Letter

Near-theoretical fracture strengths in native and oxidized silicon nanowires

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Abstract

In this letter, fracture strengths $\sigma_f$ of native and oxidized silicon nanowires (SiNWs) were determined via atomic force microscopy bending experiments and nonlinear finite element analysis. In the native SiNWs, $\sigma_f$ in the Si was comparable to the theoretical strength of Si(111), $\approx 22$ GPa. In the oxidized SiNWs, $\sigma_f$ in the SiO$_2$ was comparable to the theoretical strength of SiO$_2$, $\approx 6$ to 12 GPa. The results indicate a change in the failure mechanism between native SiNWs, in which fracture originated via inter-atomic bond breaking or atomic-scale defects in the Si, and oxidized SiNWs, in which fracture initiated from surface roughness or nano-scale defects in the SiO$_2$.

Keywords: fracture strength, silicon nanowires, atomic force microscopy, rapid thermal oxidation, reliability

(Some figures may appear in colour only in the online journal)

1. Introduction

Silicon nanowires (SiNWs) have recently attracted significant attention in a number of application areas, in large part due to their unique mechanical [1], electrical [2], optical [3], piezoelectrical [4], and thermoelectrical [5] properties. To take advantage of these properties in commercially-viable SiNW-based devices, the structural or load-bearing reliability of SiNWs over the intended device lifetimes is critical. Such reliability depends on the fracture strength of the SiNWs, which, in turn, depends greatly on phenomena that are significant only at the nanoscale SiNW dimensions. The fracture strength $\sigma_f$ of SiNWs has been shown to approach the theoretical strength of Si [6], which is 17 to 26 GPa depending on the crystallographic orientation [7]. This $\sigma_f$ range is only possible with critical flaw sizes on the order of a few nm [8], indicating that the strength of native SiNWs is dictated by intrinsic planar defects in the Si such as stacking faults or twin boundaries. Strength control by such volume defects is only possible in SiNWs that have surfaces with small areas or near-ideal structures. Furthermore, it has been demonstrated that $\sigma_f$ values for SiNWs can drop precipitously from the theoretical levels through the development of larger, extrinsic flaws due to changes in: (1) surface area or (2) processing conditions [8]. On point (1), there have been several reports on the dependence of $\sigma_f$ on surface area $A_s$ [9–11], with all in agreement that $\sigma_f$ decreases as $A_s$ increases. The mechanism behind the trend is well-defined: a given processing method produces a particular distribution of defect sizes, and the probability of a component containing a larger defect increases with $A_s$, a phenomenon often described by Weibull size-scaling analyses [12]. On point (2), there have been far fewer reports, although most notably the effects of oxidation on $\sigma_f$ have been considered. In one study, the authors assessed $\sigma_f$ for both as-grown and fully-oxidized SiNWs, and showed that $\sigma_f$ decreased by a factor of three on oxidation [13].
However, the investigation lacked \( \sigma_f \) data for partially-oxidized SiNWs, and was therefore unable to comment on the intermediate trends or the mechanism behind the reduction. Moreover, the strength calculations neglected nonlinear elastic effects, despite the large deformations in the SiNWs.

In this letter, \( \sigma_f \) of native and partially-oxidized SiNWs were measured using atomic force microscopy (AFM) bending experiments. Rapid thermal oxidation (RTO) was performed at 1000 °C for times \( t \) of 0 to 30 min to form SiO\(_2\) layers on the SiNWs. Dispersed SiNWs were supported on Si(100) substrates and bent by AFM manipulation until fracture occurred. Nonlinear finite element analysis (FEA) was used to convert curvature at fracture \( \kappa_f \) to \( \sigma_f \). As \( t \) increased, the AFM-based bending tests showed that \( \sigma_f \) decreased from 22 to 12 GPa. More importantly, it was found that the decrease in \( \sigma_f \) was non-monotonic. Instead, \( \sigma_f \) decreased significantly at small \( t \) and gradually increased at large \( t \), consistent with the idea that \( \sigma_f \) is initially dictated by inter-atomic bond breaking or atomic-scale defects in the Si but later defined by roughness or nano-scale defects in the SiO\(_2\).

2. Materials and methods

SiNW growth from the vapor-liquid-solid (VLS) process was catalyzed with commercially-available 60 nm Au nanoparticles randomly dispersed on poly-L-lysine-functionalized Si(111) substrates. Growth was performed at 900 °C and 80 kPa (600 Torr) using 30 sccm (standard cm\(^3\) min\(^{-1}\)) of SiCl\(_4\) and 200 sccm of H\(_2\) diluted with N\(_2\) to a total flow rate of 1000 sccm. The Au droplets on the SiNW tips were removed with the following process: (1) etched in a 1:10 HF: deionized (DI) water solution for 10 s, (2) rinsed in DI water, (3) etched in an aqueous KI:KI\(_2\) solution for 5 min, (4) rinsed in DI water, and (5) dried in an N\(_2\) flow. RTO of SiNWs was performed at 1000 °C for \( t \) from 0.5 to 30 min using a 1:10 O\(_2\):Ar mixture [14]. SiNWs were released via ultrasonic agitation in isopropyl alcohol and the solution was deposited on grids and Si(100) substrates to assess the oxidation kinetics and fracture properties, respectively.

SiNW length and cross-section were investigated via scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. SEM was conducted with an accelerating voltage of 20 kV at a 30° tilt. TEM was executed at an accelerating voltage of 200 kV, with the SiNWs tilted to a two beam condition and the images created with a diffraction vector \( g = \{111\} \). SiNW oxidation kinetics were assessed via annular dark field (ADF) scanning transmission electron microscopy (STEM) images at an accelerating voltage of 200 kV and inner and outer collection angles of 90 mrad and 370 mrad, respectively. For STEM, the SiNWs were tilted to the Si [110] zone axis and focused such that the Si dumbbells characteristic of the [110] zone axis were clearly visible. During the SiO\(_2\) layer thickness measurements, the SiO\(_2\) was distinguished from the Si based on the ADF intensity difference. The cross-sectional shapes of the SiNWs were determined by first calculating the dimensions of a base as-fabricated hexagonal SiNW with SiO\(_2\) thickness \( t_{\text{ox}} = 0 \) nm using the STEM measurements of the native SiNW and the molar volumes of Si and SiO\(_2\). The exterior (angular) cross sections of the oxidized SiNWs were attained using the nanowire radius \( R_{\text{NW}} \) and \( t_{\text{ox}} \) values from the STEM images and linear interpolation between the (radial) dimensions of the as-fabricated SiNW and the \( t = 30 \) min SiNW of assumed cylindrical section. The interiors of the cross-sections were determined by radial scaling of the exterior cross-sections from the STEM data. The facet radii and relative Si and SiO\(_2\) volumes were assessed by fitting circles to, and numerical integration of, the interpolated profiles, respectively.

SiNW fracture properties were determined via AFM bending tests using probes with single-crystal Si cantilevers and integrated tips (tip radius \( R \approx 20 \) nm, spring constant \( k \approx 48 \) N m\(^{-1}\)). Detailed descriptions of the AFM bending protocol can be found in previous work [6, 13]. In short, the AFM bending tests alternated between topography images and manipulation steps. Initially, each SiNW was straight, and a hook was created at one end by dragging the AFM tip along the Si(100) substrate and moving the SiNW in a prescribed direction. After a hook was created, the curvature \( \kappa \) was increased by moving the shorter end towards the longer end. The manipulation displacements spanned from 1 \( \mu m \) down to 50 nm, with the size decreasing as the number of manipulation steps increased to allow for better resolution of \( \kappa_f \). To determine \( \kappa_f \), the SiNW neutral axis just prior to fracture was traced [15] and the \( x \) and \( y \) coordinates from this process were utilized to calculate \( \kappa \) via \( \kappa = \frac{4}{\pi} \frac{r^2 y}{dx^2} / (1 + \frac{dy}{dx^2})^3/2 \).

FEA simulations of the bent SiNWs were utilized to convert \( \kappa_f \) to \( \sigma_f \) and account for two main phenomena: (1) changes in the SiNW cross-section with \( t \) and (2) nonlinear effects associated with large \( \kappa \). In detail, FEA was used to model the mechanical deformation in a thin slice of each SiNW via quadratic wedge-shaped elements [16]. A relative rotation was applied to each cross-section to find the maximum longitudinal Cauchy stress \( \sigma_{\text{max}} \) versus \( \kappa \). Geometrical and material symmetry were consistent with zero-warping assumptions. Constitutive material behavior was modeled as nonlinear hyperelastic with the energy versus Green strain formulation:

\[
U = \frac{1}{2} \epsilon_{ij} \epsilon^{ij} + \frac{1}{2} c_{ijkl} \epsilon^{ijkl} \epsilon_{ijkl} + \frac{1}{2} c_{ijklm} \epsilon^{ijklm} \epsilon_{ijklm} + \cdots
\]

where repeated indices suggest summation, and \( \epsilon^{ijkl} = 2 \epsilon_{ijkl} \). Si was modeled to order three in \( \epsilon_{ijkl} \) with \( c_{ijkl} \) and \( c_{ijklm} \) values from ultrasound experiments [17]. SiO\(_2\) was modeled to order four in \( \epsilon_{ijkl} \) with \( c_{ijkl} \) and \( c_{ijklm} \) values from ultrasound and shock-loading data [18, 19]; these constants were used to simulate nanopillar compression with good experimental agreement [20]. The full set of \( c_{ijkl} \) values were generated from the published constants using rotational symmetry. Plastic deformation in the SiO\(_2\) was neglected due to the compressive stress not exceeding the compressive yield stress of \(-6.8 \) GPa (calculated via [20]) and plasticity not being observed in tension [20, 21].

3. Results and discussion

Figure 1 shows representative SEM, TEM, and STEM images of native SiNWs (\( t = 0 \) min) produced via the VLS growth
process. From figure 1(a), SiNW lengths were found to be 25 to 30 μm for the prescribed growth conditions; these lengths were large enough to ensure adhesion between the end of a SiNW fixed to the Si(100) substrate during bending tests, but small enough to minimize changes in the cross-sectional area during VLS growth. Typical native SiNW cross-sections were near-hexagonal in shape as revealed by the fringes [22] in the TEM image (diffraction vector g = (111)) in figure 1(b), with nearly-flat {112} facets as depicted elsewhere [23]. Additional high-resolution STEM images indicated a defect-free lattice (figure 1(c)) and a {111} growth direction, the latter of which was confirmed by the 0.32 nm lattice spacing and Fourier transforms of the STEM images (figure 1(c) inset). Furthermore, $R_{NW}$ and $t_{ox}$ for the native SiNWs were 30.6 nm ± 2.4 nm and 1.8 nm ± 0.2 nm, respectively. As such, $2R_{NW}$ and $t_{ox}$ are in good agreement with the diameters of the Au nanoparticles used for VLS growth and reported values for native SiO$_2$ on SiNWs [24], respectively. On oxidation, $R_{NW}$ and $t_{ox}$ increased at small $t$, but converged to steady-state values at large $t$, as shown in the images in figures 2(a)–(f) and the resulting values for $R_{NW}$ and $t_{ox}$ in figure 2(g). At small $t$, the increases in $R_{NW}$ and $t_{ox}$ can be explained by assuming 1 mol of Si is transformed into 1 mol of SiO$_2$, and noting the greater molar volume of SiO$_2$ relative to Si [25]. It is also important to comment on the convergence of $R_{NW}$ and $t_{ox}$ at large $t$: previous studies on the oxidation of SiNWs also revealed this so-called self-limiting oxidation, and demonstrated that the final values for $t_{ox}$ were dependent on $R_{NW}$ and $t$ [26]. Two main theories have been developed to explain the decrease in oxidation rate at large $t$. In the first theory, the oxidation is diffusion-limited, due to an increase in the activation energy for diffusion to the Si/SiO$_2$ interface [27]. In the second theory, oxidation is reaction-limited, and based on a decrease in the reaction rate at the Si/SiO$_2$ interface [28] as described by a two-dimensional non-planar model for Si [29]. Interestingly, both theories cite the radial compressive stress at the Si/SiO$_2$ interface for the self-limiting behavior. Regardless of the mechanism, it is clear from figure 2 that the steady-state $R_{NW}$ and $t_{ox}$ values for these particular SiNWs were reached at $t$ of ≈7 min and 30 min, respectively.

The fracture properties of the SiNWs were measured by AFM bending tests for all $t$. The AFM topography images of bent SiNWs just prior to fracture are shown in figures 3(a)–(f). In most cases, the SiNW fractured after the next manipulation step, as confirmed by the subsequent topography image. On occasion, the SiNW fractured during a given image, as shown in figure 3(e). The scan direction for the image was bottom to top, and hence captured the profiles of the bent SiNW just prior to fracture followed by the broken SiNW end just after fracture. In both cases, the longer end of the broken SiNW returned to its near-original position and exhibited no signs of permanent deformation, implying that failure was due to brittle fracture. The calculated values for the local $κ$ in the bent SiNWs are superimposed on the AFM
Figure 3. AFM topography images of SiNWs just prior to fracture for times $t$ of (a) 0 min, (b) 0.5 min, (c) 1.5 min, (d) 4 min, (e) 7 min, and (f) 30 min. The images are taken with different tips and at random points in the tip wear process, and therefore do not exhibit the observed increase in $R_{NW}$ with $t$ (figure 2), due to varying degrees of tip convolution. The local values for $\kappa$ are shown at 100 nm increments, where $\kappa_{meas}$ is $3.5 \mu m^{-1}$ for (a) and $2.5 \mu m^{-1}$ for (b)–(f). (g) AFM curvature at fracture as a function of $t$. $\kappa_t$ decreased non-monotonically as $t$ increased. Mean values and standard deviations are based on at least 10 measurements. Solid line is a guide to the eyes. (h) AFM cross-sectional profiles at various $t$. At small $t$, $R_t$ was large and the facet edges were distinct, while at large $t$, $R_t$ approached $R_{NW}$ and the facet edges were smooth.

The vertical arrows in figure 5(a) indicate the $\kappa_t$ values for the two oxidation states from figure 3(g). The $\sigma_{max}$ values from the linear FEA can be compared to previous SiNW $\sigma_t$ measurements by noting that $\sigma_t = \sigma_{max}$ at $\kappa = \kappa_t$ for $t = 0$ min, $\sigma_t = 18.9$ GPa in the Si, which compares to $\sigma_t = 18$ GPa as reported earlier [6]; for $t = 30$ min, $\sigma_{max} = 8.1$ GPa in the SiO$_2$, which compares to $\sigma_t = 6.2$ GPa as reported earlier [13]. Therefore, linear deformation interpretations of $\sigma_{max}$ at $t = 0$ min and $t = 30$ min are in agreement with earlier $\sigma_t$ based on similar linear-elastic interpretations. However, the large $\kappa_t$ suggest that $\sigma_t$ are more appropriately determined from a nonlinear analysis.
Figures 5(b)–(g) show contours of stress in the SiNWs calculated using a full nonlinear analysis at the measured $\kappa_f$. On initial oxidation, $\sigma_{\text{max}}$ appears in the Si. As oxidation proceeds, however, the stress in the Si diminishes considerably, and $\sigma_{\text{max}}$ moves to the SiO$_2$. To interpret the shifting contours, $\sigma_{\text{max}}$ values need to be compared to the sustainable stresses of the materials. Figure 5(h) shows $\sigma_{\text{max}}$ in the Si and SiO$_2$ as a function of $t$. For the native SiNWs, $\sigma_{\text{max}}$ in the Si is comparable to the theoretical strength of Si $\langle 111 \rangle \approx 22$ GPa, shown by the shaded band. However, $\sigma_{\text{max}}$ in the SiO$_2$, $\approx 12$ GPa, is considerably greater than the SiO$_2$ theoretical strength of $E/10 \approx 7$ GPa, where $E$ is Young’s modulus. Hence, it is ambiguous whether failure initiated in the Si or SiO$_2$ for the native SiNWs. In either case, these stress, and hence strength, values are some of the largest reported for both materials, and are clearly in the realm of theoretical strengths controlled by either inter-atomic bond breaking [32] (if the SiNWs are defect-free, as suggested in figure 1(c)) or atomic-scale defects [33] (if the SiNWs have defects not detected in the STEM). On initial oxidation, $\sigma_{\text{max}}$ in the Si and SiO$_2$ decrease substantially. However, the stress in the Si was reduced significantly relative to the theoretical strength of Si, whereas the stress in the SiO$_2$ remained comparable to theoretical strength of SiO$_2$. The implication is
that failure is now initiated in the oxide, likely from surface roughness at the SiNW exterior on the newly-formed SiO₂ surface. Continued oxidation led to almost monotonic decrease in σ_{max} in the Si at failure and gradual increase in σ_{max} in the SiO₂. The increase in σ_{max} in the SiO₂ suggests a related reduction in the potency of the strength-limiting defects, perhaps from a smoothing of the SiO₂. The overall decrease in σ₁ is in good agreement with recent molecular dynamic simulations of the fracture of Si with surface steps; in that study, σ₁ decreased from 23 to 14 GPa as the number of surface steps increased from 1 to 6 [34]. The authors suggested that the decrease in σ₁ is due to a transient process, in which the roughness initially increases on SiO₂ nucleation but then decreases with complete SiO₂ formation [35].

Altogether, the data presented herein and elsewhere [34, 36] suggest that the σ₁ versus t trend for Si is dependent on the length scales of the component and the strength-limiting flaw sizes, a hypothesis originally presented in a recent review paper [8]. For nanoscale components with native σ₁ close to the theoretical limit (≈22 GPa) that are defect-free or with atomic-scale defects, it was shown here that σ₁ decreased at small t and only partially recovered at large t, indicating that the oxidation process led to an irreversible roughening of the Si surface. For nanoscale components with moderate native σ₁ (≈9 to 13 GPa) and critical flaw sizes on the order of a few to tens of nm, a recent report showed that σ₁ decreased at small t and then fully recovered at large t, signifying that the roughness of the oxidized Si surface was close to that of the native Si surface (i.e., the initial oxidation-induced roughening of the Si surface was reversible) [34]. For microscale components with relatively small native σ₁ (≈1 to 5 GPa) and critical flaw sizes on the order of tens to hundreds of nm, another study showed that σ₁ increased with oxidation, presumably due to the formation of oxygen bridges between the critical flaws induced from the fabrication process [36].

4. Conclusions

In conclusion, the strength of SiNWs has been measured as a function of oxidation state. On initial oxidation, the very thin oxide layer on the near-hexagonal native SiNWs extended outward and inwards, leading to an increase in both R_{NW} and t_{ox} and a transformation to a circular section. SiNW strengths were calculated from nonlinear FEA simulations and AFM-based measurements of σ_e. For native SiNWs, σ_{max} in the Si was comparable to the theoretical strength of Si(111), ≈22 GPa. In the oxidized SiNWs, σ_{max} in the Si was much less than this value, but σ_{max} in the SiO₂ was comparable to the theoretical strength of SiO₂, ≈6 to 12 GPa. The measurements point to a change in the failure mechanism between native SiNWs, in which fracture originated via inter-atomic bond breaking or atomic-scale defects in the Si, and oxidized SiNWs, in which fracture is initiated from roughness or nano-scale defects in the SiO₂. In all, the σ_{max} and hence σ_e values are approximately equal to the theoretical strengths for both Si and SiO₂, and an order of magnitude greater than those for microscale Si [37–39] and SiO₂ [40, 41] components.

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Specific commercial equipment, instruments, and materials that are identified in this report are listed in order to adequately describe the experimental procedure and are not intended to imply endorsement or recommendation by the National Institute of Standards and Technology (NIST). Contribution of NIST, an agency of the US government; not subject to copyright. Unless otherwise noted, experimental uncertainties are one standard deviation of the mean.

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