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Si nanowires synthesized by laser ablation of mixed SiC and SiO_2 powders

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Abstract

By using a KrF excimer laser to ablate a target of SiC powder mixed with 10 wt.% SiO_2 powder at 1400°C, Si nanowires were deposited on the inner wall of a ceramic tube. Transmission electron microscopy shows that the nanowires are around 14 nm in diameter and co-exist with a small amount of nanoparticles. High-resolution transmission electron microscopy shows that the nanowires are crystalline Si nanowires and the nanoparticles are cubic SiC. The intergrowth of heterocrystal nanowires and nanoparticles verifies that the oxide-assisted growth model of Si nanowires is reasonable.

1. Introduction

Quasi one-dimensional Si nanowires (SiNW) have attracted much attention [1–4]. As the miniaturization of present microelectronics continues, future nanoelectronics need nanoscale functional semiconductor materials. SiNWs naturally become one of the promising candidates. Current research on SiNWs focuses primarily on growth methods and starting materials. The reported growth methods include electron beam (EB) lithography [5], reactive ion etching [6], the scanning tunneling microscope (STM) [7], thermal evaporation [8,9] and laser ablation [1,2]. Among these methods, laser ablation seems to be the most promising for synthesizing SiNWs because this method can produce free-standing nanoscale materials in high yield with controllable experimental conditions. Other nanoscale materials, including C_{60} [10], β-C_3N_4 [11], single-wall carbon nanotubes [12], were first synthesized by this method. The starting materials for deposition of SiNWs by the laser ablation method include Si powder mixed with catalyst [1] or Si powder with SiO_2 powder [13]. However, a target made of SiC powder mixed with SiO_2 powder is interesting since electronic-grade silicon (EGS) is made from the reaction of SiC powder and SiO_2 powder [14]. EGS is a polycrystalline material of high purity which is the raw material for the preparation of single-crystal silicon. In this Letter, we report the synthesis of SiNWs by using KrF excimer laser to ablate the target of SiC powder mixed with 10 wt.% SiO_2 powder at 1400°C.

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2. Experimental

A schematic diagram of the equipment used is shown in Fig. 1. The target was made by pressing SiC powder mixed with 10 wt.% SiO_2 at 150°C for 24 h under a hydraulic press. After the target was placed in the high-temperature zone inside the ceramic tube, the tube was evacuated by a mechanical rotary pump. Argon gas was kept flowing through the tube at a rate of 50 sccm (standard cubic centimeter) and a pressure of 700 Torr. After the temperature achieved 1400°C, the laser ablation process was started. A KrF excimer laser beam (248 nm) of 400 mJ per pulse and a pulse width of 34 ns at 10 Hz ablated the target. The total duration of ablation was 2 h and the size of the laser spot on the target was about 1×3 mm. Two layers of sponge-like webs, a yellow web and a green web, were deposited on the inner wall of the tube as shown in Fig. 1. The yellow web was 5 times more abundant than the green web by weight. The products were mounted on copper grids for transmission electron microscopy (TEM) observations (Philips FEGCM200).

3. Results and discussion

The TEM micrograph in Fig. 2a shows the typical morphology of the materials in the yellow web. It can be seen that the product consists of nanowires with an average diameter of 14 nm. Most of the SiNWs are consist of straight and smoothly curved parts. The morphology is a common characteristic of various nanowires, such as SiC nanowires [15] and carbon nanowires [16]. Although the nanowires have a high ratio of length to diameter, the diameter remains the same throughout the entire nanowire. The inset is a selected-area electron diffraction (SAED) pattern taken from the nanowires. The diffraction rings match well with the (111), (220) and (311) diffraction rings of silicon with a diamond structure. Analysis using energy dispersive X-ray spectroscopy (EDS) equipped on TEM confirmed that the nanowires have a crystalline Si core and an amorphous silicon oxide outer layer. Fig. 2b is a micrograph of high-resolution TEM (HRTEM) of a typical SiNW. It further confirms that the nanowires are crystalline SiNWs. Two groups of crystal lattices have the angle in 70° which means the spots consisted by {111} crystalline planes. Thus the growth direction is along [111].

In addition to the yellow web as the main product, there still exists a green web, which has not been

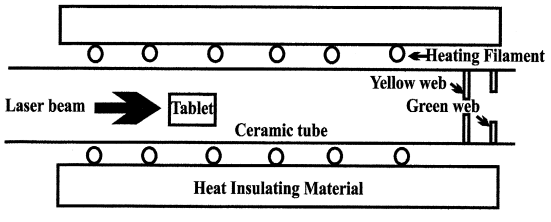

Fig. 1. The schematic diagram of the laser ablation apparatus.

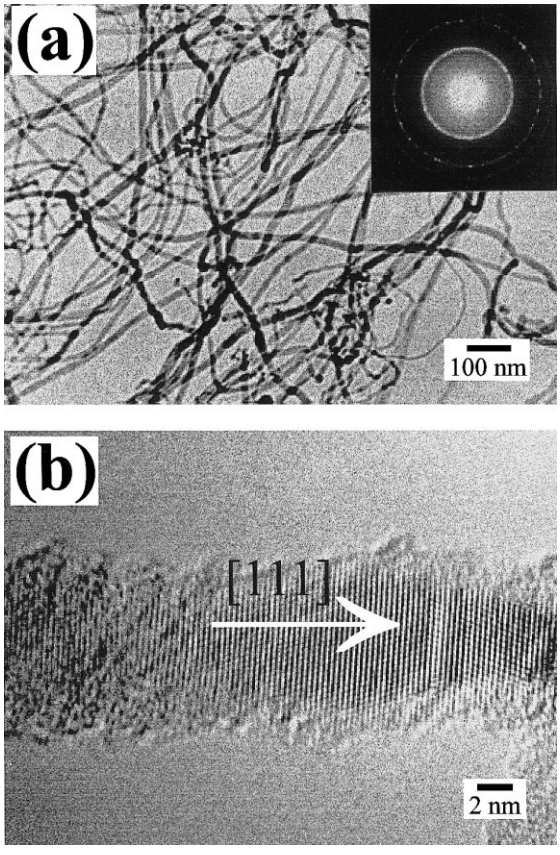

Fig. 2. Morphology of Si nanowires taken from the yellow product. (a) Low-magnitude TEM image of Si nanowires. The inset is SAED pattern. (b) HRTEM image of a typical Si nanowire. The growth direction goes along [111].

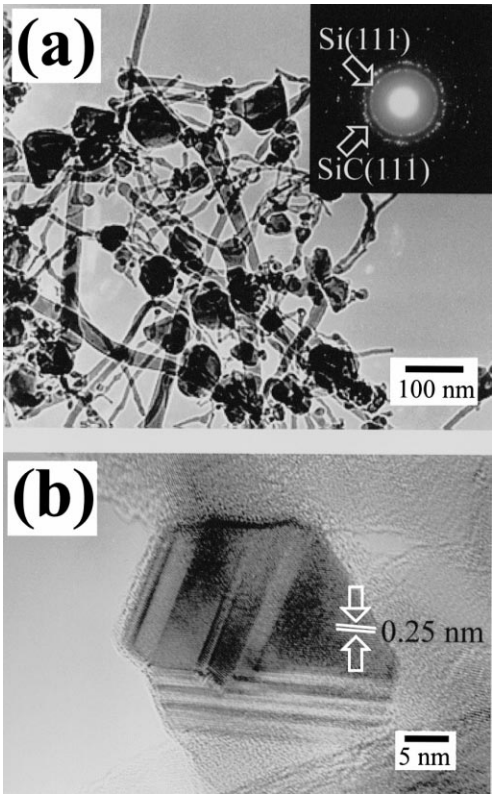

Fig. 3. TEM images of the green web in which Si nanowires coexist with SiC nanoparticles. (a) Small amount of SiC nanoparticles which attach Si nanowires. The inset is SAED pattern. (b) HRTEM image of the β-SiC nanoparticles. The fringes are {111} lattice planes with a spacing of 0.25 nm.

found in the SiNWs products by using other starting materials [13]. The results of HRTEM show that the green web is a mixture of SiNWs and cubic SiC (β-SiC) nanoparticles as shown in Fig. 3a. Fig. 3a shows that some nanoparticles co-exist with the Si nanowires. The sizes of the nanoparticles range from several nanometers to 80 nm. The nanoparticles possess irregular outlines. The inset SAED pattern shows there are two sets of rings. One consists of the (111), (220) and (311) rings of silicon. The other corresponds to the (111), (220) and (311) rings of β-SiC. This confirms that the sample is a mixture of SiNWs and β-SiC. The results of HRTEM show that the nanowires are SiNWs as shown in Fig. 2b. The nanoparticles are β-SiC nanoparticles whose typical morphology are shown in Fig. 3b. In this figure, the fringes are {111} crystalline planes with a lattice spacing of 0.25 nm. This value fits with the standard {111} crystalline plane of β-SiC. Grain boundaries and microtwins are the main defects observed.

The results of XRD and Raman analysis also give the same conclusions. Fig. 4a shows the XRD spectrum of the green product. The XRD measurements was carried out by using Cu $K\alpha$ radiation at room temperature in a Siemens D500 system. The spectrum shows two sets of peaks. One set consists of the (111), (220) and (311) peaks of Si which are from the SiNWs. The other set consists of the (111), (220) and (311) peaks of β-SiC which are from the β-SiC nanoparticles. The positions of the peaks fit the values in the standard XRD handbook [17]. The Raman scattering measurement was performed at room temperature using a micro-Raman Renishaw 2000 system with 1 cm^{-1} resolution and 0.4 cm^{-1}

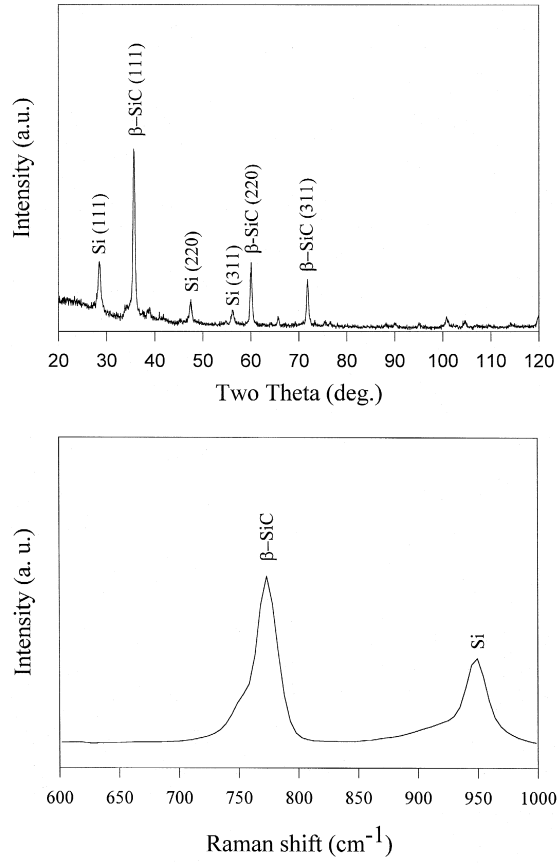

Fig. 4. The spectrum of X-ray diffraction and the Raman spectrum recorded from the green web.

reproducibility. The excitation source was the 514.5 nm line of an argon ion laser with a spot size of 10 μm in diameter and a power of 4 mW. The Raman result is shown in Fig. 4b. The peak at 780 cm^{-1} is the characteristic peak of β-SiC [18]. The other peak at 950 cm^{-1} is second-order peak of Si. The peak of SiC is asymmetric. This is possibly due to the nanoscale size effect of the SiC nanoparticles [19,20].

We propose that the growth mechanism of the Si nanowires can be explained by the oxide-assisted growth model [8,13] recently proposed by us. In this model, a liquid SiO layer was formed on the tip of the Si nanowire. It is this SiO liquid layer which assists the nanowire growth. In the present case, SiO came from the chemical reaction between SiC and SiO_2. Analogous to the synthesis of industrial silicon, the overall reaction [14] was

$$\mathrm{SiC(solid)} + \mathrm{SiO_2(solid)} = \mathrm{Si(solid)} + \mathrm{SiO(gas)} + \mathrm{CO(gas)}\,.$$

The reaction was activated by the excimer laser. The SiO vapor was carried by the flowing gas and deposited forming Si nanowires according to the oxide-assisted growth model [8,13].

It should be mentioned that no SiC nanowires were found in the product. Moreover, the β-SiC nanoparticles were only formed inside the second web (green web). Since no β-SiC nanoparticles can be found in the first web (yellow web), it implies that the β-SiC nanoparticles were also grown by the vapor reaction and not by direct ablation. Otherwise, they should also be formed inside the first web which was closer to the target. Their growth only inside the second web may be due to the suitable growth temperature. β-SiC nanoparticles can be readily formed by the chemical reaction between SiO and CO. Unlike Si which grows as the one-dimensional nanowires, β-SiC can not grow one-dimensionally but remain as three-dimensional nanoparticles. We suspect that this is probably due to the fact that β-SiC can not form a semi-melting phase at the relatively low temperature ($\sim 950°C$). According to the oxide-assisted growth model [8,13], one-dimensional growth became impossible without the liquid phase at the tip. This opinion can be understood by comparing the Fig. 3b with Fig. 2b. As we can see, the outer shells of the two materials are obviously different. The Si nanowire shown in Fig. 2b has a thick amorphous silicon oxide outer layer which is formed from the semi-melting SiO layer. However, the β-SiC nanoparticle shown in Fig. 3b has nearly no amorphous outer layers. So the one-dimensional growth of β-SiC can not be achieved.

4. Conclusions

We have synthesized Si nanowires from SiC powders mixed with SiO_2 powders which are used to synthesize single crystalline silicon in the present semiconductor industry. The crystalline Si nanowires are around 14 nm in diameter and co-exist with small amounts of β-SiC nanoparticles. The growth of the nanowires is proposed to be via the intermediate material SiO which was generated by the chemical reaction between SiC and SiO_2. The experimental results indicate that the reaction to synthesizing industrial silicon can also be that of Si nanowires. This experiment also gives support to the oxide-assisted growth model of SiNWs.

Acknowledgements

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