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Size Effects on the Stiffness of Silica Nanowires**

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The stiffness of silica, a covalently bonded network solid, has not been found to be a function of physical dimensions for bulk specimens and microscale fibers of diameter $>5\ \mu\text{m}$. However, recent indirect mechanical characterization of drawn silica nanowires suggested a substantial and unexplained decrease in the Young's elastic modulus E for diameters D below 100 nm. We present new data from direct mechanical characterization using a scanning probe microscope (SPM), and show that silica wires with diameters as small as 280 nm exhibit the stiffness of bulk silica. Further, we present results from molecular dynamics simulations that predict an increase in stiffness for diameters up to 6 nm. Together, these results suggest that the elastic weakening of silica nanowires of intermediate diameters (43 to 98 nm) cannot be explained solely by recourse to the intrinsic properties of amorphous silica as captured either by direct measurements on drawn nanowires of smaller surface-area-to-volume ratios, or by classical molecular dynamics simulations of silica nanowires of larger surface-area-to-volume ratios.

Silica nanowires have promising applications in optoelectronic nanodevices, due to the optical waveguide properties of this material's structure^[1] and the capacity of such wires to exhibit small radii of curvature without fracture.^[2] Application of this material will require improved understanding of the mechanical properties of such covalently bonded nanostructures. In general, material fibers or wires of nanometer-scale diameter exhibit much higher strength than the corresponding bulk materials.^[3] However, indirect measurements of elastic moduli have suggested that amor-

phous silica nanowires can be much more compliant than the corresponding bulk material,^[4,5] while fibers of micrometer-scale diameter exhibit the stiffness of bulk silica.^[6] This work aims to elucidate the transition between bulk and nanoscale behavior and investigate possible mechanisms for the size effect on stiffness in such covalent network solids.

In addition to suitability for emerging technologies, silica structures of such small physical dimensions provide an opportunity to understand chemical/mechanical interactions in materials, owing to inherently high ratios of surface area to volume and nearly defect-free microstructures. An important example of such interactions is stress corrosion, in which water dramatically reduces the tensile strength of silica.^[7] Moreover, nanowires represent material structures that can bridge experimental and simulation length scales, since the estimation of the theoretical strength through molecular dynamics simulation is usually restricted to systems that are too small to investigate by conventional experimental means. A reliable mechanical characterization of these wires is essential for the interpretation of strength measurements.

Mechanical properties of conventional silica fibers can be determined via conventional experiments such as two-point bending.^[8,9] Wires of smaller diameter, however, present significant experimental challenges, due to difficulties in simultaneously imaging, gripping, applying, and measuring the nanoscale forces and displacements. For silica wires of diameter $<1\ \mu\text{m}$, only indirect measurements of elastic moduli E via resonant frequency measurements have been reported.^[4,5]

At the nanoscale, several methods have been proposed to measure mechanical properties. Among these, direct measurement of force during controlled displacement of a compliant cantilevered probe within a scanning probe microscope (SPM) has been implemented to measure the stiffness and strength of carbon nanotubes and nanorods, as well as nanowires made of silicon carbide,^[10] gold,^[3] silver,^[11] and manganese oxide,^[12] among others. The force-displacement behavior is interpreted according to continuum beam theory in order to obtain the stiffness and strength of the material.

In this work, we apply this method to determine the elastic moduli E of silica wires with uniform diameters ranging from 280 to 1950 nm. We relate these results to predictions of E as a function of nanowire diameter via classical molecular dynamics simulations for diameters from 3.7 to 6 nm.

Figure 1 shows effective bending stiffness of the silica wires P/d calculated from vertical-force experiments. Points are irregularly spaced due to the manual positioning of the SPM cantilever. Figure 2 shows the effective bending stiffness of the silica wires P/d calculated from in-plane loading experiments. Note that regular spacing of acquired force-displacement responses in x was provided by the xy piezoelectric scanner (see Experimental Section). Fitting of both sets of experimental results via Eq. (2) (see below) identifies the corresponding elastic modulus E for each wire, as summarized in Table 1.

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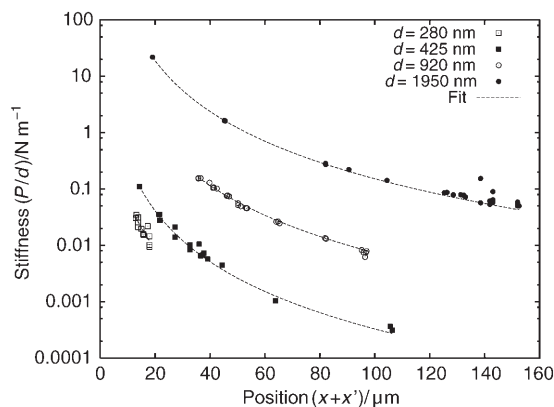


Figure 1. Bending stiffness versus force application point for vertical loading. Dashed curves are best fits using Eq. (2).

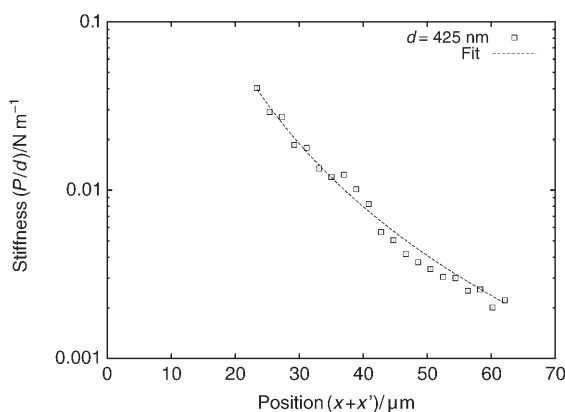


Figure 2. Bending stiffness versus force application point for in-plane loading. The dashed curve is a best fit using Eq. (2).

Table 1. Stiffness of silica nanowires for vertical (E_v) and in-plane (E_i) tests.

Wire	Diameter [nm]	E_v [GPa]	E_i [GPa]
280	281 ± 10	76 ± 45	–
425	426 ± 4	68 ± 5	105 ± 12
920	920 ± 10	70 ± 6	–
1950	1948 ± 25	72 ± 23	–

No general trend in stiffness was observed for the range of diameters tested in this work, as shown in Figure 3. Within the accuracy of the method, all wires exhibit the stiffness of bulk silica. The value fitted using the lateral wire deflection was larger than the corresponding value obtained using vertical wire deflection. However, a nonlinear fit of these data (with the assumption that $E = 72$ GPa) still exhibits a very reasonable fit (although not best fit), which suggests that the results obtained via lateral deflection are not incompatible with those obtained via vertical deflection.

Our molecular dynamics simulations predict an elastic modulus E in the range of 89–101 GPa for nanowires with $D = 3.7$ – 6.0 nm and for a thin film of thickness 3.8 nm, while simulations of the bulk sample prepared with the same procedure exhibited an E of 75 GPa, consistent with experi-

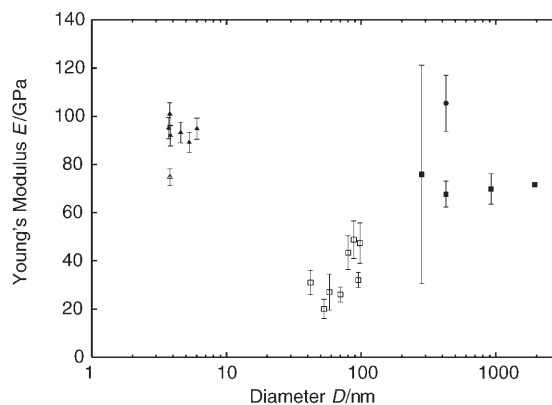


Figure 3. Young's modulus E of silica wires versus diameter D for different techniques: vertical experiments (■), in-plane experiment (●), resonant frequency experiments (□),^[4,5] MD simulations of nanowires and thin films (▲), and MD simulation of bulk silica (△).

mental measurements on bulk amorphous silica.^[13] Note that the simulated bulk silica result in Figure 3 is represented as a point (of dimensions 3 nm × 3 nm × 3 nm) to reflect the fact that “bulk” in molecular dynamics simulations still comprises less than one mole of atoms. The standard deviation of E for multiple simulations attempted for wires of the same average diameter was about 5%, indicating that the increase in E predicted for nanowires in this range of diameters is statistically significant.

The elastic stiffness of bulk amorphous silica is 72 GPa.^[13] This value has been confirmed for silica wires over the wide range of diameters accessible via conventional tensile testing ($D > 5$ μm).^[8,9] However, for silica wires of sub-micrometer diameter, results are inconsistent. Several researchers have used the resonant frequency of the wires, an indirect but well-studied evaluation of elastic compliance, to determine the elastic modulus E . Chen et al.^[6] validated this technique using larger silica wires ($D > 23$ μm), which exhibited the modulus of bulk silica, as expected. Wang et al.^[4] obtained $E = 27 ± 7$ GPa for diameters between 43 and 95 nm, and Dikin et al.^[5] measured $E = 47 ± 7$ GPa for D between 80 and 98 nm (see Figure 3). The present study provides evidence through direct measurement that nanowires of $D > 280$ nm still exhibit the stiffness of bulk silica. These intermediate values are important in understanding the transition to the lower stiffness observed at $D < 100$ nm and in validating existing results.

In order to understand the physical origin of this size-dependent elastic response of silica, classical molecular dynamics simulations were implemented to consider much smaller wire diameters ($D < 6$ nm), predicting an increase in E at those length scales. A similar effect has been reported in the simulation of gold nanowires,^[14] while the opposite was observed in simulations of copper nanowires.^[15] This elastic stiffening can be understood on the basis of surface-constrained elasticity,^[16] where tensile stresses are generated at the material surface. These stresses contract the wire and increase the stiffness of the core material within the wire, due ostensibly to nonlinear elasticity effects. However, this increase in elastic stiffness is detectable only at very small diameters. Further, surface elasticity cannot predict the dra-

matic decrease in stiffness observed by Dikin et al.^[5] for silica nanowires with diameters as large as 100 nm, as the surface-area-to-volume ratio of such nanowires is too great for this effect to be appreciable. In fact, as amorphous silica is a covalently bonded network, it is expected that surface elasticity effects would be more pronounced than in metal nanowires for which interatomic potentials are more short-range. Thin-film simulations with larger thicknesses are ongoing to determine the range where this effect is relevant for amorphous silica.

Based on the results presented herein, we suggest that the low elastic moduli measured by Wang et al.^[4] and Dikin et al.^[5] may not be explained solely by recourse to the intrinsic properties of amorphous silica nanowires. The reasons for this apparent discrepancy may be attributable in part to differences in initial material structure, or to a size effect in covalently bonded networks for $D < 100$ nm that is not captured by current simulated approximations of amorphous silica. We note that the samples of Wang et al.^[4] and Dikin et al.^[5] were obtained by vapor–liquid–solid methods, while our samples were obtained by drawing (see Experimental Section). The latter method is more similar to the process used for larger fibers, lending confidence to our results. In addition, the measurements of Wang et al.^[4] and Dikin et al.^[5] were performed indirectly through the excitation of vibration modes of the wires. This indirect method relies on additional parameters (geometry, boundary conditions, and material density) that may introduce errors, but is in general an accepted approach for an estimation of E that recovers the result of bulk silica for micrometer-scale, drawn silica wires.^[6] Of course, a more definitive conclusion will require some overlap between the diameters available through the two fabrication techniques and the diameters measurable via the two testing methods. As discussed below, direct mechanical measurement of nanowires in this range of diameters requires several considerations.

Direct bending of fibers and wires using SPM cantilevers has been employed to measure the stiffness and strength of nanobeams, nanotubes, and nanowires as small as 21 nm.^[10] One of the most important obstacles is obtaining reliable and well-characterized samples, with geometries and boundary conditions that are accessible to the SPM cantilevered probe. The cantilevered nanowire geometry employed here is the simplest to analyze via continuum analysis. However, such simply supported structures are very compliant, which can obfuscate experimental measurements. Another important consideration in SPM-enabled measurements is the calibration of the nanowire displacements and the cantilevered SPM probe stiffness; the latter is required to accurately infer the force required to deflect the nanowire. If forces are applied in the vertical (z) direction, calibration is fairly straightforward, while in-plane force calibrations require special care (see Experimental Section). For wires with diameters > 500 nm, it is feasible to position the probe manually and apply vertical forces. For smaller wires, however, contact forces can induce longitudinal stresses, actually causing stretching or buckling that mask the bending forces of interest. Therefore, it is necessary to apply the load very close to the support—within a few micrometers of the

clamped end for the wire diameters considered herein. In these cases, manual positioning of the probe is unreliable and in-plane force application should be used.

Although the plastic and fracture processes of these nanowires were not evaluated as a function of diameter in the current study and cannot be inferred directly from considerations of elastic properties, analogy to nanocrystalline materials predicts that yield and fracture strengths will generally increase as the characteristic length scale of the material (grain diameter in nanocrystalline metals or nanowire diameter in the present case) decreases.^[17–20] Weibull statistical analysis of brittle solids also predicts increased failure strength with decreased physical dimensions, due to the lower concentration of critically sized defects. We are currently exploring whether plastic strengthening to the extent reported for metallic nanowires^[3] can be predicted and observed as a function of nanoscale diameters for covalent network solids such as amorphous silica.

We have demonstrated two direct, nanomechanical approaches to determine the elastic mechanical properties of amorphous silica nanowires. For nanowire diameters ranging from 2 μm to 280 nm, such nanowires exhibit the stiffness of bulk silica. In contrast, our molecular dynamics computations recover the mechanical properties of bulk silica, but predict elastic stiffening of thin films and nanowires, consistent with surface elasticity arguments. These findings are relevant to consideration of the length-scale-dependent mechanical behavior of silica nanowires, as our results predict a 30% increase in stiffness as diameter decreases from ≈ 100 nm to ≈ 10 nm, due to the increased surface-area-to-volume ratio of the network solid. Further, this mild effect on the elastic behavior of silica nanowires is required for interpretation of the more technologically relevant deformation states of plasticity and fracture, especially as increasingly small silica nanostructures will be considered as optical waveguides in chemical environments that may compromise strength.^[21]

Experimental Section

All amorphous silica wires used in this work were obtained from larger silica fibers via the two-step drawing process developed by Tong et al.;^[2] this technique reduces the diameters to the sub-micrometer scale. In contrast, conventional high-temperature drawing^[22] typically produces wires larger than 10 μm . Nanometer-scale diameters have also been produced through various vapor–liquid–solid (VLS) techniques.^[23,24] Both techniques produce reasonably straight and amorphous silica wires, but drawn wires exhibit lower surface roughness and more uniform diameters – assumptions implicit in the continuum analysis employed to extract mechanical properties.

The wires were mounted as clamped cantilevers via placement on steel supports and fixed at one of the extremities, leaving the rest of the wire free. The length and diameter of each wire was measured over at least ten points along the wire length via a scanning electron microscope (JEOL JSM-5910). The wires used in this work are summarized in Table 1, indicating a $< 1\%$ variation in wire diameter for all the silica wires considered.

A commercial scanning probe microscope with xy and z displacement capabilities (3D-Molecular Force Probe, Asylum Research, Santa Barbara, CA) was used to acquire the force–displacement response of the silica wires. We used silicon nitride cantilevers (Veeco Inc., Sunnyvale, CA) of nominal spring constants k between 0.01 and 0.50 Nm^{-1} , except for experiments on the wire of 1950 nm diameter, which were performed using a silicon cantilever (Olympus AC240) of $k=1.3 \text{ Nm}^{-1}$ (owing to the greater structural stiffness of this thicker wire). The optical lever sensitivity (nmV^{-1}) was calibrated by deflecting the SPM cantilever against a glass surface and the cantilever spring constant k was then calculated from the thermal vibration spectrum.^[25–27]

In the first set of experiments, vertical loading, the SPM cantilever was positioned manually over different points along the length of the cantilevered silica wire (hereafter, wire) and the z -piezo was actuated to apply a vertical displacement z (see Figure 4). The wire was perpendicular to the cantilever to minimize the effect of longitudinal forces. The deflection δ of the SPM cantilever was recorded, giving the force through $P_v = k\delta$.

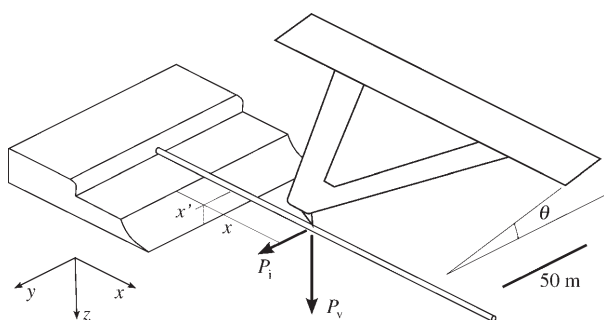


Figure 4. Force application scheme for vertical loading (P_v) and in-plane loading (P_i) at the position $x+x'$. The triangular SPM cantilever is inclined by an angle θ with respect to the horizontal plane. Dimensions are approximate.

Continuum beam theory predicts that the displacement $d = (z - \delta)$ of a cantilever beam subject to a force P is given by:

$$P = \frac{3EI}{x^3} d \quad (1)$$

where E is the Young's elastic modulus of the material, I is the moment of inertia (for a cylinder of diameter D , $I = \pi D^4/64$) and x is the distance from the application point to the support. Measuring the bending stiffness P/d at different points x , it is possible to estimate the effective elastic modulus E with higher accuracy.

The position x was obtained from a simultaneously acquired high-magnification optical image (Pulnix CCD camera on a Nikon TE200 inverted optical microscope). The real support point is not visible due to the inverted optics used to image the wire, therefore a reference point, such as the wire tip (if visible), was used to measure x . An additional distance x' corresponds to the invisible part of the wire and needs to be determined indirectly. We use a nonlinear fitting procedure to determine E and x' simultaneously from:

$$\frac{P}{d} = \frac{3EI}{(x+x')^3} \quad (2)$$

A second set of measurements was obtained by loading the beam in the horizontal (xy) plane. The SPM cantilever was positioned perpendicularly to the long axis of the wire. The xy piezo scanner was set to acquire a large number of points in the fast-scanning (y) direction, in which the wire was bent. Movement in the slow-scanning (x) direction caused the force application to occur at different positions on the wire. The resulting data and interpretation is similar to that of the vertical loading experiments discussed above. However, here the in-plane load P_i is calculated from the vertical load P_v , which is measured directly:

$$P_i = \frac{P_v}{\tan \theta} \quad (3)$$

where θ is the angle of the SPM cantilever with respect to the horizontal plane. This formula is obtained by considering that the contact force P between the probe and the wire can be decomposed into $P_v = P \cos \theta$ and $P_i = P \sin \theta$. This introduces the parameter (θ), which may introduce additional errors. We assumed $\theta = 10^\circ$.

The accuracy of the calculated elastic stiffness P/d or modulus E will depend on the quality of several independent measurements. For the experiments presented herein, the main source of error was the range in experimentally measured P/d values (5–20%). Other relevant sources of error are the SPM system calibration (optical lever sensitivity and cantilever stiffness each contribute $\approx 3\%$ standard error), the wire diameter measurement (1–2.5% standard error) and the determination of testing position along the wire length x when manually positioning the point of vertical force application ($\approx 1\%$ standard error).

Classical molecular dynamics simulations of amorphous silica nanowires (diameters from 3.7–6 nm) were implemented using the BKS interatomic potential.^[28] Amorphous silica structures were obtained by computationally annealing and then quenching (crystalline) quartz wires of the same approximate diameter. Periodic boundary conditions were enforced in the longitudinal direction only. The amorphous systems were strained in the longitudinal direction at a rate of 10^{10} s^{-1} , under a constant simulation temperature (300 K) enforced via a Nosé–Hoover thermostat. The stress on the wires was calculated by normalizing the force by the initial cross-sectional area of the nanowire. A bulk sample and a thin film sample of 3.8-nm thickness were prepared using the same annealing/quenching procedure for comparison and consideration of surface elasticity effects.

Keywords:

mechanical properties • molecular dynamics • nanowires • scanning probe microscopy • silicates

- [1] J. Y. Lou, L. M. Tong, Z. Z. Ye, *Opt. Express* **2005**, *13*, 2135–2140.
- [2] L. M. Tong, R. R. Gattass, J. B. Ashcom, S. L. He, J. Y. Lou, M. Y. Shen, I. Maxwell, E. Mazur, *Nature* **2003**, *426*, 816–819.
- [3] B. Wu, A. Heidelberg, J. J. Boland, *Nat. Mater.* **2005**, *4*, 525–529.
- [4] Z. L. Wang, R. P. Gao, P. Poncharal, W. A. De Heer, Z. R. Dai, Z. W. Pan, *Mater. Sci. Eng. C* **2001**, *16*, 3–10.

- [5] D. A. Dikin, X. Chen, W. Ding, G. Wagner, R. S. Ruoff, *J. Appl. Phys.* **2003**, *93*, 226–230.
- [6] X. Q. Chen, S. L. Zhang, G. J. Wagner, W. Q. Ding, R. S. Ruoff, *J. Appl. Phys.* **2004**, *95*, 4823–4828.
- [7] C. R. Kurkjian, P. K. Gupta, R. K. Brow, N. Lower, *J. Non-Cryst. Solids* **2003**, *316*, 114–124.
- [8] P. W. France, M. J. Paradine, M. H. Reeve, G. R. News, *J. Mater. Sci.* **1980**, *15*, 825–830.
- [9] M. J. Matthewson, C. R. Kurkjian, S. T. Gulati, *J. Am. Ceram. Soc.* **1986**, *69*, 815–821.
- [10] E. W. Wong, P. E. Sheehan, C. M. Lieber, *Science* **1997**, *277*, 1971–1975.
- [11] X. D. Li, H. S. Gao, C. J. Murphy, K. K. Caswell, *Nano Lett.* **2003**, *3*, 1495–1498.
- [12] A. Kis, D. Mihailovic, M. Remskar, A. Mrzel, A. Jesih, I. Piwonski, A. J. Kulik, W. Benoit, L. Forro, *Adv. Mater.* **2003**, *15*, 733–736.
- [13] H. Scholze, *Glass: Nature Structure, and Properties*, Springer-Verlag, New York, **1990**.
- [14] J. K. Diao, K. Gall, M. L. Dunn, *J. Mech. Phys. Solids* **2004**, *52*, 1935–1962.
- [15] H. Y. Liang, X. G. Ni, X. X. Wang, *Acta Metall. Sin. (Engl. Lett.)* **2001**, *37*, 833–836.
- [16] R. C. Cammarata, *Prog. Surf. Sci.* **1994**, *46*, 1–38.
- [17] J. Schiøtz, K. W. Jacobsen, *Science* **2003**, *301*, 1357–1359.
- [18] J. Schiøtz, *Scripta Mater.* **2004**, *51*, 837–841.
- [19] H. Van Swygenhoven, A. Caro, *Nanostruct. Mater.* **1997**, *9*, 669–672.
- [20] H. Van Swygenhoven, A. Caro, *Appl. Phys. Lett.* **1997**, *71*, 1652–1654.
- [21] T. Zhu, J. Li, X. Lin, S. Yip, *J. Mech. Phys. Solids* **2005**, *53*, 1597–1623.
- [22] R. Brückner, G. Pähler, in *Strength of Inorganic Glass* (Ed.: C. R. Kurkjian), Plenum, New York, **1985**, pp. 329–349.
- [23] B. Zheng, Y. Y. Wu, P. D. Yang, J. Liu, *Adv. Mater.* **2002**, *14*, 122–124.
- [24] Z. W. Pan, Z. R. Dai, C. Ma, Z. L. Wang, *J. Am. Chem. Soc.* **2002**, *124*, 1817–1822.
- [25] J. L. Hutter, J. Bechhoefer, *Rev. Sci. Instrum.* **1993**, *64*, 1868–1873.
- [26] H. J. Butt, M. Jaschke, *Nanotechnology* **1995**, *6*, 1–7.
- [27] J. P. Cleveland, S. Manne, D. Bocek, P. K. Hansma, *Rev. Sci. Instrum.* **1993**, *64*, 403–405.
- [28] B. W. H. van Beest, G. J. Kramer, R. A. van Santen, *Phys. Rev. Lett.* **1990**, *64*, 1955–1958.

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