Quantum-confined and tunable optical emission from sub-10-nm silicon oxide nanowires in aqueous suspension

Z. Y. Zhang
National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China

X. L. Wu
National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, People’s Republic of China and Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

J. C. Shen and L. L. Xu
National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China

Paul K. Chu
Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

(Received 2 July 2007; accepted 17 October 2007; published online 9 November 2007)

Silicon oxide nanowires (SiONWs) smaller than 10 nm were synthesized by vaporization of SiO2 powders without catalytic assistance. The SiONWs resemble bamboos and the knots comprise Si nanocrystals of different orientations. A SiONW water suspension prepared ultrasonically was subjected to photoluminescence and photoluminescence excitation spectral examinations. Strong blue emission which arises from band-to-band recombination in the quantum confined Si nanocrystals in the knots is observed. Our results show that the emission characteristics can be tuned by adjusting the size of the knots. © 2007 American Institute of Physics. [DOI: 10.1063/1.2806228]

Since the fabrication of the first carbon nanotubes in 1991,1 one-dimensional nanomaterials such as nanowires,2 nanotubes,3 and nanobelts4 have been investigated extensively. Silicon is an important semiconductor in microelectronics and optoelectronics, and thus silicon nanowires (SiNWs) have also received attention.2,5 Many methods such as vapor-liquid-solid (VLS),2,6 solid-liquid-solid,7,8 and oxide-assisted growth (OAG)9,10 have hitherto been proposed to synthesize SiNWs and their optical properties have been studied.11–16 Most of the photoluminescence (PL) results show a green to red emission13–16 and only a few reports describe blue emission arising from oxygen-related defects in SiNWs.11,12 In order to widen their applications in modern optoelectronics, it is important to obtain blue emission from SiNWs via the quantum confinement effect (QCE). In this letter, we report the PL characteristics of bamboo-shaped silicon oxide nanowires (BSSiONWs) produced by a facile thermal evaporation technique. The SiONWs which are several micrometers long have diameters less than 10 nm. The structure comprises Si nanocrystals (SiNCs) in the knots connected by amorphous SiONWs in the trunk. These BSSiONWs dispersed in de-ionized water by ultrasonic vibration exhibit strong blue emission. Spectroscopic analyses suggest that the blue emission arises from the QCE of the SiNCs in the BSSiONWs.

The BSSiONWs were produced on silicon (100) wafers in an alumina tube inside a furnace. The vapor consisting of pure SiO (99.99%) powders (without metal catalysts) was introduced into an alumina crucible that was placed in front of an alumina boat. Si wafers were placed on the alumina boat at distances of 10 and 14 cm from the alumina crucible to collect the products. The alumina crucible with the vapor source was placed at the center of the alumina tube in the furnace. The system was pumped down to a pressure of 1 × 10−3 Pa with a diffusion pump before the alumina tube was heated to 1300 °C under flowing 99.99% Ar [20 SCCM (SCCM denotes cubic centimeter per minute at STP)] at a typical pressure of ~20 Pa. The crucible was held at 1300 °C for 2 h and then the alumina tube was cooled gradually to room temperature under Ar. A yellow spongelike product was formed on the Si wafers. The schematic diagram of the experimental setup is the same as that reported in Ref. 6.

Transmission electron microscopy (TEM) was performed on an FEI Tecnai G2 20 S-TWIN TEM and x-ray diffraction (XRD) spectra were acquired using a Rigaku 3015 single crystal diffractometer using Cu Kα radiation. PL and PL excitation (PLE) spectra were obtained on a Jobin-Yvon FluoroMax-2 spectrophotometer equipped with a 150 W Xe lamp as the light source. Raman scattering spectra were acquired on a T64000 triple Raman system. Bulk quantities of BSSiONWs can be obtained by our method that utilizes vaporization of pure SiO powders in the absence of a metal catalyst. This procedure is different from those reported previously.17–20 Figure 1 depicts the TEM image of the bamboo-shaped nanowires which have micrometer lengths. The nanowire diameters are nonuniform, generally ranging from 5 to 13 nm (see the arrows in Fig. 1). SiNCs are present in the knots of the bamboos, and the trunks are composed of amorphous SiONWs, as shown by the high-resolution (HR)-TEM image of a knot in the inset of Fig. 1.
The knot shows obvious \{111\} lattice fringes of Si and the adjacent area has an amorphous structure, indicating that the SiNC is embedded in an amorphous environment. Other HR-TEM images reveal that each SiNC has its own growth orientation implying no association among the SiNCs during growth. This is understandable. Because no catalyst assists, these SiNCs randomly deposit and cannot connect together into a nanowire. The experimental results suggest that the growth of these BSSiONWs is via the OAG model.\(^9,\)\(^{10}\) At a high temperature, the silicon oxide in the source sublimes into molecular species composed of Si atoms and stoichiometric SiO\(_2\) molecules (\(2\text{SiO} \rightarrow \text{Si} + \text{SiO}\_2\)). Their separation leads to the formation of SiNCs (the nuclei of nanowires). When the \{111\} surface of a SiNC is parallel to its growth axis, the system energy will be reduced significantly.\(^5,\)\(^{10,21}\) Hence, if the directions of some Si nuclei are parallel to the axis of the nanowire, Si will grow rapidly forming a continuous Si nanowire core. Otherwise, the SiNC growth is terminated and the renucleation occurs at other positions. This is the reason why knots are formed in the BSSiONWs.\(^{10}\) That is to say, renucleation leads to the formation of the BSSiONWs and the growth mechanism of the BSSiONWs is a result of the renucleation of SiNC suggested by the OAG model.

The BSSiONWs are different from normal Si nanowires that consist of continuous nanocrystalline Si core and surface silicon oxide sheath.\(^{22}\) To further investigate the composition of the BSSiONWs, XRD is conducted on the yellow spongelike product and the results are shown in Fig. 2(a). For comparison, the XRD results acquired from normal SiNWs synthesized by the VLS method are displayed in Fig. 2(b).\(^{15}\) Figure 2(b) displays three strong diffraction peaks from crystalline Si (111), (220), and (311) and one weak broad peak at 0.411 nm from amorphous Si oxide [the Si (100) peak arises from the Si substrate]. Figure 2(a) shows two evident broad peaks at 0.411 and 0.258 nm originating from amorphous Si oxide and three other broad peaks from crystalline Si (111), (220), and (311), indicating that the sizes of Si nanocrystalline cores are smaller and the Si oxide content in the BSSiONWs are higher compared to those of normal SiNWs. These results are consistent with our TEM observations and corroborate that the BSSiONWs consist of silicon oxide nanowires and embedded Si NCs.

To study the optical property of the BSSiONWs, the powder product is immersed in an ultrasonic de-ionized water bath to disperse the BSSiONWs. The corresponding PL and PLE results from the water suspension are depicted in Fig. 3 (the sharp peaks in the PL and PLE spectra are the Raman scattering signals from the water because the OH vibration band of water is at around 3480 cm\(^{-1}\)). The PL spectrum in Fig. 3(a) shows blue emission, and the peak position changes from 410 to 450 nm with increasing excitation wavelength from 300 to 360 nm. The PLE spectrum

![FIG. 1. Typical TEM image of the BSSiONWs. The inset shows the HR-TEM image of a knot in which the SiNC has \{111\} lattice fringes.](image1)

![FIG. 2. XRD spectra of (a) BSSiONWs and (b) normal SiNWs.](image2)

![FIG. 3. (Color online) (a) PL spectra with peak wavelengths at 415, 422, 434, and 446 nm obtained from the water suspension with BSSiONWs excited by the 300, 320, 340, and 360 nm lines of a Xe lamp, respectively. (b) PLE spectra with peak wavelengths at 318, 327, 336, and 346 nm obtained from the water suspension with BSSiONWs excited by the 400, 420, 440, and 460 nm lines, respectively. Note that the sharp peaks in (a) and (b) are the Raman signals of water.](image3)
Since small SiNCs exist in the BSSiONWs, it can be inferred that the PL intensity weakens and the peak position slightly blueshifts. When the BSSiONWs were stored in air for several minutes, the blue PL intensity of small BSSiONWs in the product is dispersed in de-ionized water, BSSiONWs with a blue emission. These BSSiONWs are expected to have potential applications in biotechnology and nano-optoelectronics.

In order to fathom the discrepancy between the experiments and the theory, we examine the Raman spectra obtained from the Si wafer coated with the BSSiONWs shown in Fig. 4. The Si Raman peaks from different positions in the sample exhibit different shifts (three Raman peaks at 518, 507, and 502 cm\(^{-1}\) are shown). It indicates that the SiNCs in the BSSiONWs have different sizes. Here, we can exclude the effect of strain on the Raman blueshift according to the XRD result. In Fig. 2(a), the diffraction angle of the (111) plane is slightly toward the low-angle side from 2\(\theta\) = 28.47\(^\circ\) in the single crystal to 28.34\(^\circ\) in the sample. Hence, the elastic tensile strain is calculated to be less than 0.5\% and, consequently, the Raman blueshift caused by the strain is less than 2 cm\(^{-1}\).\(^{27}\) The influence is thus negligible. According to the relationship (\(d = 2\pi \sqrt{B/\Delta \omega}\)),\(^{27,28}\) where \(\Delta \omega\) is the shift of Raman peak of the nanocrystal compared to that of c-Si and \(B = 2.0\) cm\(^{-3}\) nm\(^2\), the Si Raman peaks at 518, 507, and 502 cm\(^{-1}\) correspond to SiNC sizes of 5.1, 2.3, and 2.0 nm, respectively. There is an evidence that small SiNCs with sizes of \(\sim 2\) nm do exist in the BSSiONWs. Such small SiNCs are difficult to observe by TEM due to the coexistence of large BSSiONWs in the product. However, when the product is dispersed in de-ionized water, BSSiONWs with very small diameters can more easily suspend in the medium, which increases the density of small-size SiNCs, whereas the big BSSiONWs tend to sink to the bottom of the container. With the increasing storage time of the suspension, the density of small-size SiNCs decreases. This leads to the decrease of the PL intensity and the blueshift of its peak positions, as observed in our previous experiments.\(^{29}\) Hence, the suspension behavior is a key parameter to observe the blue emission.

In summary, we have synthesized sub-10-nm BS-SiONWs using the OAG method without the use of a metal catalyst. HR-TEM shows that the BSSiONWs comprise SiNCs in the knots, and the trunks are composed of amorphous SiONWs. When the BSSiONWs are dispersed in de-ionized water ultrasonically, strong blue emission is observed and can be attributed to the band-to-band recombination of the photoexcited carriers in the knots (SiNCs) of the BS-SiONWs. These BSSiONWs are expected to have potential applications in biotechnology and nano-optoelectronics.

This work was jointly supported by grants (60576061, 60476038, and BK2006715) from the National and Jiangsu Natural Science Foundations as well as the City University of Hong Kong Strategic Research Grant (SRG) (7001238). Partial support was from the State Key Program for Basic Research of China under Grant No. 2007CB936300.