Available online at www.sciencedirect.com
SCIENCE DIRECT®
Chemical Physics Letters 367 (2003) 339–343
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

A simple large-scale synthesis of very long aligned silica nanowires

J.Q. Hu [1], Y. Jiang, X.M. Meng, C.S. Lee, S.T. Lee *

Department of Physics and Materials Science, Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong SAR, China

Received 13 August 2002; in final form 11 October 2002

Abstract

A simple method based on the thermal oxidation of Si wafers has been discovered to provide a large-scale synthesis of very long, aligned silica nanowires. The as-grown product was characterized by scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy, and photoluminescence. The obtained SiO_2 nanowires had no metal contaminations, ultralong lengths of millimeters, and most diameters of ~50 nm. The PL spectra of the SiO_2 nanowires showed a strong and stable green emission at 540 nm. The nucleation and growth of the SiO_2 nanowires were investigated.

1. Introduction

In the development of nanotechnology, nanoscale optical wires are of both scientific and technological interest because of their potential applications for localization of light, low-dimensional waveguides, and scanning near-field optical microscopy (SNOM) [1]. As an important candidate material, silica (SiO_2), particularly its synthesis and optical properties, has been actively studied for a long time. The photoluminescence (PL) band of bulk SiO_2 or SiO_2 films has a peak around 1.9–4.3 eV [2,3]. Yu et al. [1] have synthesized SiO_2 nanowires using an excimer laser ablation method and investigated their intense blue light emission. Other methods, such as carbothermal reduction [4], catalyzed thermal decomposition [5], and sublimation of SiC in an O_2 flow [6], have also been applied for the synthesis of SiO_2 nanowires. However, the obtained SiO_2 nanowires by these routes were randomly distributed on the substrates. The lack of alignment in the SiO_2 nanowires has hampered their experimental characterization and applications for high-resolution optical heads of SNOM and as nanointerconnects in integrated optical device. Thus, it is of interest to synthesize aligned and long SiO_2 nanowires that can be explored for further applications. Wang et al. [7] have observed a variety of silica

* Corresponding author. Fax: + 852-2784-4696.
E-mail address: apannale@cityu.edu.hk (S.T. Lee).
[1] Present address: National Institute for Materials Science, Advanced Materials and Nanomaterials Laboratory, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan.

0009-2614/02/$ - see front matter
PII: S0009-2614(02)01697-4

nanostructures including SiO_2 nanofiber 'bundled' arrays produced by pyrolysis of mixture of Si and SiO powders. Recently, Pan et al. [8] have developed a molten gallium-catalyzed vapor–liquid–solid (VLS) process for the growth of bundles of highly aligned and packed SiO_2 nanowires. In this Letter, we report the production of large-quantities of high-purity (no metal catalysis contamination) and ultralong (millimeters) SiO_2 nanowires (most of the wires have uniform diameters of ~50 nm, while some of them have thinner diameters of 5–10 nm) using a simple thermal oxidation route and silicon wafers as a source material. We further investigate the optical properties of the SiO_2 nanowires and their growth mechanisms.

2. Experimental

The synthesis of aligned SiO_2 nanowires was carried out in a high-temperature tube-furnace. Briefly, an alumina tube (outer diameter: 42 mm, length: 80 cm) was mounted horizontally inside the tube furnace. More than 10 strip-like polished Si (1 0 0) wafers (about 10 mm in width and 50 mm in length) were ultrasonically cleaned in acetone for 20 min and then placed one by one on a long alumina plate (35 cm in length and 30 mm in width) to act as the starting material and growth substrate. After transferring these wafers together with the alumina plate into the tube (one end of the plate was at the center of the tube and the other end was near the tube's downstream end), the tube was evacuated by a mechanical rotary pump to a base pressure of 6×10^{-2} Torr. The furnace was heated at a rate of 10 °C/min to 800 °C and kept at this temperature for 30 min, and then further heated to and kept at 1300 °C for 5 h. During the experiment, high-purity argon (99.99%, $H_2 < 1$ ppm, $H_2O <$ or $= 20$ ppm, $O_2 <$ or $= 20$ ppm, hydrocarbon $<$ or $= 6$ ppm) was kept flowing through the tube at a rate of 50 sccm and a pressure of 300 Torr. The temperature at the deposition position was measured by a movable thermocouple mounted inside a thinner alumina tube that was inserted into the larger tube. One end of the thinner tube was closed and located at the center of the furnace, while the other end was open and extended outside the furnace. After the furnace was cooled naturally to room temperature, the grown material was collected and characterized by scanning electron microscopy (SEM; Philips XL 30 FEG), transmission electron microscopy (TEM; Philips, CM200/FEG, at 200 kV), energy-dispersive X-ray spectroscopy (EDAX) (attached to the TEM), and photoluminescence (PL) spectroscopy. The PL spectra were measured at room temperature in the spectral range of 300–800 nm using a He–Cd laser with a wavelength of 325 nm as the excitation source.

3. Results and discussion

After the synthesis, a large quantity of white wool-like product covering approximately a 6 cm region was formed on the silicon wafers and alumina plate in the temperature range of 1100–1200 °C. For SEM investigations, the Si wafers were directly transferred to the SEM chamber, without disturbing the original nature of the products on the wafers. Fig. 1a is a low-magnification cross-sectional SEM image of the tilted sample. The image shows the entire wire length from their growth roots (lower edge of this image), which is the location of the wafer (indicated by a two-way arrow). It can be seen that the as-grown nanowires on the wafer display well-aligned nature and have length of up to several millimeters. A high-magnification SEM image (Fig. 1b) clearly reveals the diameter distribution of the nanowires. As seen from this image, most of the wires have uniform diameters of ~50 nm, while some of them have thinner diameters of 5–10 nm. A high-magnification TEM image (Fig. 1c) shows that the nanowires are remarkably clean and smooth, and there are no particles at its surface. An SAED pattern (Fig. 1c, upper inset) of this wire reveals only diffusive rings and no diffraction spots, showing the amorphous nature of the synthesized nanowires. The corresponding elemental composition is confirmed by EDAX (Fig. 1c, lower inset) to be Si and O with an approximate atomic ratio of 1:2 (Cu signal comes from TEM grids). Therefore, the nanowires are identified as amorphous SiO_2. In contrast to the previous growth routes [1,4,5,8], no metal catalytic particles (contamination) have been

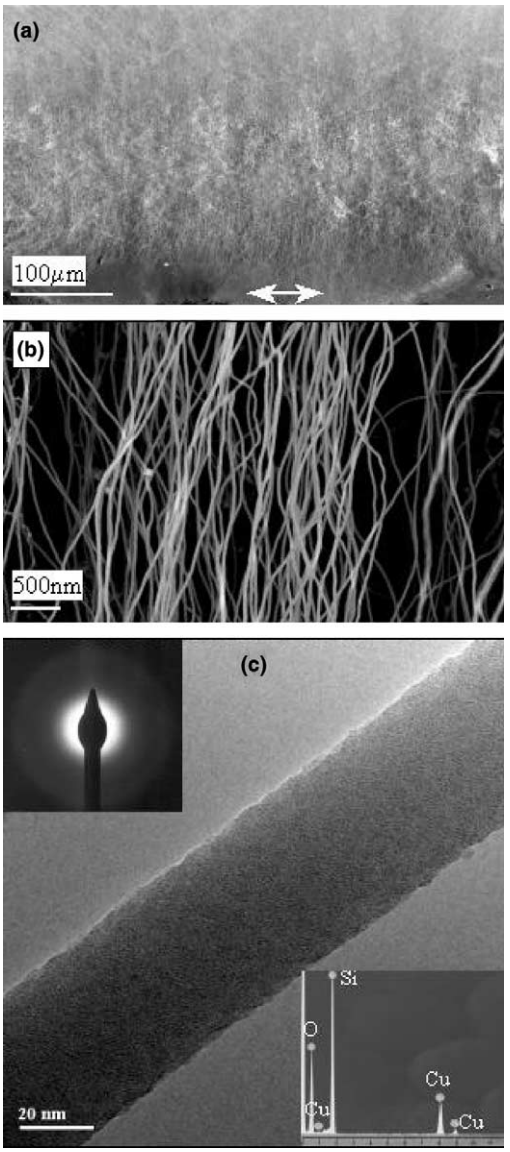

Fig. 1. (a) Low-magnification cross-sectional SEM image with the arrow indicating the wafer. (b) High-magnification SEM image, and (c) TEM image (the insets show the SAED and EDAX pattern, respectively), of the as-grown aligned SiO_2 nanowires.

found attached to the tips of the SiO_2 nanowires (observed from SEM and TEM images).

The PL spectrum of the synthesized SiO_2 nanowires measured at room temperature is shown in Fig. 2. The as-synthesized nanowires have a stable (even after exposure to air for about 1 year), strong green emission band centered at 540 nm, which has been ascribed to neutral oxygen vacancies [3]. Compared to the previous PL results of SiO_2 nanowires, which show an intense main peak with at least one shoulder [1,4], the present PL curve is nearly symmetrical and appears not to have any shoulder peaks. The exact nature of the PL of the synthesized aligned SiO_2 nanowires remains unclear and requires more detailed systematic investigations.

To study the growth processes of the SiO_2 nanowires, we placed several Si wafers in the region (on the alumina plate) where SiO_2 nanowire growth would occur, and heated them in the tube for different periods (1, 2, and 3 h). Fig. 3a shows the Si wafer heated for 1 h, revealing the initial nucleation stage of the SiO_2 nanowires. It seems that at the given temperature the Si wafer surface reacted with oxygen (the source of oxygen will be discussed later) and formed numerous SiO_2 nanoparticles through homogeneous nucleation in a suitable temperature region. The quantity of these SiO_2 nanoparticles was so large that they appeared as islands and covered partially the surface of the wafer. Fig. 3b, c show the Si wafers heated for 2 and 3 h, respectively, revealing the different growth stages of SiO_2 nanowires. The growth of SiO_2 nanowires appeared to start from

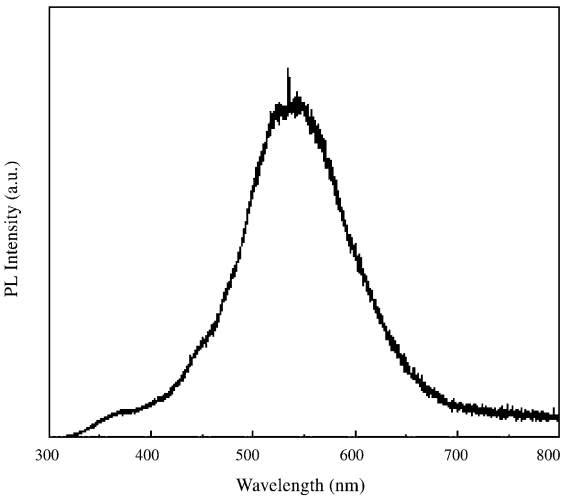

Fig. 2. Room temperature PL spectrum of SiO_2 nanowires.

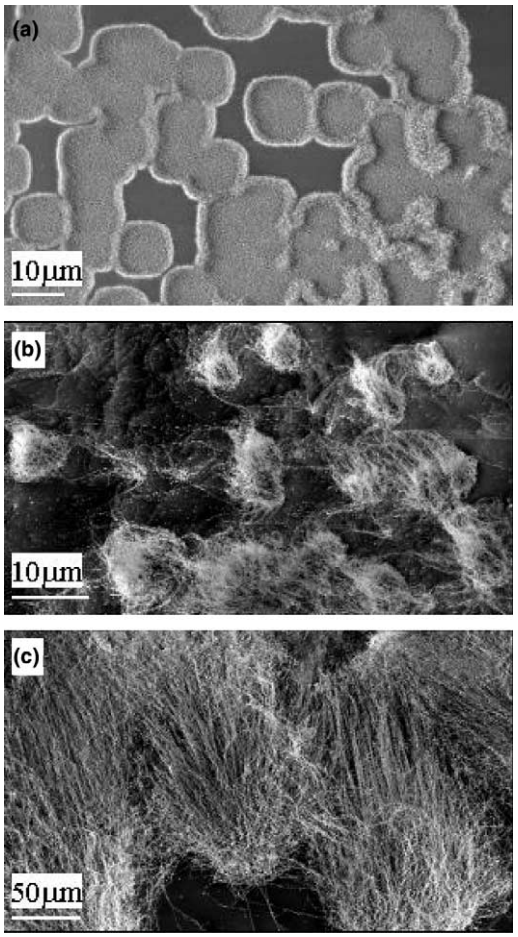

Fig. 3. The Si wafers heated for different periods: (a) 1 h, (b) 2 h, and (c) 3 h.

the formed SiO_2 nanoparticles. The high density of SiO_2 nanoparticles would lead to the concurrent growth of a large number of SiO_2 nanowires, resulting in the congested growth of SiO_2 nanowires. The overcrowding effect would confine the propagation of nanowires predominantly in the vertical direction. As a result, SiO_2 nanowires emerged as aligned bundles perpendicular to the Si wafer surface, except for those formed at the exposed edges where the SiO_2 nanoparticle islands could grow freely. The nanowire alignment due to overcrowding effect is somewhat similar to the production of aligned carbon nanotubes [9,10]. In comparison with the observation by Wang et al. [7,8], the present growth of aligned SiO_2 nanowires was based on a simple thermal oxidation of the silicon wafer. In our case, the aligned SiO_2 nanowires grew in large area (the dense SiO_2 nanowires covered the whole surface of the wafer) and had ultralong lengths approaching several millimeters. In addition, since no metal catalyst was involved, the product was free of metal catalysis contamination.

The source of oxygen that contributed to the formation of SiO_2 nanowires may have several origins. The most likely source of oxygen may come from the low content of H_2O ($\sim$20 ppm) and O_2 ($\sim$20 ppm) in the carrier gas of Ar, which can supply a constant oxygen source during the growth of SiO_2 nanowires. Another likely source is the oxygen adsorbed on the Si wafer due to air exposure during the processing. The residual oxygen may also be a source, as the base pressure (6×10^{-2} Torr) of the vacuum system was relatively high.

4. Conclusions

A simple method based on thermal oxidation of Si wafers has been suggested for the large-scale synthesis of very long aligned silica nanowires. The SiO_2 nanowires were highly pure (no metal catalysis contamination), ultralong (millimeters). Most of wires had uniform diameters of $\sim$50 nm, while some of them had thinner diameters of 5–10 nm. Room-temperature PL spectra of the synthesized SiO_2 nanowires showed a strong and stable green emission peaking at 540 nm. By selecting suitable gas source, e.g., NH_3 or CH_4, it is reasonable to expect that the aligned SiO_2 nanowires (acting as a template or solid source material) can be converted to other important material aligned nanowires, e.g., SiC or Si_3N_4.

Acknowledgements

The authors express their gratitude to Dr. Q. L. Liu (from Institute of Physics, Center for Condensed Matter Physics, Chinese Academy of Sciences) for making available photoluminescence measurements. The work was supported by a grant

from the Research Grants Council of the Hong Kong SAR, China [Project No. CityU 3/01C (8730016)] and a Strategic Research Grant of the City University of Hong Kong [Project No. 7001175].

References

[1] D.P. Yu, Q.L. Hang, Y. Ding, H.Z. Zhang, Z.G. Bai, J.J. Wang, Y.H. Zou, Appl. Phys. Lett. 73 (1998) 3076.
[2] L.S. Liao, X.M. Bao, X.Q. Zheng, N.S. Li, N.B. Min, Appl. Phys. Lett. 68 (1996) 850.
[3] H. Nishikawa, T. Shiroyama, R. Nakamura, Y. Ohiki, K. Nagasawa, Y. Hama, Phys. Rev. B 45 (1992) 586.
[4] X.C. Wu, W.H. Song, K.Y. Wang, T. Hu, B. Zhao, Y.P. Sun, J.J. Du, Chem. Phys. Lett. 336 (2001) 53.
[5] Z.Q. Liu, S.S. Xie, L.F. Sun, D.S. Tang, W.Y. Zhou, C.Y. Wang, W. Liu, Y.B. Li, X.P. Zou, G. Wang, J. Mater. Res. 16 (2001) 683.
[6] H. Takikawa, M. Yatsuki, T. Sakakibara, Jpn. J. Appl. Phys. 38 (1999) L401.
[7] Z.L. Wang, R.P. Gao, J.L. Gole, J.D. Stout, Adv. Mater. 12 (2000) 1938.
[8] Z.W. Pan, Z.R. Dai, C. Ma, Z.L. Wang, J. Am. Chem. Soc. 124 (2002) 1817.
[9] W.Z. Li, S.S. Xie, L.X. Qian, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao, G. Wang, Science 274 (1996) 1701.
[10] M. Terrones, N. Grobert, J. Olivares, J.P. Zhang, H. Terrones, K. Kordatos, W.K. Hsu, J.P. Hare, P.D. Townsend, K. Prassides, A.K. Cheetham, H.W. Kroto, D.R.M. Walton, Nature 388 (1997) 52.