force field model (solid lines) and the elastic beam model (dashed lines). Inset: the Young’s modulus versus diameter for KSiNWs with arm length 13.30 nm, where calculation results (points) are fitted to an exponential function (solid line) and compared with the elastic beam model (dashed line). The diameter limit is sandwiched between the Young’s modulus in bulk silicon along the ⟨110⟩ and ⟨112⟩ directions. This result can be understood from the fact that the KSiNW is constructed by ⟨110⟩ (the arm) and ⟨112⟩ (the kink) silicon nanowires.

We also calculate the Young’s modulus of KSiNWs from the continuum theory based on the finite element method. We use the Euler–Bernoulli beam model [23–25] in our calculation. Finite element calculations are performed using the commercial ANSYS 12.0 package with a 2-node BEAM188 element. The only input parameters required by this package are the Young’s modulus and Poisson ratio for bulk silicon from the above calculation based on the Stillinger–Weber empirical potential. Figure 3 shows the Von Mises stress distribution from the elastic beam model for two KSiNWs with arm length 13.30 nm and diameter 1.54 nm in (a), and arm length 26.60 nm and diameter 1.54 nm in (b). The applied tensile displacements are the same in both structures. The stress in the thinner KSiNW in (b) is roughly one quarter of that in the KSiNW in (a), because the Young’s modulus and the strain in the thinner KSiNW in (b) are both about half of that in the KSiNW in (a).

We note that the Euler–Bernoulli beam model neglects the shear strain, while this shear strain is considered in the Timoshenko beam model. We have also tested the Timoshenko beam model, and a similar size dependence of the Young’s modulus is obtained while the value is overall smaller. An interesting phenomenon in figure 3 is the distinct stress concentration at kinks. The stress concentration may lead to the generation of a fracture around the kink in the KSiNW under large tension. This stress concentration phenomenon also affects the accuracy of the predicted Young’s modulus. An important parameter in such a calculation is the stress concentration ratio (SCT), i.e. the ratio of the stress concentration length to the total length. The SCT is less than 30% in both KSiNWs shown in figure 3. This is important. It is because the Saint-Venant principle says that it is crucial for the SCT to be less than 30% for an accurate prediction of the Young’s modulus [26, 27]. According to the Saint-Venant principle [26], a more accurate Young’s modulus can be obtained from a smaller SCT, because the stress is distributed uniformly in more areas within the system in the case of smaller SCT. From the comparison of these two KSiNWs in figure 3, the SCT decreases with increasing arm length. As a result, the Young’s modulus from the finite element method should be more accurate for KSiNWs of longer arm length. Indeed, figure 2 shows a better agreement between the Young’s modulus from the finite element method and the molecular mechanics approach for KSiNWs of longer arm length.

Results for the set of KSiNWs of diameter 1.54 nm are shown by the dashed line in figure 2. The overall tendency from the finite element calculation agrees well with the MD simulation results. The Young’s modulus decreases with increasing arm length. It should be noted that the finite element results always lie below the MD simulation results, which is probably due to the loss of part of the angle bending interactions in the beam model and also surface effects. As a result, the beam model actually mimics a system that is softer than the real material. The softness property of the beam model has been discussed in more detail in a recent work by Zhao et al [28]. The deviation between the finite element results and the MD simulations is more pronounced for KSiNWs with smaller arm length, as the Euler–Bernoulli beam model is more accurate for a thinner rod structure with a higher length to diameter ratio. There will be some systematic errors in the Euler–Bernoulli beam model if the simulated system is very thick and/or short, since the higher order terms associated with the shearing deformation are ignored in this model. The surface induced diameter dependence of the Young’s modulus from the finite element method is also shown in the inset of figure 2. Again, the general tendency of the finite element method agrees with that of the MD simulation, and the elastic method also gives a lower value for the Young’s modulus.

![Figure 2](image2.png)

**Figure 2.** The size effect on the axial Young’s modulus. The MD simulation results for the Young’s modulus versus arm length in KSiNW with diameters 1.54 nm (black points), 3.07 nm (blue triangles), and 4.61 nm (red squares). Simulation results are compared with the valence force field model (solid lines) and the elastic beam model (dashed lines).

![Figure 3](image3.png)

**Figure 3.** Von Mises stress (in unit of $10^{10}$ Pa) distribution in KSiNWs from the elastic beam model calculation. The applied tensile displacement is the same in (a) for the KSiNW with arm length 13.30 nm and diameter 1.54 nm, and (b) for the KSiNW with arm length 26.60 nm and diameter 1.54 nm. Note the stress concentration at kinks. Note that the longer nanowire in (b) has been scaled by an overall factor of 0.5.
We note that it is a usual technique to use the bulk Young’s modulus of silicon as input for finite element modeling of the mechanical properties of nanomaterials or nanostructures [29, 30]. However, there is some uncertainty in doing so, since the nanowires are anisotropic on the atomic scale. A different Young’s modulus may lead to an overall shift of the whole curve in figure 2, while the size dependence of the Young’s modulus is kept unchanged. As a result, the size dependence of the Young’s modulus from the finite element modeling still agrees with that from the molecular mechanic method, although the input Young’s modulus for the finite element modeling varies. This size dependence is more important in the present work. In this sense, it is appropriate to use the bulk properties of silicon for the finite element modeling of the kinked silicon nanowires.

3.2. Analysis based on valence force field model

The above size dependence for the axial Young’s modulus can be understood in a valence force field model. Considering its zigzag configuration, the KSiNW can be simplified as a series of springs representing its arm length and kink angle, as shown in figure 4. The arm-spring has a force constant of $k_b$, while the kink-spring has a force constant of $k_0$. The potential of these two springs gives the most important interaction for such a zigzag structure. Due to the translation invariance, we only need to consider the interaction within a single kink in the KSiNW. The kink angle bending ($V_b$) and the arm length stretching ($V_b$) potentials are [31–36],

$$V_{tot} = V_θ + V_b = \frac{k_0}{2} (\cos θ - \cos θ_0)^2 + \frac{k_b}{2} (b - b_0)^2,$$

where $θ$ is the kink angle and $b$ is the arm length. Variables with subscript 0 correspond to their values in the equilibrium configuration without strain. For uniaxial strain applied in the horizontal direction, figure 4 shows a relationship among geometrical variables

$$c = b \sin \frac{θ}{2}.$$

There is only one independent degree of freedom in the tensile KSiNW. We choose the kink angle $θ$ as the free variable. From the energy minimum condition $\partial E/\partial θ = 0$, we have

$$k_0 (\cos θ - \cos θ_0) \sin θ \sin^2 \frac{θ}{2} + \frac{1}{2} k_b (c - b_0 \sin \frac{θ}{2}) \cos \frac{θ}{2} = 0.$$

The solution of equation (3) yields the equilibrium structure of the KSiNW under mechanical strain $ε$. For small strain, the kink angle is also small, so it deviates only slightly from its equilibrium value, i.e. $θ = θ_0 + δ_0$. Applying standard perturbation theory to equation (3) up to $(δ_0)^2$, we get

$$α δ_0^2 + β δ_0 + γ = 0,$$

where the three coefficients are:

$$α = k_b c \left( \frac{\sqrt{3}}{8} b_0 - \frac{1}{16} c \right),$$

$$β = \left[ k_b c \left( \frac{1}{4} b_0 - \frac{\sqrt{3}}{4} c \right) - \frac{3 \sqrt{3}}{16} k_0 \right],$$

$$γ = k_b c \left( \frac{1}{2} c - \frac{\sqrt{3}}{4} b_0 \right).$$

The solution of the equilibrium equation is then obtained analytically,

$$δ_0^2 = -\frac{β ± \sqrt{β^2 - 4αγ}}{2α}.$$

It can be shown that the elastic properties are dominated by the first-order term in the Taylor expansion of the angle variation $δ_0$ in terms of $ε$. We thus expand the three coefficients in equation (5) to the Taylor series of $ε$:

$$α ≈ α_0 + α_1 ε,$$

$$β ≈ β_0 + β_1 ε,$$

$$γ ≈ γ_0 + γ_1 ε,$$

where

$$α_0 = \frac{9}{32} k_b b_0^2,$$

$$β_0 = -\frac{3 \sqrt{3}}{16} k_b b_0^2 - \frac{9 \sqrt{3}}{16} k_0,$$

$$γ_0 = 0.$$

Inserting these equilibrium coefficients into equation (6), we obtain the angle variation without strain: $δ_0^0 = [δ_0 - δ_0^0]$. Obviously, only $δ_0^0$ is the physical solution, because the angle variation should vanish without strain. For the first-order term, we have

$$α_1 = \frac{\partial α}{\partial ε} |_{ε=0} = \frac{3}{32} k_b b_0^2,$$

$$β_1 = \frac{\partial β}{\partial ε} |_{ε=0} = -\frac{\sqrt{3}}{4} k_b b_0^2,$$

$$γ_1 = \frac{\partial γ}{\partial ε} |_{ε=0} = \frac{3}{8} k_b b_0^2.$$

The angle variation is:

$$δ_0 = \frac{γ_1}{|β_1|} ε = \frac{1}{\sqrt{\frac{3}{6} + \frac{3 \sqrt{3}}{2} η}} ε,$$

where $η = \frac{k_0}{k_b b_0^2}$. According to this formula, the kink angle variation is determined by the competition between kink angle and arm length potentials. It is smaller for KSiNW with larger $k_0$, or smaller $k_b$, which is physically correct. A rigid arm ($k_b → +∞$) results in the largest angle variation of $δ_0 = 2\sqrt{3} η$.

Inserting the kink angle variation into the total strain energy in equation (1), and making a linear approximation, we obtain the elastic strain energy density,

$$V_ε ≈ \frac{1}{2} \frac{3}{8} k_b b_0^2 + \frac{1}{2} k_b b_0^2 \left( ε - \frac{\sqrt{3}}{6} b_0 \right)^2 \equiv \frac{1}{2} γ ε^2.$$
Geometrical variables are related to each other by $c$ (inside the box) is highlighted in its equilibrium structure without strain (solid, black) and under mechanical strain (dotted, blue). with $b$ the opposite phenomenon should be observed in KSiNW Young’s modulus increases with increasing arm length; while $c$ where coefficients $k$ and $\theta$ are independent of the arm length, but increase rapidly with increasing diameter. These two force constants are effective values for the whole KSiNW system, so they can be quite different from the force constants in the potential for an actual chemical bond. For instance, $k_b$ for KSiNWs with diameter 1.54 nm is about 20 times larger than that describing C–C–C angles in carbon nanotubes [35], while $k_b$ is half of that in the C–C bonds in carbon nanotubes [31, 33]. From the energy point of view, each silicon atom in the system is connected to its neighbors by small springs within the linear approximation. $k_b$ and $k_\theta$ are actually the summation over these small springs between silicon atom pairs. For KSiNWs with larger diameter, there are more small springs that are in parallel connection, so the two effective force constants $k_b$ and $k_\theta$ are larger. For KSiNWs with longer arm length, there are an increasing number of small springs that are in series connection, which should not affect the effective force constants. As a result, $k_b$ and $k_\theta$ is sensitive to the diameter of the KSiNW, while they are independent of its arm length.

4. Conclusion

To summarize, we first pointed out a lattice constraint on the diameter of the KSiNW. Then we performed extensive MD simulations and finite element methods to study the Young’s modulus of the KSiNW. The Young’s modulus is found to decrease rapidly with increasing arm length. The size sensitivity is explained by a valence force field mode, where we derived an analytic formula for the axial Young’s modulus of the KSiNW with different arm length, i.e. \( Y = c_1/\left(b + c_2\theta^2\right) \). We show that the size dependence of the Young’s modulus in KSiNW is governed by two different types of potentials stored inside its zigzag configuration, which lead to the two terms in the denominator.

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