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Chainlike silicon nanowires: Morphology, electronic structure and luminescence studies

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The chainlike silicon nanowires SiNWs have been synthesized by fluctuating the pressure of the carrier gas in the growth process. The chainlike SiNWs comprise crystalline Si nanoparticles interconnected by amorphous silicon oxide wires. In addition to the sphere, other interesting shapes such as rectangular and triangular Si nanoparticles in chainlike SiNWs were also observed. X-ray absorption fine structure shows that the Si nanoparticles in the chainlike SiNWs are crystalline silicon and that the wire has a significantly larger Si oxide to crystalline Si ratio and disorder compared to the normal SiNW. X-ray excited optical luminescence and photoluminescence spectroscopy show that the relatively strong luminescence from the chainlike SiNWs compared to normal SiNWs arises mainly from silicon oxide in the chainlike SiNWs. © 2004 American Institute of Physics. [DOI: 10.1063/1.1782958]

I. INTRODUCTION

In recent years, considerable efforts have been made in the fabrication and characterization of silicon nanowires (SiNW)s because SiNW’s exhibit different properties corresponding to bulk silicon and their potential application in future nanoelectronics. Many synthesis strategies to obtain bulk quantities of SiNWs have now been developed using both gas phase and condensed phase procedures.1–3 SiNWs show a variety of morphologies depending on the synthesis strategy and the growth conditions.4–8 It has been recognized that the electronic and optical properties of SiNWs exhibit morphology dependence, which may be employed for different fields of applications.9–15 One of the challenging issues in producing nanomaterials is to fabricate and control the morphology of the as-prepared nanostructures with a well-organized arrangement, for example, equally spaced nanocrystallites and to specify their structural dependent electronic and optical properties. Unlike strong luminescence observed from porous silicon16 and other Si-based multilayer superlattices17 and nanoclusters,18 weak and complex luminescence from SiNWs with emission wavelength ranging from 420 to 820 nm have been observed due to the wide variation of morphology of SiNWs.12–15 The luminescence peaks have been ascribed variously to the quantum confinement effect, the defect centers surrounding the SiNW crystalline core, the silicon oxide surface, and the silicon-silicon oxide interface, or combinations thereof. In this paper, we report the synthesis of the chainlike silicon nanowires by simply fluctuating the pressure of the carrier gas during the growth of SiNWs, which exhibit unique and well-organized morphology comparing to the normal continuous SiNWs as revealed by high-resolution transmission electron microscopy (HRTEM). Further, we conducted a comparative study of the electronic and optical properties of the chainlike SiNW with those of the normal continuous SiNW using x-ray absorption fine structure (XAFS), x-ray excited optical luminescence (XEOL), and photoluminescence (PL) spectroscopy. The XEOL technique20 monitors the optical response of a light-emitting material by tuning the x-ray energy to a specific excitation channel (often at the x-ray absorption edge of a element of interest) and monitoring the luminescence with an optical monochromator (typically in a range of 200–900 nm). The relative quantum yield of the luminescence chromophore, which is either due to excitons, the recombination of a hole in the valence band and an electron in the conduction band or due to defects, depends strongly on the site and chemical environment of the absorbing atom. The photoluminescence yield (PLY) can in turn be used to record XAFS that provides structural information for the absorption site responsible for the luminescence.20,21 Combining the XEOL and PLY spectra, we have been able to obtain the structural dependence of the luminescence.

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II. EXPERIMENT

The SiNWs used in this work were synthesized by thermal evaporation of SiO as previously described. The pressure in the system was kept oscillating in the range of 200–700 Torr in the growth process of SiNWs. The light yellow spongelike SiNWs were collected from the wall of the alumina tube where the temperature was approximately 930–950 °C. The morphology and microstructure of the nanowire products were investigated by a Philips CM200 FEG HRTEM operating at 200 kV. The HRTEM samples were prepared by dispersing the product on a TEM grid with carbon holey film. The XAFS of the as-prepared chainlike SiNWs dispersed on a stainless steel substrate was carried out at the double crystal monochromator (DCM) beamline of the Canadian Synchrotron Radiation Facility (CSRF) located at the Synchrotron Radiation Center, University of Wisconsin-Madison. Total electron yield (TEY), fluorescence yield (FLY), and PLY were used to monitor the absorption. At these photon energies, TEY is sensitive to the surface and the near-surface region of the specimen while both FLY and PLY are sensitive to the bulk. The XEOL of the as-prepared chainlike SiNWs and their HF-etched samples excited with photon energy across the Si K-edge were also obtained at the DCM beamline of CSRF, using a JY 100 monochromator to monitor the optical photons. A normal SiNW sample (smooth surface, ~20 nm in diameter) was also studied for comparison. The PL of the as-prepared chainlike SiNWs and normal SiNWs were obtained by a micro-Raman spectrometer (Reniashaw 2000 micro-Raman spectrometer) at room temperature. The 514.5 nm emission from an argon ion laser was used to excite the luminescence.

III. RESULTS AND DISCUSSIONS

The chainlike SiNWs had been previously observed as the by-product in the fabrication of normal SiNWs by both the laser ablation and thermal evaporation method. Bulk quantity of Si nanosphere chains had also been prepared by annealing normal SiNWs in high temperature via a spheroidization mechanism or by heating a gold-coated silicon substrate via an extension of the vapor-liquid-solid mechanism. These chainlike SiNWs were formed by silicon nanoparticles (actually, silicon nanospheres were observed in all previous studies), which are encapsulated and connected by a continuous outer layer of silicon dioxide. Figure 1 shows a typical TEM image of the chainlike SiNWs synthesized in this study. From Fig. 1, we see that the nanoparticles in the chainlike SiNWs have an average diameter of 16 nm and are connected by ~20 nm long oxide wires. The morphology and microstructure of the chainlike SiNWs are shown in the HRTEM images in Fig. 2. Clearly, the nanoparticles are single silicon crystallites as confirmed by electron diffraction. The outer shells of the nanoparticles and interconnects are amorphous silicon oxide. It is interesting to note that the silicon nanoparticles in the chainlike SiNWs exhibit a variety of shapes. In addition to the sphere shape observed in previous studies, shown in Fig. 2(a), the rectangle and triangle shapes of silicon nanoparticles were also observed, as shown in Figs. 2(b) and 2(c), respectively. From the HR-TEM images, we find that the Si nanoparticles exhibit (111) crystal planes with a 3.1 Å d spacing. In recently study, the horizontal cross section of a chainlike SiNW was obtained and it was found that some nanoparticles, measuring 16–20 nm in diameter, exhibited polyhedral shapes such as hexagons and octagons in the cross-sectional view. These observations are in contrast to previous studies in which only Si nanospheres were observed. Obviously, the mechanism of spheroidization of cylindrical nanowires of semi-infinite length at high temperature cannot give a satisfactory explanation for the formation of silicon nanoparticles with polyhedral shapes. We believe that the fluctuation of the pressure in the SiNW growth process is a main factor contributing to the formation of the chainlike SiNWs in our experiments. The details of the mechanism await further investigation.

Figure 3 shows the TEY and FLY Si K-edge XAFS of the as-prepared chainlike SiNW and normal SiNW specimens. The spectra have been normalized to unity edge jump and shifted vertically for clarity. All spectra exhibit a resonance at 1841 eV and an intense resonance at ~1847.5 eV. The first resonance at ~1841 eV arises form the crystalline Si nanoparticles in the chainlike SiNWs and the Si core of the normal nanowires. The intense resonance at ~1847.4 eV in all TEY, but a much-reduced intensity in all FLY, is characteristic of a Si to 3p (t_2 orbital in a Td symmetry) transition of SiO_2 and is due to the outer silicon oxide layer of the SiNWs. It is worthy noting that both chainlike SiNWs and normal SiNWs exhibit a larger intensity ratio of Si (1841 eV) to SiO_2 (1847.5 eV) in FLY than those in TEY. This is due to the fact that TEY is a surface sensitive technique, which is more sensitive to the surface oxide than the encapsulated Si, whereas FLY is bulk sensitive. These results confirm that the oxide is on the surface of the nanowire, and that the intense resonance at ~1841 eV in all TEY can be attributed to the Si core of the normal SiNWs.
The perhaps most noticeable feature in Fig. 3 is that the chainlike SiNWs exhibit a much stronger SiO\textsubscript{2} resonance, in both TEY and FL Y than that of the normal SiNWs. This is due to a larger ratio of Si (oxide) atom to elemental atom in the former. This observation indicates that the nanoparticles in the chains are embedded entirely in silicon oxide as observed by HRTEM. Another feature worthy nothing in Fig. 3 is that the resonances between 1850 and 1900 eV in Si K-edge result for the chainlike SINW shows silicon oxide dominant features.

The XEOL of the chainlike SiNWs compared to the normal SiNWs excited with photon energies at Si K-edge (1841 eV) and SiO\textsubscript{2} resonance position (1848 eV) is shown in Fig. 4. Two emission bands in the green and blue regions peaking at 460 nm (2.7 eV) and 530 nm (2.34 eV), respectively are observed. The chainlike SiNWs exhibit much stronger emission intensity than the normal SiNWs. The in-

![HRTEM images of the chainlike SiNW's](image)

**FIG. 2.** The HRTEM images of the chainlike SiNW’s. (a) A spherical Si nanoparticle, (b) a rectangular Si nanoparticle, and (c) a triangular Si nanoparticle, in the chainlike SiNW’s, respectively.

![TEY and FL Y Si K-edge XAFS](image)

**FIG. 3.** TEY and FL Y Si K-edge XAFS of the chainlike SiNW and normal SiNW specimens.
The intensities of the two peaks increased remarkably, especially in the chainlike SiNWs when the K-edge channel of silicon oxide turns on at 1847.5 eV. The peak at 2.7 eV is similar to the results observed in the silica nanowires\textsuperscript{12} and can be attributed to the neutral oxygen vacancy in the oxide, while the peak at 2.34 eV is less straightforward to assign. Close examination of the branching ratio (intensity of an individual emission over the overall emission intensity) of the two peaks in the chainlike SiNW spectra excited at 1841 and 1847.5 eV reveals that the 530 nm emission is noticeably more intense at the 1841 eV excitation (by 25%). Also, when the silicon oxide channel turns on, the intensity increase of the peak at 2.34 eV is less than that at 2.7 eV. It indicates that the 2.34 eV peak is at least not completely associated with the Si oxide. It may arise primarily from the small Si crystallites embedded in the SiNW (according to the quantum confinement model, the crystallite size has to be smaller than 2 nm\textsuperscript{23–25}) or from the defects surrounding the silicon nanoparticles. Thus the 530 nm emission is likely to have some quantum confinement origin. This is consistent with a recent observation.\textsuperscript{19}

Figure 5 shows the PLY at the Si K-edge XAFS of the chainlike SiNW sample monitored with total (zero-order) and wavelength-selected (460 nm) luminescence. The TEY and FLY are also shown. Both PLY spectra show similar spectral features to those observed in TEY and FLY spectra except for the intensity of the elemental Si whiteline (~1841 eV) which decreases noticeably in the zero-order PLY and nearly disappears at the 460 nm (2.7 eV) PLY. As discussed above, TEY is surface sensitive while FLY and PLY are bulk sensitive. This observation indicates that the total luminescence (zero-order) PLY arises mainly from silicon oxide as expected from Fig. 4. The disappearance of the elemental Si whiteline and an enhanced oxide feature in the 460 nm PLY show that the luminescence at 460 nm (2.7 eV) is primarily from silicon oxide. The weaker luminescence at 530 nm prevented the accumulation of satisfactory statistics for the 530 nm PLY measurement, but the difference in the intensity of the elemental Si K-edge whiteline between the zero-order and 460 nm PLY clearly indicates that the 530 nm one should at least have some contributions from the quantum-confined Si crystallites. Another evidence for the oxide dominant luminescence in chainlike SiNWs comes from XEOL recorded after the complete removal of silicon oxide by HF solution. After HF-etching, no luminescence can be observed in either chainlike SiNWs or normal SiNWs under the same experimental conditions.

Finally, the PL spectra of the chainlike and normal SiNWs excited at 514.5 nm with an argon ion laser are shown in Fig. 6. The PI spectral features for both samples are similar except for the much stronger emission in the chainlike SiNW. A strong PI peak around 560 nm with a broad shoulder at 620 nm was obtained for the chainlike SiNW sample. We attribute the PI to the defects in silicon oxide or interface between silicon oxide and nanoparticles. It is interesting to note that the 460 nm emission observed in XEOL is not accessible with the laser.

In conclusion, the chainlike silicon nanowires synthesized by fluctuating the pressure in the process of growth of...
SiNWs are reported. HRTEM shows that the chainlike SiNWs comprise crystalline Si nanoparticles of an average diameter of 16 nm and interconnecting 20 nm long silicon oxide wires. In addition to at the sphere, rectangle and triangle shapes of Si nanoparticles in the chainlike SiNWs were observed. XAFS studies reveal a significantly larger ratio of Si in oxide to Si in elemental crystallite in the chainlike SiNWs consistent with the HRTEM observation. XEOL and PL results show that the major portion of the luminescence from the chainlike SiNW arises primarily from the silicon oxide while only a minor component is from quantum-confined silicon luminescence, in contrast to porous silicon luminescence.

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