INSTITUTE OF PHYSICS PUBLISHING NANOTECHNOLOGY
Nanotechnology **16** (2005) 1445–1448 doi:10.1088/0957-4484/16/9/004

Self-modulated taper drawing of silica nanowires

Limin Tong[1,2,4], **Jingyi Lou**[3], **Zhizhen Ye**[3], **Geoff T Svacha**[2] **and Eric Mazur**[2]

[1] State Key Laboratory of Modern Optical Instrumentation, Zhejiang University, Hangzhou 310027, People's Republic of China
[2] Department of Physics and Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA
[3] State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, People's Republic of China

E-mail: phytong@zju.edu.cn

Received 8 April 2005
Published 29 June 2005
Online at stacks.iop.org/Nano/16/1445

Abstract
We report a self-modulated taper-drawing process for fabricating silica nanowires with diameters down to 20 nm. Long amorphous silica nanowires obtained with this top-down approach present extraordinary uniformities that have not been achieved by any other means. The measured sidewall roughness of the wires goes down to the intrinsic value of 0.2 nm, along with a diameter uniformity better than 0.1%. The wires also show high strength and pliability for patterning under optical microscopes. The ability to prepare and manipulate highly uniform silica nanowires may open up new opportunities for studying and using low-dimensional silica material on a nanometre scale.

1. Introduction

Owing to their excellent physical and chemical properties, silica materials in the forms of fibres, tapers or wires with nanometric diameters show great promise for optical, mechanical, chemical and biomedical applications [1–7]. Existing methods for synthesizing one-dimensional nanostructures such as vapour–liquid–solid growth can yield silica nanowires with small diameters [5–15], but usually present difficulties in achieving high uniformities and pristine surfaces. For using as building blocks for nanoscale photonic, mechanical and biological components and tools, unwanted light scattering and stress concentration due to surface roughness, defects and diameter fluctuations may seriously degrade the nanowire's optical and mechanical properties that are crucial to nanodevice applications [16–18]. Also, physical and chemical research on the morphology of silica nanostructures [19–21], surface roughness of silica glass [22–24] and intrinsic strength of silica materials [25, 26] favours high uniformities and/or pristine surfaces for both molecular dynamical simulations and experimental investigations.

[4] Author to whom any correspondence should be addressed.

2. Self-modulated taper drawing of silica nanowires

Recent work has shown that highly uniform silica nanowires can be fabricated with a two-step taper-drawing method [1]. Relying on a balance kept between the surface tension (the force tending to break the wire) and molecular bonding (the cohesive force that connects the wire) at the softening temperature of silica (around 2000 K), nanowires with diameters down to 50 nm have been fabricated by taper drawing micrometre diameter wires with constant forces. Wires obtained with this technique show excellent diameter uniformity and surface smoothness, and the physical drawing (rather than a chemical reaction) approach makes it possible to obtain pristine surfaces. However, the effort required to fabricate nanowires thinner than 50 nm, which are desired for a variety of purposes such as structural, dynamical and catalytic investigations of silica nanowires, has proven problematic due to the increased susceptibility of the drawing process as a result of the decreased wire diameter; the pulling force that is suitable for drawing a thick wire during the initial stage is excessively large for handling a thinner one afterward. When there are slight fluctuations in drawing conditions (e.g. wobbles in the drawing temperature), wire drawing with a constant force or speed usually leads to an abrupt taper or a sudden

break, especially for wires thinner than 100 nm. Here we show that, by introducing self-modulations to the drawing force and speed, silica nanowires with much smaller diameters and intrinsic surface roughness can be obtained.

A schematic diagram of the self-modulated taper drawing is shown in figure 1. Firstly, as was done in previous work [1], we heat and draw a standard silica fibre (e.g. SMF-28 from Corning Inc.) to a micrometre diameter wire, and wrap the wire on the tip of a tapered sapphire fibre. Secondly, to introduce the self-modulation, we hold the silica fibre (to which the smaller-diameter wire is connected through a taper) parallel to the sapphire taper (see figures 1(A) and (B)) without breaking the connection between the silica wire and the sapphire taper. We then tauten the wire to form a 90° elastic bend around the taper of the silica fibre and thereby produce a tensile force perpendicular to the sapphire and silica fibres, which can be used for self-modulation. Since the sapphire taper is thicker and much stiffer than the silica fibre taper, the elastic bend always occurs around the taper area of the silica fibre. As shown in figure 1(C), during the initial stage, when we draw a thick wire that requires a relatively large force, the bending centre (around which the sharpest bend is centred) occurs at the thicker part of the taper; as the wire is elongated and the wire diameter goes down, the bend loosens and the bending centre moves towards the thin end of the taper, resulting in smaller forces for drawing thinner wires, which we found to be critical for drawing uniform wires with very small diameters. Also, when there are unpredictable undulations in drawing conditions, for example a slight temperature fluctuation that may cause large variation in the viscosity of silica [27], the elastic bend can instantly modulate the drawing speed by shifting the bending centre to and fro to avoid sudden changes in wire diameter, whereas a constant-force drawing may cause an abrupt taper or even breakage of the wire. In addition, a 30 mW continuous-wave He–Ne laser (633 nm wavelength) is launched into and guided along the silica fibre, fibre taper and silica nanowire to illuminate the taper and nanowire, which facilitates the real-time monitoring and controlling of the drawing process.

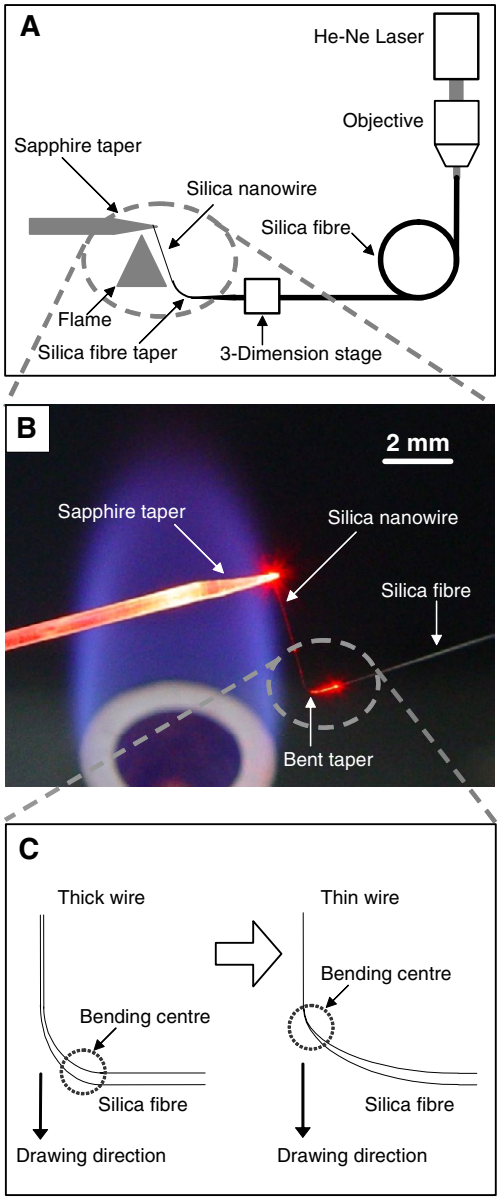

Figure 1. (A) Schematic diagram of the self-modulated taper-drawing system. A three-dimension stage is used to mount and adjust the silica fibre taper to form a 90° bend, and a He–Ne laser is launched into the silica fibre for illuminating the nanowire and monitoring the drawing process. (B) Close-up photograph of the nanowire drawing assisted with a bent taper for self-modulation. The red light shining around the nanowire and tapers is from the He–Ne laser. (C) Schematic diagram of the self-modulation realized by shifting the bending centre. The bending centre is marked around the sharpest bend with a red circle.

3. Characterization of as-drawn silica nanowires

Silica nanowires with diameters down to 20 nm are obtained with the self-modulated taper-drawing method. Generally, the wire contains three parts: an obviously tapered start (millimetres long), a uniform wire (up to centimetres) and an abruptly tapered end (usually several to tens of micrometres in length). Shown in figure 2(A) are the measured diameter D and diameter uniformity U_D of a typical nanowire with respect to its length (starting from the thin end), where we define $U_D = \Delta D/L$, with L the length over which the wire gives a maximum diameter deviation ΔD from the central diameter D. Although it exhibits an overall monotonic tapering tendency, neglecting the obvious initial and end tapered regions, the wire shows a very high uniformity. For example, at $D = 30$ nm, $U_D = 1.2 \times 10^{-5}$, which means that if we cut a 80 μm length wire with its diameter centred around 30 nm, the maximum diameter difference between the two ends is less than 1 nm; such a tiny tapering effect is acceptable in most applications. The high uniformity of the wire can also be seen in figures 2(B) and (C), in which 25 nm diameter (TEM image in figure 2(B)) and 100 nm diameter (SEM image in figure 2(C)) wire segments are cut from the same wire; although they can be viewed as composite parts of a long taper on the whole, the two pieces are very uniform by themselves. If we set $U_D < 10^{-3}$ (that is 0.1%) as a criterion for uniformity, the thinnest uniform nanowire we obtain is about 20 nm in diameter.

The small diameter of the nanowire makes it possible to investigate the surface roughness with a TEM. Shown in

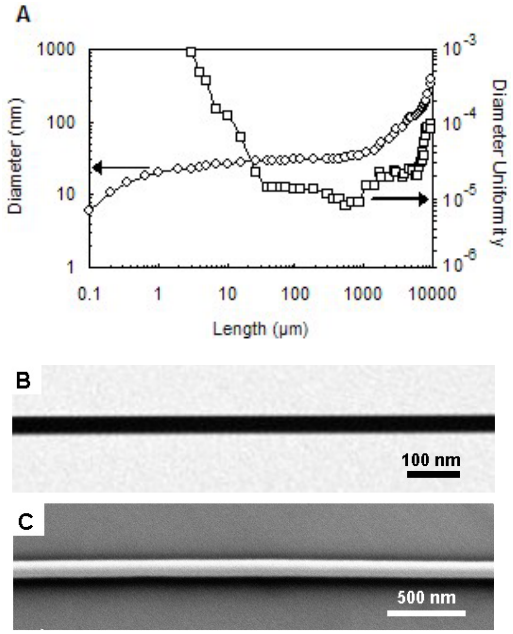

Figure 2. (A) Measured diameter D and diameter uniformity U_D of a self-modulated taper-drawn silica nanowire with respect to its length. The length starts from the distal end. (B) TEM image of a 25 nm diameter silica nanowire. (C) SEM image of a 100 nm diameter silica nanowire. Nanowires shown in (B) and (C) are different parts of a same long wire.

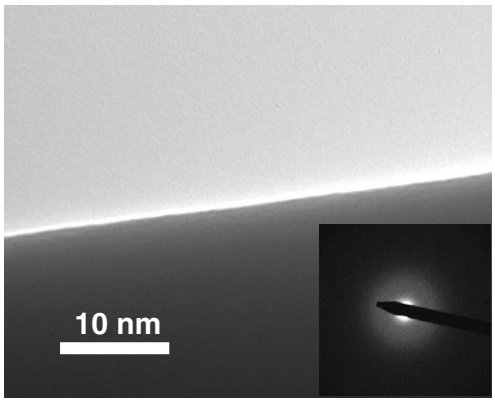

Figure 3. High-magnification TEM investigation of the surface roughness of a 35 nm diameter silica nanowire. The dark area is the silica core and the bright area is vacuum. Inset: the electron diffraction pattern shows that the nanowire is amorphous.

figure 3 is a typical image taken at the edge of a 35 nm diameter nanowire. No obvious irregularity and defect can be seen along the sidewall of the wire. For nanowires with diameters smaller than 50 nm, measured root mean square (RMS) surface roughness ranges from 0.15 to 0.20 nm, which is much better than that of thicker wires (around 0.5 nm) reported previously [1], and representing the intrinsic roughness of melt-formed glass surfaces [22, 23].

Because of the large length, silica nanowires obtained here can be clearly identified under an optical microscope. The optical visibility of the nanowires makes it possible to manipulate silica nanowires individually under optical microscopes in air, which should greatly facilitate the handling

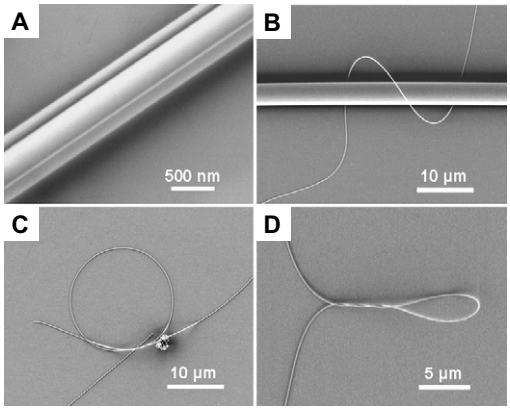

Figure 4. (A) SEM image of three silica nanowires placed in a bundle. The diameters of the nanowires are 140, 510 and 30 nm (from top left to bottom right respectively). (B) SEM image of a 150 nm diameter silica nanowire wrapped around a 4 μm diameter fibre to form a spiral coil. (C) SEM image of an 18 μm diameter loop assembled with a 65 nm diameter silica nanowire. (D) SEM image of a rope-like twist formed with a 120 nm diameter silica nanowire.

of these nanowires for practical applications. Also, because of its excellent uniformity, these nanowires present high mechanical strength and pliability for patterning without breaking. Using probes from an STM to hold and manipulate nanowires under an optical microscope, we have successfully assembled silica nanowires into various patterns. As shown in figures 4(A)–(C), we bundle three nanowires with diameters of 30, 140 and 510 nm in parallel with the help of van der Waals attraction (figure 4(A)), wrap a 150 nm diameter silica nanowire around a 4 μm diameter fibre to form a spiral coil (figure 4(B)), and assemble a 65 nm diameter silica nanowire into an 18 μm diameter nanoring. Using tilted probes, we can also rub and twist the nanowires on a finely polished substrate without breaking them. Shown in figure 4(D) is a rope-like twist formed with a 120 nm diameter silica nanowire on a silicon substrate; the 'nanorope' keeps its shape when it is lifted up from the substrate, indicating that the nanowire can also withstand shear deformation to a certain degree.

4. Conclusions

In conclusion, we have demonstrated a self-modulated taper-drawing method for fabricating amorphous silica nanowires with diameters down to 20 nm. Nanowires obtained with this top-down approach present excellent diameter uniformity and intrinsic surface smoothness, and they are sturdy and flexible enough to be manipulated and patterned under an optical microscope. As silica is one of the fundamental materials for building components and tools in optical, mechanical, biological and many other applications, the ability to prepare and manipulate highly uniform silica nanowires may attract broad interest in studying and using low-dimensional silica material on a nanometre scale.

Acknowledgments

The authors acknowledge the support from the Natural Science Foundation of China (60425517 and 60378036) and the US National Science Foundation (PHY-9988123).

References

[1] Tong L M, Gattass R R, Ashcom J B, He S L, Lou J Y, Shen M Y, Maxwell I and Mazur E 2003 *Nature* **426** 816
[2] Domachuk P and Eggleton B J 2004 *Nat. Mater.* **3** 85
[3] Tong L M, Lou J Y and Mazur E 2004 *Opt. Express* **12** 1025
[4] Brambilla G, Finazzi V and Richardson D J 2004 *Opt. Express* **12** 2258
[5] Yu D P, Hang Q L, Ding Y, Zhang H Z, Bai Z G, Wang J J, Zou Y H, Qian W, Xiong G C and Feng S Q 1998 *Appl. Phys. Lett.* **73** 3076
[6] Wang Z L, Gao R P P, Gole J L and Stout J D 2000 *Adv. Mater.* **12** 1938
[7] Wang Z L 2004 *Annu. Rev. Phys. Chem.* **55** 159
[8] Zhu Y Q, Hsu W K, Terrones M, Grobert N, Terrones H, Hare J P, Kroto H W and Walton D R M 1998 *J. Mater. Chem.* **8** 1859
[9] Pan Z W, Dai Z R, Ma C and Wang Z L 2002 *J. Am. Chem. Soc.* **124** 1817
[10] Sun S H, Meng G W, Zhang M G, Tian Y T, Xie T and Zhang L D 2003 *Solid State Commun.* **128** 287
[11] Wang J C, Zhan C Z and Li F G 2003 *Solid State Commun.* **125** 629
[12] Hu J Q, Jiang Y, Meng X M, Lee C S and Lee S T 2003 *Chem. Phys. Lett.* **367** 339
[13] Lee K H, Lee S W, Vanfleet R R and Sigmund W 2003 *Chem. Phys. Lett.* **376** 498
[14] Elechiguerra J L, Manriquez J A and Yacaman M J 2004 *Appl. Phys.* A **79** 461
[15] Niu J J, Sha J, Zhang N S, Ji Y J, Ma X Y and Yang D R 2004 *Physica* E **23** 1
[16] Markel V A and George T F 2000 *Optics of Nanostructured Materials* (Hoboken: Wiley)
[17] Wang Z L 2003 *Nanowires and Nanobelts: Materials, Properties and Devices* (New York: Kluwer–Academic)
[18] Prasad P N 2004 *Nanophotonics* (Hoboken: Wiley)
[19] Roder A, Kob W and Binder K 2001 *J. Chem. Phys.* **114** 7602
[20] Zhu T, Li J, Yip S, Bartlett R J, Trickey S B and De Leeuw N H 2003 *Mol. Simul.* **29** 671
[21] Litton D A and Garofalini S H 1997 *J. Non-Cryst. Solids* **217** 250
[22] Jackle J and Kawasaki K 1995 *J. Phys.: Condens. Matter* **7** 4351
[23] Radlein E and Frischat G H 1997 *J. Non-Cryst. Solids* **222** 69
[24] Gupta P K, Inniss D, Kurkjian C R and Zhong Q 2000 *J. Non-Cryst. Solids* **262** 200
[25] Brow R K, Lower N P, Lang A J and Kurkjian C R 2002 *Glass Sci. Technol.* **75** 133
[26] Proctor B A, Whitney I and Johnson J W 1967 *Proc. R. Soc.* A **297** 534
[27] Bansal N P and Doremus R H 1986 *Handbook of Glass Properties* (Orlando, FL: Academic)