First-principles study of the Young’s modulus of Si <001> nanowires

Byeongchan Lee and Robert E. Rudd

Lawrence Livermore National Laboratory, University of California, L-415, Livermore, California 94551

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We report the results of first-principles density functional theory calculations of the Young’s modulus and other mechanical properties of hydrogen-passivated Si <001> nanowires. The nanowires are taken to have predominantly {100} surfaces, with small {110} facets. The Young’s modulus, the equilibrium length and the residual stress of a series of prismatic wires are found to have a size dependence that scales like the surface area to volume ratio for all but the smallest wires. We analyze the physical origin of the size dependence, and compare the results to two existing models.

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Nanoscale mechanical devices have been proposed for applications ranging from nano-electro-mechanical systems (NEMS) such as high frequency oscillators and filters[1] to nanoscale probes[2] to qubits for quantum computation[3]. The process of design and fabrication of these devices is extremely challenging, complicated in part by uncertainties about how even ideal devices should behave. The mechanical response of structures at the nanoscale is known to be different than that of their macroscopic analogs and surface effects in these high surface-to-volume devices are important[4], but a predictive theory of nanomechanics remains an open problem.

Much of what is known about mechanics of nanodevices has been learned from atomistic calculations based on empirical potentials. The first such calculations were done for single-crystal alpha quartz beams, finding that the Young’s modulus decreased with decreasing size[6, 7]. These and calculations of the Young’s modulus for various other materials have found a size-dependent modulus with an additive correction to the bulk value that scales like the surface area to volume ratio[5, 8, 9]. A few studies claim an additional contribution that scales like the edge to volume ratio (cf. 6), and such a contribution, with a factor of the logarithm of the separation of the edges, has been discussed for epitaxial quantum dots[10, 11]. An intuitive way of understanding these effects is that there is a layer of material at the surface (and edges) whose mechanical properties differ from those of the bulk including different elastic moduli and eigenstrains. This layer could be chemically distinct from the bulk, such as an oxide layer or a hydrogen-passivated surface, but the effect may be entirely due to the structural difference at the surface, such as a bare reconstructed surface. The formalism of nanoscale mechanics based on the surface energy and its first two strain derivatives (the surface stress and modulus) has been developed[12]. Recently it has been proposed that the size dependence of the Young’s modulus can be due to the anharmonicity (non-linearity) of the bulk elastic moduli together with the strain resulting from the surface stress[13].

To date experimental data on the size dependence of nanostructure mechanics are very limited. Atomic force microscopy (AFM) measurements of the Young’s modulus ($E$) of cast metallic nanowires show a strong size dependence[14]. Recent experiments have also found a strong size dependence for $E$ of ZnO nanowires[15], and other mechanical properties of ZnO and GaN nanowires[16]. Measurements of $E$ for silica nanobeams have demonstrated that the way in which the beam is clamped (i.e. the boundary conditions) affects the apparent value[18]. A study using a different AFM technique reported a value of $E$ of 18 ± 2 GPa for a <10 nm Si [100] nanowire[19]: for 100-200 nm Si[111] wires, $E$ has been found to be consistent with the bulk value[20]. Experimental challenges measuring the intrinsic nanoscale Young’s modulus make this a topic of continued activity, leveraging earlier work on the mechanics of nanotubules[21].

In the absence of definitive experimental data, first-principles quantum mechanical calculations can provide robust predictions of nanowire mechanical properties, but few results have been reported. One quantum study based on an empirical tight-binding technique has been published[22]. The electronic and optical properties of nanowires have been studied using first-principles techniques, leading to interesting predictions about size-dependent phenomena as evidenced by an increase in band gap due to quantum confinement[23], and a switch from an indirect, to a direct, band gap[24, 25]. We are not aware of any $ab$ initio calculations of nanowire moduli.

Here we present first-principles calculations of the mechanical properties of silicon nanowires, studying the Young’s modulus due to its direct relevance in the function of nanoscale devices such as flexural-mode mechanical resonators[1] and as an archetype for a variety of mechanical properties. We address several important open questions in nanomechanics. Is the modulus size dependent? Does it soften or stiffen at the nanoscale? What physics cause the effect? We focus on prismatic Si <001> nanowires with a combination of {100} and {110} H-passivated surfaces, and single crystal cores as in experiment[1, 27]. We have chosen the [001] orien-
Surfaces at their minimum energy separation. The cross-sectional area is defined as the square-root of the cross-sectional area. A vacuum space in the transverse directions. To calculate the longitudinal axis because of its relevance to the NEMS devices. Si nanowires grown rather than etched typically have different orientations. Hydrogen passivation results from rinsing the oxidized Si surfaces with HF, and it provides a standard system suitable for a systematic study of size dependence in nanomechanics. With other surface conditions the band gap can vary greatly, and nanowires can go from semiconducting to metallic; but the H-passivated wires remain semiconducting and the surfaces do not change the nature of Si-Si chemical bonding from its covalent character.

First-principles density functional theory (DFT) has been employed: specifically, the Vienna Ab-initio Simulation Package using the projector augmented-wave method within the generalized gradient approximation (GGA). The energy cutoff for the plane wave expansion is 29.34 Ry and higher, and 6 points in the one-dimensional irreducible Brillouin zone are used for k-point sampling. Each supercell is periodic, is one Si cubic unit cell long along the wire and has more than 10 Å vacuum space in the transverse directions.

To calculate $E$, we define the cross-sectional area to be the area bounded by the centers of the outermost (H) atoms. This choice is motivated by the fact that the volume excluded by the wire from access by outside atoms is determined from the forces arising from electron interactions. Most of the electron density is enclosed by the boundary formed by H atoms and the electron density from Si atoms essentially vanishes beyond this point. The positions of the nuclei are well defined and not subjective. Other definitions of the bounding surface exist, for example the mid-plane between two identical H-passivated surfaces at their minimum energy separation.

The cross-sectional shape of the Si [001] wire is a truncated square with four {100} facets and four {110} facets. Some wires studied have no {100} facets; for those that do, the ratio of the facet areas is taken to be roughly in accordance with the Wulff shape for a bare wire with (110)-(1x1) and (100)-p(2x2) surface reconstructions; i.e. the ratio of {100} to {110} area is 3.5:1. For each of the nanowire geometries shown in Fig. the Si atoms were initially positioned at their bulk lattice sites and hydrogens were added to terminate the bonds at the surfaces, and this configuration was relaxed. The system was relaxed to its zero-temperature minimum energy with the DFT total energy, is indicative of the residual stress in a doubly clamped beam etched from a single-crystal substrate. It is plotted in Fig. 2.

Next the relaxed total energy was calculated for each wire in a series of longitudinal strains, at increments of roughly 0.5%. These total energy values were fit to a polynomial. The minimum of the polynomial gives the equilibrium length, and the value of the curvature at the minimum gives the Young's modulus, $E = V^{-1} \partial^2 U/\partial \varepsilon_{zz}^2 |_{\varepsilon_{zz, min}}$. The equilibrium elongation and modulus are plotted in Figs. 2 and 3 respectively.

The calculated Young's modulus of the 1.49 nm wire is tabulated in Table I. The table gives an indication of the sensitivity to the order of the polynomial fit. For the given order, a higher cutoff energy offers little improvement. We find that the second order fit with 29.34 Ry energy cutoff is reasonably good, differing by less than 2% compared with all the higher-order combinations tested.
The extrinsic contribution is most important, as we now see, since the dangling Si bonds are well terminated with H and the Si-Si bond order is not significantly different than in the bulk. The small magnitude of the intrinsic stress is best seen in the case of the 1.39 nm wire for which the elongation is less than 0.1% compared to ∼1.5% of the 1.49 nm wire. The absence of {100} facets on this wire leads to a small extrinsic stress since the H-H separation on the {110} facets is relatively large. The vacant Si sites above the facets are filled by one and two H atoms on {110} and {100}, respectively, and the double occupancy, albeit with ∼2 Å H-H separation due to the shorter Si-H bond, leads to more repulsion for {100}.

The extrinsic surface stress due to the H-H repulsion on the {100} facets quantitatively accounts for both the compressive residual stress σ_{zz}(L_0) and the elongated equilibrium length L_{eq} of the nanowires. They are related to leading order through the linear elasticity:

\[
\sigma_{zz}(L_0) = \sigma_{zz}(\text{core}) + \frac{1}{A} \sum_i r_{zz}^{(i)} w_i (L_0 - L_{eq}) / L_{eq} \sim \sigma_{zz}(L_0) / E
\]

where \(A\) is the cross-sectional area, \(w_i\) is the width, \(r_{zz}^{(i)}\) is the longitudinal surface stress of facet \(i\), and \(L_0\) is the bulk length of the beam. \(E\) is the Young’s modulus of the beam. For constant surface stress, the second term in Eq. (1) is proportional to the surface area to volume ratio; the core stress is too, since the surface stress causes a transverse expansion of the wire that induces a tensile core stress. We now use much smaller periodic slabs to quantify these contributions and compare with the nanowire results. Using H-passivated slabs we calculate in DFT the surface stress of the ground-state cant(100) surface to be -55.0 meV/Å^2, and that of the (110) surface to be -1.3 meV/Å^2[36]. The negative stress indicates compression. The core stress may be estimated through a generalized Young-Laplace law to be \(\sigma_{zz}(\text{core}) \approx -8 \nu \tau_{zz}^{(100)} / \pi w\), where \(\nu = C_{12} / (C_{11} + C_{12})\) is the Poisson ratio. The details of these calculations will be given elsewhere[35]. Using these values in Eq. (1) gives predictions in very good agreement with the full nanowire calculations as shown in Fig. 2. The scatter for 1.49 and 2.05 nm wires may be accounted for by small edge effects. The 0.61, 1.00 and 1.39 nm wires have no {100} facets and almost no elongation as described above. In the case of the second smallest (0.92 nm) wire all of the {100} atoms undergo substantial relaxation, as shown in Fig. 1, lowering the magnitude of the surface stress and the elongation. This high level of agreement gives us confidence that we understand the physics of the size dependence of the residual stress.

What about the Young’s modulus? As shown in Fig. 3 it becomes softer monotonically as the size is decreased. It drops from the bulk value (\(E_{\text{DFT}}^{\text{bulk}} = 122.53\) GPa) in proportion to the surface area to volume ratio. It does not exhibit the strong dependence on the ratio of {100} to {110}.
to \{110\} area seen in the equilibrium length. As with the residual stress, the Young’s modulus may be decomposed into intrinsic, core and extrinsic contributions. From continuum mechanics neglecting edge and non-local effects, the modulus can be expressed, slightly generalizing Ref. 6, as

\[ E = E(\text{core}) + \frac{1}{A} \sum_i S^{(i)} w_i \]  

(3)

where \( S^{(i)} \) is the surface elastic constant, a strain-derivative of the surface stress including both extrinsic and intrinsic parts. The insensitivity to the facet ratio suggests several conclusions: The extrinsic contribution to the modulus (which is strongly facet dependent) is small; the core anharmonicity is irrelevant since the modulus is not correlated with the equilibrium elongation; and the intrinsic surface contribution dominates and its \{100\} value may be nearly sufficient to determine \( E \).

To study the core stress further, we calculated that the Young’s modulus of the bulk crystal increases by only 1.6% when strained \( \sim 1.5\% \) to match the most strained (0.92 nm) wire. This change is negligible compared to the observed softening (contrary to claims that the bulk anharmonicity is dominant \([13]\)). The extrinsic effect is also small, but not negligible. Based on silane interaction forces for the cantled \{100\} surface geometry we have estimated that the extrinsic contribution is \( \sim 8 \) GPa for the 1.49 nm wire \([35]\), roughly equal to \( E(1.49 \text{nm}) - E(1.39 \text{nm}) \), i.e. the difference in the moduli with and without \{100\} facets. We have also calculated the size dependence of the modulus using Eq. (3) based on the surface elastic constant \( S^{(100)} \) from a separate slab calculation \([35]\). The results, shown in Fig. 3, are in good agreement with the full first-principles calculation, and adding the core contribution slightly improves the agreement. Also plotted in the figure is the best fit curve of Ref. \([3]\) from Stillinger-Weber (SW) empirical molecular statics calculations. The SW bulk Young’s modulus is 13\% lower and the coefficient \( C \) of the \( 1/w \) term is 29\% lower than the DFT values. The errors compensate for each other leading to reasonable agreement for the nanoscale wires, which is unexpected since the SW potential does not have the relevant nanophysics in its functional form or its fitting database.

In conclusion we have found that calculation of several mechanical properties of silicon wires reveals a size dependence at the nanoscale, allowing analysis of the magnitude of surface and edge effects in the nanowire Young’s modulus from first principles for the first time. In each case the size dependence scales roughly as the surface area to volume ratio, but for different reasons. For the equilibrium length and residual stress it is due to the extrinsic surface stress from interactions in the H passivation layer; for the Young’s modulus it arises from the intrinsic contribution to the surface elastic constant. Surface parameters from slab calculations capture most, but not all, of the physics. The size effect is not strong for the H-terminated surfaces studied here: the Young’s modulus is softened by about 50\% for a 1 nm diameter wire. It may be possible to measure this effect directly using either AFM deflection or resonant frequency measurements in a double clamped configuration. Another interesting possibility is that the effect could be substantially stronger in silicon nanowires with different surfaces, such as bare or oxide surfaces, making measurement easier. For those systems, the balance of core, intrinsic and extrinsic contributions could be different, and indeed, new functional forms may be needed for the smallest wires.

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\* Electronic address: robert.rudd@llnl.gov

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