Evolution of core-shell silicon nanowires grown on silicon substrates by pulsed laser ablation

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***Abstract*- Si nanoparticles and nanowires have been synthesizd on Si substrates by pulsed laser ablation (PLA). The Si nanowires which have a crystalline core with an amorphous shell have been grown on the Si nanoparticles with increase of the ablation time. The obvious blue shift has been observed from the photoluminescence (PL) spectrum.**

I. INTRODUCTION

The recent observations has revealed that Si nanowire nuclei consisted of a polycrystalline Si core with a high density of defects which are challenging problems for the scientific community [1,2]. In this paper, we describe the evolution of a Si nanowire grown from a crystalline Si nanoparticle. The core-shell microstructure and morphology of Si nanowire have been investigated.

II EXEPERIMENTAL

Nanoparticles and nanowires were prepared by PLA technique in argon atmosphere at 300 Torr. The target for laser ablation was made by mixing Si (70 at.%) and SiO_2 (~30 at.%) powders and was hot-pressed into a disk of 15 mm in diameter and 5 mm thick. The furnace temperature was kept at around 1250 ℃. A KrF excimer laser was focused to a $1\times2mm^2$ rectangular spot on the target which rotated at 2rpm.

The samples were examined by a field emission scanning electron microscope (SEM, Hitachi S4800), high-resolution transmission electron microscope (HRTEM), energy dispersive X-ray (EDX) spectrometer and X-ray photoelectron spectroscopy (XPS)

III RESULTS AND DISCUSSIONS

Four samples have been prepared on Si substrates with the ablation time of 1h, 2h, 4h and 8h, respectively. The Si nanoparticles with a diameter ranging from 10~100nm have been initially synthesized and the nanowires with a diameter about 20nm and length up to a few hundred microns have been then grown from these Si nanoparticles.

SEM images in Fig. 1(a) clearly depict the Si nanoparticles with the homogenous size and shape at the initial stage. When the furnace temperature was heated up to 1250℃ and ablation time was long enough, nanowire began to grow from the tip of the Si nanoparticles, as seen in Fig. 1(b) and 1(c). After 8h ablation of the mixture target in the furnace, numbers of Si nanowires have been obtained. Fig. 1(d) shows the large amount of Si nanowires which have been grown along the surface of the silicon substrate.

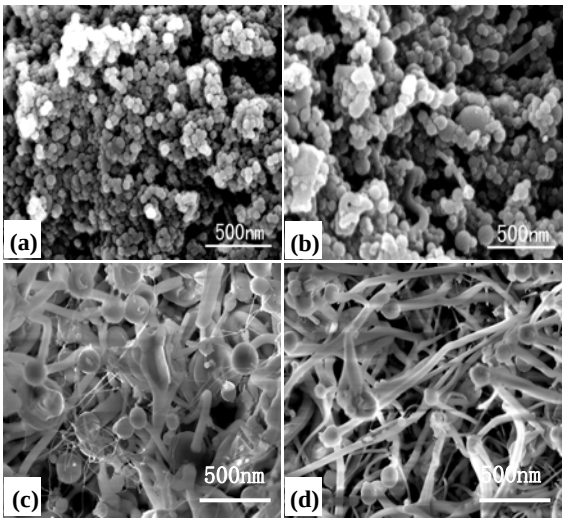

Fig. 1 SEM images of Si nanostructures produced by pulsed laser ablation at 1250℃ for different ablation time from 1h to 8h. (a)1h, typical morphology of Si nanoparticles with homogeneous size; (b) 2h, Si nanoparticles with few nanowires; (c) 4h , Si nanowires with the chain-like structure; (d) 8h, Si nanowires with the pinlike structure.

The original nanoparticles were scratched from the Si substrate and ultrasonically cleaned in ethanol and then dispersed on carbon film for TEM measurement. In the present experiment, a mixture target consisted of SiO_2 has been ablated by the laser to form nanoparticles. The nucleation of nanoparticles may involve different decompositional reactions of the Si oxide vapor phase at a relatively low temperature of 930°C [3].

The decompositions have resulted in the precipitation of the silicon nanoparticles (the nuclei of Si nanowires) surrounded by shells of silicon oxide. Based on the oxygen assisted mechanism, SiO_x can be formed by reaction

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$2SiO \rightarrow 2SiO_x + (1-x)O_2$ during the ablation process in the hot furnace [4,5]. Therefore, the amorphous shells are possibly formed from the reaction. Most of these sphere-like nanoparticles are single crystals as revealed by the HRTEM image. The outside region of the Si nanoparticle is coated by oxidized surface layer. EDX measurement can be focused on the individual Si nanoparticle. The strong Si signal and weak O signal demonstrate the presence of Si and silicon oxide.

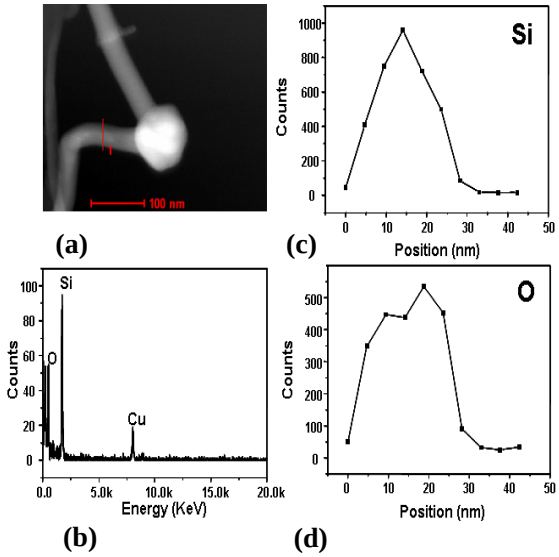

Fig. 2 (a) A dark field scanning TEM image. EDX line scan is operated along the cross-section of a Si nanowire (mark 1); (b) EDX spectrum of the nanowire, Si peak is dominant, O peak is due to contamination and surface oxide, Cu peak is also seen because the sample was mounted on a Cu substrate for the analysis; (c) The distribution pattern of Si element; (d) the distribution pattern of O element.

With the increase of ablation time, numbers of agglomerated Si nanowires are observed by TEM and results are in agreement with those in the reports [6,7]. The Si nanowires consist of a crystal core with a thick amorphous SiO_2 shell and this core-shell structure is confirmed by EDX measurements. The EDX line scanning is operated along the cross section of the nanowire to investigate the distribution of Si and O. The presence of Si and O elements has been observed and the graph c and d in Fig. 2 confirm the existence of a silicon oxide shell and a silicon core.

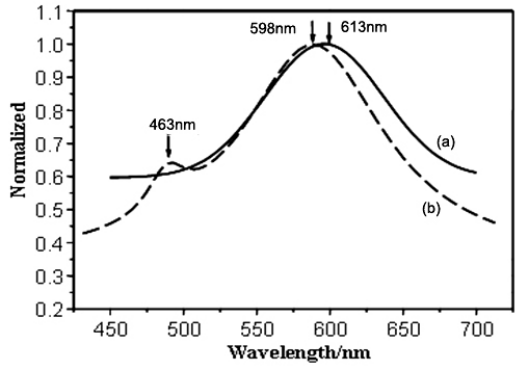

Fig. 3 Normalized PL spectra for Si nanoparticles (sample 1, curve a) and Si nanowires (sample 2, curve b)

The nucleation and growth of Si nanowires are controlled by oxygen assisted growth mechanism [8]. The involvement of oxygen element in the ablated target is the key role during the growth of the Si nanowires.

We have investigated the PL properties of the Si nanowires. The typical room temperature PL spectra of the Si nanoparticles samples synthesized in Ar atmosphere by PLA are illustrated by curve (a) in Fig. 3, which is dominated by broad PL spectral features with the peak centering at 613nm, and the FWHM about 110 nm. Fig. 3 also shows the double peaks PL spectra of chain-like and core-shell Si nanowires where a shoulder is located at 436nm. These two PL bands are generally believed to arise from different mechanisms: (1) the 463nm band is from the defect-related SiOx layer through the recombination of carriers at defects; (2) the 598nm band is attributed to the recombination of the confined excitons in Si nanoparticles.

CONCLUSIONS

In summary, PLA technique has been developed for preparation of Si nanowires through an oxygen assisted mechanism. The morphology of silicon nanowires is chain-like structures observed by SEM. And the Si nanoparticles are regarded as nuclei for growth of Si nanowires without any metals catalysts. TEM images and EDX results show that homogeneous silicon nanowires with a core-shell structure which consists of the crystalline silicon core (20 nm in diameter on average) covered by the amorphous silicon oxide shell (~5 nm thick on average). The PL spectrum of chain-like structural Si nanowiers illustrates a double peak at 463 and 598nm respectively, which are due to the defect related oxidation process. The present research finding enhances the understanding of quasi-one-dimensional Si quantum structures.

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