# Si nanotubes fabricated by wet etching of ZnO/Silicon Core-Shell nanowires

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### **INTRODUCTION**

Bulk silicon does not show good optical properties because of its indirect band gap. However, when the size of silicon is reduced to nanoscale, the optical properties can be improved. There are many kinds of silicon nanomaterials, such as silicon nanoparticles (SiNPs), silicon nanowires (SiNWs), and silicon nanotubes (SiNTs). SiNPs and SiNWs have already been well investigated, while the research of SiNTs is still very limited, In this study, we focus on the SiNTs. Due to their very high surface area to volume ratio and novel physical properties, SiNTs have good application prospects in many fields. For example, it can be applied to the anode material in lithium ion battery [1], transistors [2], and light emitted diodes [3].

Our aim is to fabricate SiNTs and apply them to the above-mentioned device.

#### EXPERIMENTAL PROCESS

As shown in the Fig. 1 (a), we grew arrays of ZnO NWs by a hydrothermal synthesis method. The reaction materials include 2.5 mM hexamethylenetetramine (HMTA), Zinc of nitrate (5 mM) and ammonia (1 mL). Then, we use chemical vapor deposition process to form Si layer on the ZnO nanowires. The temperature and time are varied from 650 to 700°C and 6 to 15 min, respectively. Next, the samples were wet etched by phosphoric acid (85%) to remove ZnO NWs and to form SiNTs. We characterized SiNTs by scanning electron microscopy (SEM), (TEM), transmission electron microscopy energy dispersive X-ray spectroscopy (EDS), X-ray (XRD) diffraction and Raman spectroscopy.

#### **RESULTS AND DISCUSSION**

Fig. 2 (a) shows the SEM image of the SiNTs after wet etching. To further confirm the formation of the Si shell, we performed TEM measurements. From Fig. 2 (b) and (c) we could clearly see a hollow space in the middle which proves the tubular shape and observe Si formation from the increase of NWs diameter.

Fig. 3 is the result of the EDS linescan of a SiNTs, showing no zinc peaks. Fig. 4 shows that the ZnO peaks disappeared after etching, which is consistent with the result of EDS. Fig. 5 shows the crystallization of the SiNTs after annealing which increases the applicability of the device. Based on these results we could prove the fabrication of the amorphous- and crystalline-SiNTs structures.

[1] Wen, Zhenhai, et al. Electrochem. Commun. 29 (2013) 67.

[2] Fahad, Hossain M., and Muhammad M. Hussain. Sci. Rep. 2 (2012) 475.

[3] Taghinejad, Mohammad; Taghinejad, Hossein. Nano Lett. 13 (2013) 889.



Fig 1. Schematic illustration of the full procedure of the fabrication of SiNTs: (a) Synthesis of ZnO NWs on a Si substrate with a ZnO seed layer. (b) formation of Si layer on the ZnO core. (c) Etching of ZnO by H<sub>3</sub>PO<sub>4</sub> and SiNTs was fabricated.



Fig 2. (a) 30° titled SEM image of the SiNTs arrays. (b) Magnified TEM image of the SiNTs. (c) Cross-section of SiNTs.



Fig 3. EDS linescan for Si and Znic in the SiNTs.



Fig. 4 XRD results of the SiNTs before and after etching.



Fig. 5 Raman spectra of the SiNTs before(dot line) and after(solid line) annealing.