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Anomalous surface states modify the size-dependent mechanical properties and fracture of silica nanowires

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Abstract
Molecular dynamics simulations of amorphous silica nanowires under tension were analyzed for size and surface stress effects on mechanical properties and for structural modifications via bond angle distributions. Their fracture behavior was also investigated beyond the elastic limit. The Young’s moduli of silica nanowires were predicted to be about 75–100 GPa, depending on the nanowire size. The ultimate strength was calculated to be ~10 GPa, depending on the diameter, which is in excellent agreement with the experiments. The dependence of the Young’s modulus on nanowire diameter is explained in terms of surface compressive stress effects. The fracture behavior of nanowires was also found to be influenced by surface compressive stresses. Bond angle distribution analysis of various nanowires reveals significant compressive surface states, as evidenced by the appearance of a secondary peak in the Si-O-Si bond angle distribution at ~97°, which is absent in bulk silica. The strain rate was found to have a negligible effect on the Young’s modulus of the silica nanowires, but it has a critical role in determining their fracture mode.

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Keywords: mechanical properties of nanoscale systems, nanowires, molecular dynamics simulations

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

1. Introduction

Amorphous silica (SiO$_2$) is an exceptional material that owes its versatile properties to its non-crystalline and covalent-ionic bonding nature. Silica is also an important scientific material used as a model structure for the investigation of other complex disordered materials [1]. Bulk silica is routinely used in a wide range of technological applications such as waveguide devices, laser lenses and optical fibers. Its equation of state (pressure-volume behavior) has been extensively studied both experimentally [2, 3] and theoretically [4]. The experiments performed on this glass have produced key findings such as an anomalous equation of state at high pressure [2, 3]. Molecular dynamics (MD) simulations have successfully reproduced the experimental pressure-volume relationships of silica glass under compression [4]. In that study, structural transformations in the bulk silica samples were determined up to 25 GPa via ring size distributions, in which ring size $N$ is the shortest loop formed by $N$ Si-O bonds [5]. Compressive loads have been found to modify the structure of bulk silica and broaden this ring size distribution [1, 4]. Independent experiments on compressed silica glass [6, 7] have indicated an enhancement of Raman lines associated with the smaller rings via specific vibration frequencies. Modern synthesis efforts have been able to readily produce various types of oxide nanostructures, such as silica nanowires (SNWs), silica nanosprings, etc., with precise morphologies, depending on various factors including temperature [8–10].

When materials reduce in size down to the nanoscale, many unique phenomena emerge that lead to novel material properties and functionalities. For example, due to the quantum confinement effect, the electronic density of states of
nanowires, nanoribbons and nanodots show distinct spectra compared to their bulk counterparts. This electronic property enables these materials to have promising applications in nanoelectronics and efficient energy conversion devices. The mechanical behavior of nanoscaled materials is also unique, not only due to the failure of the continuum assumption of material structures that has been successful at the macro- and microscales, but also to the increased surface area-to-volume ratio, which leads to significant surface stress effects that affect their mechanical strength.

Experimental studies have shown that the Young’s moduli of SNWs are between 60–100 GPa [11–13] for nanowire diameters ranging from 40 to 100 nm. With an increasing demand for the fabrication of higher-density nanoelectronics, smaller SNWs are expected to be better candidates for the next generation of nanoelectromechanical device applications. Therefore, understanding the mechanical properties of such SNWs is not only of scientific importance but is also critical for device design and manufacturing.

While experimental approaches have limitations at the nanoscale, predictive methods, such as theory and MD simulations, play an increasingly important role in the study of silica nanostructures, with only a few publications on this topic available to date [14–16, 18, 19]. MD simulations by Davila et al [14] had found that SNWs under compression were more deformable as they decreased in diameter. In that study, ring size distribution analysis showed that SNWs underwent unique structural transformations, which led to their distinct response to mechanical loadings compared to that of compressed bulk silica glass. Previously, MD simulations by Silva et al [15] had reported the Young’s moduli of selected SNWs under tension to be ~85–110 GPa, with a general trend of increasing strength as the SNWs decreased in diameter. A recent MD simulation by Yuan and Huang using different preparation methods confirmed these findings in SNWs [16]. Hence, the combined MD studies above revealed a unique finding, namely that as SNWs decrease in diameter, they become more deformable under compression but stronger under tension. This mechanical response of SNWs is opposite to the behavior observed in bulk silica, which is commonly stronger under compression [17]. Furthermore, results from the above MD studies [14, 15] agree with the unique mechanical behavior of thin SNWs, as predicted earlier using elasticity calculations [18, 19]. Overall, the nanowire diameter and loading sense were found to determine the resulting behavior of the SNWs. More insights into the underlying mechanisms that rule the nanomechanics of SNWs are certainly still needed. Most significantly, theoretical work by Shankar et al [18] anticipated that at the nanoscale, surface stress effects would play a dominant role in modifying the strength of SNWs under different loadings. Simulations on the compression of SNWs [14] have partially verified this analytical prediction; however, the influence of such effects on their tensile behavior has not yet been investigated via atomistic modeling, and the characterization of such surface states is limited. It is expected that such surface stress effects will have a major impact in modifying the fracture modes of the SNWs.

In this study, systematic MD simulations were performed to study the tensile behavior of amorphous SNWs for size and surface stress effects on strength, ultimate strength and fracture modes and for local structural modifications and surface state calculations using bond angle distributions.

2. Methods

MD simulations were performed in this investigation using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) open-source code [20] and the van Beest–Kramers–van Santen (BKS) interatomic pair-potential [21], which is computationally efficient and has fitted parameters that reproduce the experimental structure and elastic constants of crystalline silica. The BKS interatomic potential has been widely used to investigate several dynamic and thermodynamic properties of silica in many forms and under different conditions [15, 22–24]. In this study, the general approach involved creating an amorphous bulk silica model, generating several SNW models from the bulk silica, relaxing the SNWs to obtain an initial state, and applying tension. The Young’s modulus of these SNWs was evaluated for size and surface stress effects on strength and for structural changes using bond angle distributions.

A bulk silica glass structure (14.32 x 14.32 x 14.32 nm³) was created via a standard simulated melt-quench procedure [4, 5, 25]. Solid SNWs (diameters D = 3.7–10 nm, lengths L = 4–14.32 nm) were carved out from the bulk glass to consider various length-to-diameter ratios (L/D = 0.4–3.9). This method of creating SNWs has previously been found [14] to produce a very small (<0.5%) number of ‘defects’ (unbonded atoms) on the lateral surfaces of the nanowires; hence, these are assumed to be negligible in this study. The obtained SNWs were subsequently relaxed for 0.25 ns at 300 K using the NVT ensemble before subjecting them to tensile deformation, with a random number used to generate the initial temperature based on a Gaussian distribution. The potential energy variation during the relaxation was closely examined, and the results showed that the potential energy saturates at its lowest level within 0.25 ns, indicating that the SNWs were fully relaxed. Periodic boundary conditions (PBCs) were applied along the loading axial (z-) direction only. Stretching of the SNWs was carried out at 300 K using a time step of 0.5 fs by: (1) increasing the length (z-direction) of the periodic box size by a 2% increment, (2) relaxing the model (25–75 ps), (3) measuring the resulting pressure in the cross-section area to calculate the stress and then (4) repeating steps (1)–(4). Such a loading method led to an ‘effective’ strain rate of ~10⁸ s⁻¹, which is similar to previous studies [15, 22]. Comparable techniques have been applied to study the compression of amorphous SNWs [14], metallic nanowires [26] and bulk silica glass [2, 4]. Independent studies have also suggested that stress-strain curves [27] and strength [22] are not very sensitive to variations in sample preparation conditions.

Since each SNW was uniaxially stretched along its z-axis, the resulting stress-strain (σ–ε) curve was evaluated as a
function of nanowire dimension. The Young’s modulus $E$ was calculated from the slope in the linear region of each $\sigma-\varepsilon$ curve by fitting a line between 0% and 6% strain to ensure that each nanowire was within the purely elastic region. The surface stress effect and structural transformations in the SNWs under tension were later examined via concentric virtual cylinders and bond angle distributions as a function of strain, respectively, as described below. The calculation of the bond angle distributions was accomplished by probing local nanostructural distortions (i.e. measuring the short-range and medium-range modifications via the tetrahedral bond angle and the rotation of the bridging bond angle, respectively) as the material responded to the tensile-induced transformations. Finally, several MD tensile simulations of the SNWs were performed beyond the elastic limit to investigate their fracture modes and possible correlations with the SNW dimensions.

3. Results and discussion

Each initial silica nanowire structure is fully equilibrated before any deformation is applied, with its potential energy curve becoming rapidly constant (within a few ps) upon relaxation. Figure 1(a) shows a representative SNW studied in this work. To investigate the surface stress effect on the mechanical properties of a given SNW, concentric virtual cylinders (‘cores’), each with a diameter $d_{\text{core}}$, as illustrated in figure 1(a), were created inside of the SNW, and the stress-strain behavior of the atoms inside these virtual ‘core sizes’ was examined. The stress-strain behavior of a small SNW ($D=5$ nm, $L=4$ nm) and several of its virtual ‘core sizes’ up to 8% strain is shown in figure 1(b), from which the Young’s modulus of the SNW is calculated to be 86 GPa. Similarly, the stress-strain behavior of the virtual ‘core sizes’ ($d_{\text{core}}=2$ nm, 3 nm and 4 nm) within this SNW is evaluated. The resultant Young’s moduli of these SNW core sizes are measured to be 110 GPa, 100 GPa and 87 GPa, respectively. This trend of decreasing strength with the increasing SNW core diameter $d_{\text{core}}$ is consistently observed in all of the studied SNWs, which indicates that the interior of the SNW has distinct properties compared to its surface. This is evidenced in figure 1(b), where the innermost SNW core ($d_{\text{core}}=2$ nm) displays higher stresses than those calculated in the outer SNW cores. This implies that the surface of this small SNW must be under compression for the overall stress to be balanced. It is noteworthy that for larger SNWs ($D>5$ nm, $L>7$ nm), this discrepancy is reduced. Typical examples are shown below (figures 2 and 3); in these figures, little or no...
difference is observed between the stress-strain curves in the elastic region for the SNWs and their virtual inner cores, particularly for the larger diameter SNWs ($D = 6\,\text{nm}$, $L = 14.32\,\text{nm}$).

Analysis of the MD tensile results in this study shows a distinct correlation of Young’s modulus $E$ with the SNW diameter $D$, as is evident in figure 1(c). The previous MD findings [14–15] on the behavior of SNWs under compression and tensile loads, respectively, are also plotted for comparison. The results from this study, shown in figure 1(c), are in good overall agreement with prior findings [15], which suggests that the approach used here is well suited and may provide useful insights into the nanomechanical properties of SNWs. Silva et al [15] reported the elastic modulus for bulk glass ($E \sim 75\,\text{GPa}$) and for selected SNW sizes ($D \sim 3.7–6\,\text{nm}$, $E \sim 85–110\,\text{GPa}$) under tension. The difference in the $E$ dependence reported here compared to that study [15] is attributed to the different SNW sizes ($D \sim 3.7–10\,\text{nm}$, $L = 4–14.32\,\text{nm}$) and simulated conditions (e.g. strain rates and specific elastic and plastic regimes). The MD results in this study are particularly consistent with prior findings [15] as the SNWs have higher $E$ values than the bulk glass, with a trend of increasing $E$ values for the thinnest SNWs. This is notably different from the compression behavior of similar SNWs [14].

Furthermore, an anomalous feature is observed in this study, as shown in figure 1(c): the Young’s moduli of long SNWs ($L = 14.32\,\text{nm}$, averaged over the strain rates listed in table S1) saturate at $\sim 87\,\text{GPa}$ when $D > 6\,\text{nm}$. As the SNW diameter decreases from $6\,\text{nm}$ to $\sim 4.6\,\text{nm}$, the Young’s moduli decrease below $80\,\text{GPa}$ before increasing dramatically to $\sim 89\,\text{GPa}$ when $D = 3.7\,\text{nm}$. This unique feature of high strength for thin SNWs is consistent with a previous theoretical prediction [18] that the surface stress has a profound effect on the elastic modulus when the SNW diameter is smaller than a critical size ($D \sim 4\,\text{nm}$). Our tensile simulations also detect instabilities in the ultrathin SNWs ($3.5\,\text{nm} < D < 3.7\,\text{nm}$) that were analyzed, making them undesirable for nanomechanical studies. As the diameter increases from $\sim 3.7\,\text{nm}$, the effect of the surface stress starts to play a dominant role; thus, the Young’s moduli of SNWs will be dependent on their diameters. In addition, it is found that the Young’s modulus of a virtual SNW inner core is consistently larger than that of its associated SNW, suggesting that the nanowire surface undergoes compressive stresses that counteract the tensile loadings of the SNW, which is consistent with prior findings [18]. It is also worth noting that the Young’s moduli of SNWs under compression (figure 1(c)) show a different diameter dependency compared to those under tension. This can be understood from the fact that under compression, the compressive surface stresses do not counteract the external loading as strongly as when the SNWs are under tension. This results in a smaller Young’s modulus for a given SNW under compression as opposed to tension, particularly when the diameter is very small (e.g. $D < 4\,\text{nm}$). The ultimate strength of the long SNWs ($L = 14.32\,\text{nm}$) was

![Figure 2. Tensile response of long silica nanowires ($L = 14.32\,\text{nm}$) for different diameters. Results show the calculated stress-strain relationship for each given SNW in the elastic-to-plastic regions (top), and representative images (bottom) display the structural evolution of the SNW during tensile strains up to its breakage. Specifically, the SNW dimensions and associated elastic moduli are: (a) $D = 3.7\,\text{nm}$, $E = 98\,\text{GPa}$ and plastic strains $a_1$ to $a_4$; (b) $D = 3.8\,\text{nm}$, $E = 83\,\text{GPa}$ and brittle plastic strains $b_1$ to $b_3$, and (c) $D = 4.6\,\text{nm}$, $E = 80\,\text{GPa}$ and anomalous slightly ductile plastic strains $c_1$ to $c_3$. The tensile behavior of the nanowire and its inner core sizes are shown in all three cases, with core diameters ranging from the innermost size (Core 1) to the outermost size (Core 4). The strain rate in all three cases is $2%/25\,\text{ps} ~ (\sim 8\times 10^8\,\text{s}^{-1})$.](image-url)
calculated to be \(\sim 10\) GPa for a range of diameters, as shown in figure 1(d), which is in excellent agreement with independent measurements [28]. A close examination of the variations in the ultimate strength in the thin SNWs \((D < 5\) nm, \(L = 14.32\) nm) reveals a similar pattern to that of the Young’s modulus for the equivalent SNW dimensions, as shown in the inset of figure 1(d). This behavior confirms that the mechanical properties of SNWs are unique when their diameter is \(\sim 4\) nm, likely due to the unusual surface stress effects at this small size.

Figure 2 shows typical tensile simulation results for the longest SNWs \((L = 14.32\) nm) analyzed in this study for different diameters, and it shows the same strain rate of \(2\% / 25\) ps \((\sim 8 \times 10^8\) s\(^{-1}\)) in both the elastic and plastic regimes. As discussed above, the thinnest SNW \((D = 3.7\) nm) is an exception as it has the greatest Young’s modulus \((E = 98\) GPa at this strain rate) compared to the other SNWs. This can be understood from the fact that as a nanowire diameter falls below a critical value \((e.g. D \sim 4\) nm for silica), compressive surface stresses play a major role in strengthening the nanowire, leading to an enhanced Young’s modulus in thin SNWs under tension. This is consistent with the critical SNW diameter \((D \sim 4\) nm) predicted independently using the elasticity theory [18]. This implies that as the SNW diameter increases, the effect of the surface stresses becomes negligible compared to the SNW interior stress.

Most significantly, the stress-strain curves and structural evolution during the elastic-to-plastic and plastic-to-failure regimes (figure 2) for thin and long SNWs under equal strain rates show dissimilar deformation and failure modes. The thinnest SNW \((D = 3.7\) nm) displays a typical plastic deformation behavior for ductile materials, with tensile stresses gradually decreasing, starting at \(14\%\) strain \((a_1)\) (shown in figure 2(a)), which is associated with necking within the SNW beyond the yield strain and the plastic deformation in which the SNW undergoes up to \(32\%\) strain when it fails \((a_4)\). As the SNW diameter increases slightly \((D = 3.8\) nm), the nanowire breaks apart in a characteristic brittle fracture mode, and the stresses abruptly drop to zero at \(20\%\) strain \((b_3)\), as depicted in figure 2(b). The structural images for this long SNW also confirm the two completely separated segments of the nanowire at \(20\%\) strain \((b_3)\), with no detectable necking prior to its fracture. The above results suggest the existence of a critical diameter for SNWs, which is likely between \(3.7\) nm and \(3.8\) nm, below which the surface states play a major role in modifying the mechanical properties of the nanowire, which is in excellent agreement with early theoretical predictions \((D \sim 4\) nm) [18] and MD simulations [14]. The tensile
behavior of the thinnest SNW ($D = 3.7$ nm) can be explained in terms of surface stresses. When the thinnest SNW undergoes tensile loads (figure 2(a)), its associated surface compressive stresses (described earlier) likely influence deformation modes. A possible explanation for the mechanical response of this SNW is that the inner core reaches the breaking strain ($a_D$) first while the surface strain (e.g. Core 4) is still below this critical strain. As a result, the surface layer is resistant to the direct breaking of the SNW, leading to the necking behavior observed at the breaking location. As the SNW diameter increases, although the same surface states still remain, the surface-to-volume ratio decreases; therefore, the SNWs show a transition to the brittle fracture mode. Additional tests involving varied initial simulation conditions were conducted to verify the property changes, which seem to occur for the small difference in the SNW diameter ($D = 3.7$ nm and 3.8 nm).

Further analysis of other SNWs reveals that a thicker SNW ($D = 4.6$ nm) exhibits a slightly ductile fracture mode, as seen in figure 2(c), which seems distinct from the fracture modes in figures 2(a) and (b). In fact, a closer look at the structural deformation pattern reveals that this failure mode is not the same as for the thinnest preceding nanowire ($D = 3.7$ nm). First, the stress of the thinnest SNW ($D = 3.7$ nm) gradually decreases before breaking, while the stress of the thicker SNW ($D = 4.6$ nm) decreases more sharply after cracks are nucleated in one end of the nanowire, as seen in figure 2(c) at 22% strain ($c_1$). Additionally, the fracture surface of the thicker SNW shows relatively less necking compared to that of the thinnest SNW. These results suggest that the thicker SNW ($D = 4.6$ nm) is prone to a brittle fracture mode upon tension. The seemingly ‘ductile’ fracture mode in this SNW can be attributed to the limited time allowed for each tensile deformation, as each stretching process was given 25 ps, while a complete fracture event would likely require additional time for the crack to propagate throughout the entire SNW cross section.

The shapes and stress levels of the stress-strain curves of the long SNWs are also noted in figures 2(a) through 2(c). In the case of the thinnest SNW ($D = 3.7$ nm), the stress-strain response of the entire nanowire is similar to that of its virtual ‘core sizes,’ which implies that the SNW undergoes homogeneous stresses throughout its 3D structure. For a slightly thicker SNW ($D = 3.8$ nm), the equivalent stress-strain curves show a different behavior from that of the thinnest SNW ($D = 3.7$ nm). In fact, the innermost core size (Core 1) is found to be stiffer than other core sizes, as shown in figure 1(b); hence, the SNW endures heterogeneous stresses throughout its structure, with higher stresses in the innermost core of the SNW compared to the outer core sizes. For the thicker SNW ($D = 4.6$ nm) the stress-strain curves show even more variation, and the innermost core size (Core 1) undergoes elevated stress levels compared to other thinner SNWs. Thus, heterogeneous stresses were found to characterize the thicker SNWs, with higher stresses within the nanowire core regions. In addition, it is found that diameter size does not correlate directly with fracture strain levels.

### Table 1. Fracture modes of SNWs with different diameters evaluated at different strain rates. All SNWs in this evaluation have lengths of 14.32 nm.

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This MD investigation also evaluated the strain rate effects on the tensile deformation of SNWs. As shown in figure 3, a large SNW ($D = 6$ nm, $L = 14.32$ nm) is analyzed as it stretches at different strain rates. It is apparent that with decreasing strain rates (from 2%/25 ps to 2%/75 ps), the stress levels in all cases decrease faster after the elastic (linear) region. The breaking strain also decreases from 36% at a strain rate of 2%/25 ps to 30% at a strain rate of 2%/75 ps. Typical structural images under each stress-strain plot show distinct transitions from a ductile-to-brittle fracture mode. The fracture modes of all of the SNWs under different strain rates are summarized in table 1. From this table, it is observed that except for the thinnest SNW ($D = 3.7$ nm) for which the surface stress effects dominate, other thicker SNWs (3.8 nm < $D < 6$ nm) show a clear trend of ductile-to-brittle transition with the decreasing strain rate. The critical strain rate for a SNW to break in a brittle mode decreases monotonically as the diameter increases, probably due to the increased number of atoms per cross-section area. This likely explains why a brittle fracture mode is not observed for the largest SNWs ($D > 8$ nm) at 2%/75 ps but is expected to appear at slower strain rates, which would require rather lengthy simulations. Most interestingly, the strain rate was found to have a negligible effect on the Young’s modulus, except for the anomalously thinnest SNW ($D = 3.7$ nm), as shown in the supporting materials, table S1. It is seen that for most SNWs with different diameters, the Young’s modulus remains almost unchanged at different strain rates. This would be anticipated, as the Young’s modulus is measured within the elastic region in which there are no drastic structural changes or phase transitions; hence, the structural relaxation occurs rapidly. Additionally, in the failure region of a SNW, abundant bond breaking and re-bonding processes take place; the amount of this activity is dependent on the local strain rate and time duration. Hence, as the SNW diameter increases, more time is required for the bond breaking to complete. Another analysis in this study involved the investigation of surface stress effects of SNWs under tensile conditions by monitoring local structural distortions via bond angle distributions as a function of strain. The bond angle distribution of a bulk silica glass model was first examined, as shown in figures 4(a) and (b). The unstrained bulk glass has a bridging bond angle (Si-O-Si) distribution with a peak value at about
155°, while the tetrahedral bond angle (O-Si-O) distribution has a characteristic peak value at 109°, which is consistent with previous findings [4, 5]. Under a 6% tensile strain, the bulk silica model undergoes structural transformations that affect the Si-O-Si bond angle peak, primarily by a slight shift to a higher value since this bond angle is rather flexible. The O-Si-O bond angle distribution remains essentially unchanged due to a rather rigid tetrahedral angle, which is typical of silica structures. Most notably, similar analysis of the tensile behavior of all of the SNWs reveals that both bond angle distributions have a unique secondary peak, with a characteristic result for a SNW ($D = 8$ nm, $L = 14.32$ nm) at three different strain levels. Parts (c)–(d) show the equivalent bond angle distributions for the same SNW ($D = 8$ nm, $L = 14.32$ nm) within a core region ($d_{\text{core}} = 6$ nm). The insets in (c) and (e) illustrate the SNW structures at an unstrained state and under ~24% strain. The dashed arrows in parts (c)–(e) denote the positions of secondary peaks as signs of compressive surface stresses in the SNWs.

![Figure 4](image.png)

Figure 4. Bond angle distributions of various silica glass structures under tension. These include: (a)–(b) The Si-O-Si and O-Si-O bond angle distributions for bulk silica containing 12 288 atoms under different strains. The peak positions in both bond angle distributions are denoted (black arrows) as 155° and 109°, respectively. Parts (c)–(d) depict the bond angle distributions for a thick SNW ($D = 8$ nm, $L = 14.32$ nm) at three different strain levels. Parts (e)–(f) show the equivalent bond angle distributions for the same SNW as (c)–(d) within a core region ($d_{\text{core}} = 6$ nm). The insets in (c) and (e) illustrate the SNW structures at an unstrained state and under ~24% strain. The dashed arrows in parts (c)–(e) denote the positions of secondary peaks as signs of compressive surface stresses in the SNWs.

155°, while the tetrahedral bond angle (O-Si-O) distribution has a characteristic peak value at 109°, which is consistent with previous findings [4, 5]. Under a 6% tensile strain, the bulk silica model undergoes structural transformations that affect the Si-O-Si bond angle peak, primarily by a slight shift to a higher value since this bond angle is rather flexible. The O-Si-O bond angle distribution remains essentially unchanged due to a rather rigid tetrahedral angle, which is typical of silica structures. Most notably, similar analysis of the tensile behavior of all of the SNWs reveals that both bond angle distributions have a unique secondary peak, with a characteristic result for a SNW ($D = 8$ nm, $L = 14.32$ nm), shown in figures 4(c) and 4(d). The secondary peaks are found to be independent of the applied tensile strain, with their position unchanged up to 24% strain. Moreover, the Si-O-Si bond angle distribution has a more pronounced secondary peak height compared to that of the O-Si-O bond angle distribution due to greater flexibility in the Si-O-Si bond angle with the O atoms being two-coordinated, while the Si atoms are four-coordinated.

To examine the origin of the secondary peak, additional analysis of the bond angle distributions of the inner core of a large SNW ($D = 8$ nm, $L = 14.32$ nm) was pursued, as shown in figures 4(e) and 4(f). The SNW core diameter is $d_{\text{core}} = 6$ nm. It is seen that within the elastic region, i.e. at 0% and 10% strains, the secondary peak does not appear in either bond angle distribution. This behavior demonstrates that the secondary peak arises from the surface states, primarily due to surface reconstruction, which gives rise to intrinsic surface stress that modifies the mechanical properties of SNWs. Moreover, it is observed that the secondary peak emerges for this inner core
region when the SNW begins to plastically yield. This is probably because the SNW diameter tends to shrink in the plastic deformation stage, as seen in the inset of figure 4(e). As a result, a new surface state at a strain level of ~24% emerges in the core region. This again demonstrates that the secondary peak is a result of surface states. Another feature of the secondary peak is that it is positioned at angles near 97°, which indicates that the surface Si-O-Si angle is subjected to compressive stresses because its primary peak is located at 149°, which is consistent with the previous analysis that predicted that the intrinsic unstrained SNW has a compressive surface stress [18]. Additional simulations were run to test the effect of a higher annealing temperature (e.g. 1500 K) on the secondary peak. After a structural analysis of several of the SNWs using bond angle distributions, results showed that after annealing at 1500 K and quenching to 300 K, the secondary peak remains unchanged, indicating that the surface compressive stress effect prevails following this distinct treatment. The structures in this study represent ideal high-purity SNW samples under vacuum conditions (e.g. the SNW surface is dry). Experimental SNWs will likely contain defects, impurities and even coatings under various conditions such as humidity, all of which will affect their structural and mechanical properties. Future studies would need to evaluate such factors for reproducing more complex real laboratory conditions.

4. Conclusions

In summary, systematic MD simulations of the tensile behavior of SNWs show remarkable size-dependent Young’s moduli and fracture modes, primarily due to dominant surface states. A critical SNW diameter range is identified to be 3.7–4 nm, below which surface states play a key role in modifying the mechanical properties of these oxide nanowires. Hence, the mechanical properties of SNWs with diameters smaller than 4 nm were found to be different from those of larger diameters. The strain rate was found to be important in determining the fracture mode of these nanowires but had negligible effect on their elastic properties, except for the anomalous thinnest SNW (D = 3.7 nm). Surface stress effects of the SNWs were evaluated by probing characteristic bond angle distributions in a specific SNW and in associated inner core sizes. A secondary peak was found in the bridging bond angle (Si-O-Si) distribution located at ~97° in the SNW surface layers, offering evidence of compressive surface stress. Future studies of local structural transformations occurring in the SNW and its virtual cores will be pursued to correlate the transformations with macroscopic properties and for comparison with previous studies [4, 14]. The success of future manufacturing using SNWs will depend considerably on understanding their structure, properties and performance, with implications for self-assembly and nano-manipulation processes. The nanomechanical results presented here can help toward understanding similar nanostructures, nanoscale silica foams and nanoporous self-assembled silica structures, all of which can potentially be used in a wide range of technological applications. The results of this study are also expected to have important implications in the design and fabrication of nanowire-based nanoelectromechanical devices and phononic nanodevices.

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