

Synthesis and light emission of fine and straight Si nanowires

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Using Au as catalyst, fine and straight Si nanowires (SiNWs) with diameters of 8–30 nm and lengths of several micrometers were synthesized by the self-designed chemical vapor deposition system at 480 °C. The influence of the growth pressures on the nanowire growth and morphology has been investigated by scanning electron microscopy (SEM). High-resolution transmission electron microscope (HRTEM) images indicate the growth direction of the nanowires are along the [1 1 1] with thin amorphous silicon oxide sheaths (~3 nm). The SiNWs with the Raman peak positions at 517 cm^{-1} exhibit a photoluminescence (PL) peak centered at 750 nm.

(Received July 21, 2008; accepted November 27, 2008)

Keywords: Si nanowires; VLS; Chemical vapor deposition; HRTEM; Light emission

1. Introduction

Bottom-up approaches for the growth of semiconductor nanowires (NWs) have received remarkable attention within the last decade. In particular, SiNWs have recently become of interest for potential applications in various technologies such as optics, electronics, and chemical sensors. This is the SiNWs can offer the possibility of integration with conventional Si integrated-circuit technology [1–3]. The quantum effects in the electronic and optical properties of the nanodevices are strongly related to nanostructure's dimensions [2]. Therefore, good control of the dimensions and alignments of the NWs is required to employ them as elements for nanodevices.

The vapor–liquid–solid (VLS) mechanism using Au as catalyst material was first described by Wagner and Ellis in 1964 [4] and advanced by Givargizov in 1975 [5]. The VLS growth scheme requires the presence of a metal mediating the nanowire growth and of a precursor gas. At the growth temperature, a liquid alloy droplet containing the metal and Si is formed. The silicon from the gas phase diffuses preferentially into the liquid alloy and bonds at the liquid–solid interface resulting in the growth of a wire with the liquid alloy droplet on the top. Gold is commonly used as the nucleation-inducing metal [6–8] although the use of Fe [9, 10] and other metals [11] and no catalyst at all [12] have been reported in the literature. Au and Fe catalysts have liquid eutectic temperatures with Si below the commonly used growth temperatures and hence SiNW formation is well described by the VLS scheme.

The most used method for growing SiNW is chemical vapour deposition (CVD) from SiH_4 or from Si_2H_6 . At substrate temperatures above 430 °C the original precursor molecule is not particularly important for the structures

forming on Si [13]. Among other techniques, SiNW formation by pulsed laser deposition (PLD) [9, 14], gas-phase molecular beam epitaxy (GSMBE) [15] and physical deposition [10] have also been reported in the literature. In the VLS-based NW growth processes, the diameter and alignment of the NWs can be readily controlled by the size of the catalytic metal islands and the substrate orientation [15, 16]. However, the diameters of the reported NWs did not correspond to that of the metal islands but were extensively modified with variation in growth conditions [6, 15]. Thus, detailed studies on the correlation of the growth parameters with morphological evolution of Si-NWs in the VLS processes are still required for the well-controlled growth.

In this paper, we have successfully synthesized SiNWs on Si substrates with diameters of 8–30 nm and several micrometers in length by the self-designed chemical vapor deposition system using SiH_4 as the source gas at a lower substrate temperature of 480 °C. A 3-nm-thick Au film covered on Si substrates as the catalyst to control the growth of the SiNWs. The influence of growth pressures on the morphology and dimension of the SiNWs was investigated. Finally, the PL properties of the SiNWs have been demonstrated, with a 750 nm PL peak at room temperature.

2. Experimental procedures

Si (1 0 0) wafers were employed as substrates. The substrates were ultrasonically cleaned in acetone and ethanol in turns for 10 min, dipped in 2% HF (HF: H_2O = 1:50) for 3 min, and then leached under running distilled water and dried. The cleaned substrates were transferred into a sputter system to deposit 3.0 nm thick Au films at

room temperature. Subsequently, the Au-deposited substrates were transferred to the self-designed deposition system showed in Fig. 1, which was evacuated to 1.3×10^{-5} Torr by a turbo molecular pump before the substrates were heated. After the growth temperature reached 480 °C, the substrates were exposed to SiH₄ (diluted to 20% in H₂) for 2 h. As a result, a yellow-colored spongelike product was obtained on the Si substrates.

In our experiments, scanning electron microscope (SEM) images were obtained on a JSM-6701F field emission SEM system which was equipped with energy dispersive X-ray spectroscopy (EDS). High-resolution transmission electron microscope (HRTEM) images were taken on a JEOL 2010F TEM equipment, operated at 200 kV accelerating voltage at room temperature. The structure of the NWs was further characterized by XRD on a RigakuD/Max-III C diffractometer using the 0.154 nm Cu α line. Raman spectra of the NWs were performed by using the micro-Raman Jobin-Yvon HR 800 system with the 325 nm line as excitation source. Photoluminescence (PL) spectra of the NWs were measured using He-Cd laser, with the excitation wavelength of 325 nm.

3. Results and discussion

Fig. 2 shows SEM images of the morphology of SiNWs on Si substrates at different pressures. Fig. 2(a) is the SiNWs grown at 6000 Pa, only a few, short and curving nanowires can be found. The SiNWs are tipped with an Au nanoparticle as shown by arrow, which is typical for the VLS growth mechanism. Most of the Au nanoparticles are still on the Si substrates without support the growth of SiNWs. When the grown pressure increase to atmospheric, fine and straight SiNWs with 8 ~ 30 nm diameter and several micrometres length can be observed on Si substrates in Fig. 2(b). The EDS spectrum of the SiNWs produced at atmospheric pressure is shown in the inset, which reveals that the SiNWs are comprised of Si element.

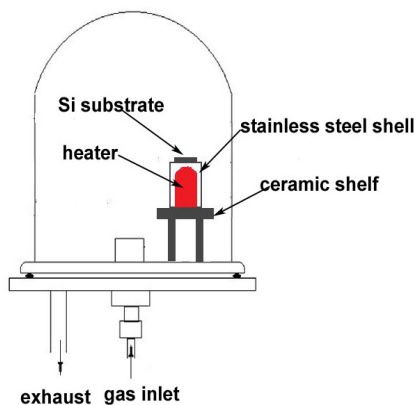


Fig. 1. Schematic diagram of self-designed deposition system for the synthesis of SiNWs.

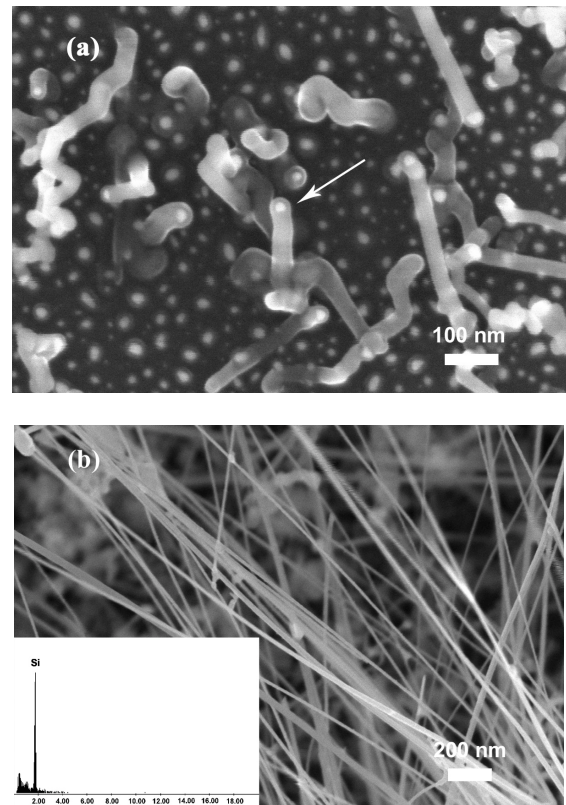


Fig. 2. SEM images of SiNWs grown at a pressure of (a) 6000 Pa and (b) atmospheric pressure.

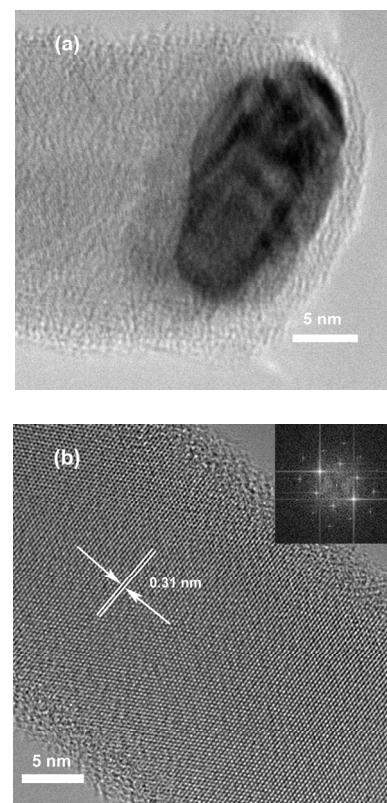


Fig. 3. (a) Au nanoparticle on the top of the SiNW, (b) HRTEM image of an individual SiNW, inset image is a FFT pattern.

The microstructure of silicon nanowires grown at atmospheric pressure was confirmed by HRTEM observations. Fig. 3(a) shows the HRTEM image of a typical nanowire with an Au nanoparticle, which is typical for the VLS growth mechanism. Fig. 3(b) gives a lattice image of a SiNW, in which we can clearly see that the SiNWs are composed of crystalline Si core and an amorphous silicon oxide sheath. The thickness of the oxide sheath is about 3 nm. The lattice fringes with a lattice spacing of 0.31 nm correspond to the (1 1 1) plane of Si and the growth of the nanowire is along the [1 1 1] direction. The FFT pattern of the SiNWs is shown in the inset in Fig. 3 (b), which further indicates that the SiNWs is single crystal with the growth direction of [111].

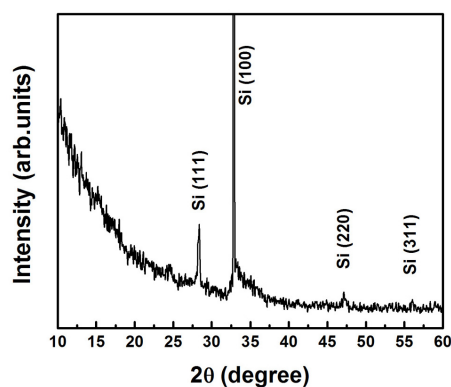


Fig. 4. XRD spectra of the synthesized SiNWs grown on Si substrates at atmospheric pressure.

To further show the crystallinity of the SiNWs grown at atmospheric pressure, we performed the XRD measurement of the Si substrates with nanowires and present the corresponding result in Fig. 4. One can see that this XRD spectrum shows four Si peaks from the (1 1 1), (1 0 0), (2 2 0), and (3 1 1) reflections. The strongest Si (1 0 0) peak is a signal of Si substrate. Note that the diffraction intensity of (220) and (311) is extremely lower than the (111), suggesting that the [111] is the major growth direction of the SiNWs. That is in good agreement with the result of HRTEM.

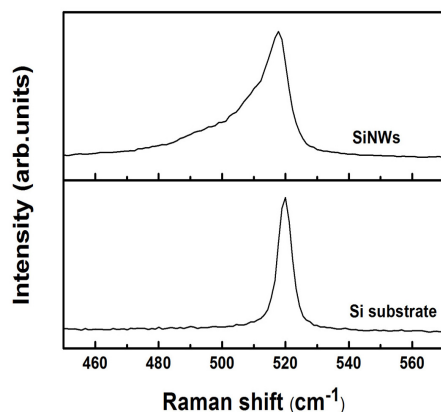


Fig. 5. Raman spectra of the SiNWs and single crystalline Si substrate.

Raman spectroscopy is very sensitive to the lattice structure and the crystal symmetry. Raman study of SiNWs had been reported in detail in [17]. Raman spectroscopy (peak energy, peak width, and symmetry) of nano-Si changes with the reduction of the size. The first-order Raman peak of single crystalline Si at 521 cm^{-1} is symmetric. The Raman spectrum of Si nanowires is asymmetric, centred at 517 cm^{-1} in our experiments, with an extended tail at low frequency (Fig. 5), which is attributed to the size confinement effect.

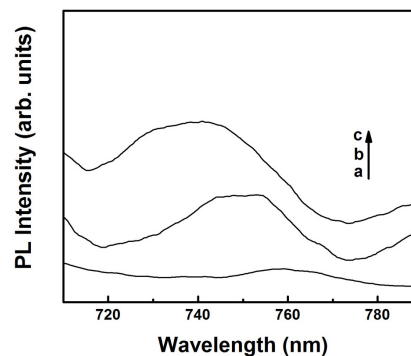


Fig. 6. PL spectra from single crystalline Si substrate (a) and SiNWs measured at room temperature (b) and 10 K (c), respectively.

To investigate the optical property of the SiNWs grown at atmospheric pressure, we carried out the PL measurements. Fig. 5 shows PL spectra of single crystalline Si substrate (a) and SiNWs at room temperature (b) and 10 K (c), respectively. For the SiNWs, the PL peak appears at $\sim 750\text{ nm}$ at room temperature and a little blueshift at 10 K. However, no peak is observed for the single crystalline substrate. Therefore, we can confirm that the 750 nm PL peak results from SiNWs. The observed 750 nm (1.65 eV) PL peak probably arises from radiative recombination of carriers in the defect states of the interface between the SiNW core and the surface silicon oxide, whereas the photogeneration of carriers takes place in the quantum confined SiNW core [18]. In fact, some theoretical calculations have indicated that the Si/SiO_x interface has a direct band gap of 1.7 eV [18, 19]. Some experimental investigations on the Si/SiO_x films such as porous silicon [20] and oxidized Si nanometer-sized spheres [19] have also shown that in these systems the Si/SiO_x interfacial region is responsible for the 1.65–1.7 eV PL peak. These results are in good agreement with our current PL peak position.

4. Conclusions

In a conclusion, we have synthesized fine and straight SiNWs with diameters of 10–30 nm and lengths of several micrometers using Au as catalyst by self-designed chemical vapor deposition system at atmosphere pressure.

HRTEM images reveal that SiNWs consist of crystalline silicon cores covered by amorphous silicon oxide sheaths (~3 nm) and growth direction of the nanowires are along the [1 1 1]. Raman spectroscopy shows an asymmetric peak around 517 cm⁻¹, with a down-shift of 4 cm⁻¹ with respect to the first-order Raman peak of single-crystalline silicon caused by the size confinement effect. The fine SiNWs exhibits a photoluminescence that peaked at 750 nm.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (No. 60776009). The authors would like to thank Dr. Huigao Duan for the HRTEM measurements.

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