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Growth of p-type Si nanotubes by catalytic plasma treatments

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Abstract

We have demonstrated a new technique to transform bulk materials into one-dimensional nanostructures. We have shown that p-type Si nanotubes (SiNTs) can be grown by a simple dual RF plasma treatment of p-type Si substrates at 500 °C. These SiNTs have diameters of ∼50–80 nm with tubular wall thickness of ∼10–15 nm. The use of Cu vapor and reactive plasma has enabled the growth of these SiNTs instead of Si nanowires.

(Some figures in this article are in colour only in the electronic version)

Silicon nanowires (SiNWs) are attractive nanomaterials because of their compatibility to state-of-the-art integrated circuit technology [1, 2]. On the other hand, silicon nanotubes (SiNTs) have attracted much attention because of their intriguing structures and mysterious properties. Theories have predicted the existence of various types of SiNT [3–8]. Experimentally, SiNTs have been grown by using anodic aluminum oxide templates and hydrothermal techniques [9–12]. The results from these works are not consistent with each other and the electronic properties of these SiNTs have not been elucidated. Here we report the growth of p-type SiNTs from p-type Si substrates without using templates. These SiNTs are grown in vertical arrays, with diameters of 50–80 nm, lengths as long as 20 μm, and tubular walls 10–15 nm thick. The results indicate that we can transform Si substrates into SiNTs that maintain similar transport characters.

The growth of our SiNTs is based on a novel dual RF plasma treatment technique (figure 1(a)). Nitrogen gas is used for the plasma generation and oxidized Si substrates serve as the Si source materials as well as the substrates. The growth of SiNTs is conducted in a stainless steel vacuum chamber (figure 1(a)) with a base pressure as low as $\sim 5 \times 10^{-7}$ mbar. A p-type Si(100) substrate is used as the source material as well as the substrate. This substrate has a nominal thermal oxide layer of ∼100 nm and is heated up to 500 °C on a ceramic heater after the chamber is back filled with nitrogen gas of 5×10^{-2} mbar. Two RF plasma generators (1 and 2 in figure 1(a)) are used for the growth of these SiNTs. Generator 1 is connected to the substrate steel holder (3 in figure 1(a)) by a copper wire. This plasma will generate dc substrate bias voltages up to −550 V at a forward power of ∼40 W. Generator 2 was connected to a molybdenum ring electrode ∼3 cm in front of the substrate (4 in figure 1(a)) with a forward power of ∼25 W (dc bias voltage −400 V). These generators were applied for 4 h in each experiment. Subsequently, the substrate is cooled to the room temperature to complete the growth processes. Bias voltages generated by the plasmas will induce bombardments of N^{2+} ions and initiate sputtering of these plasma wires and the substrates.

Figures 1(b)–(e) show a set of images obtained by scanning electron microscopy (SEM) of the as-grown SiNTs. These SiNTs are grown in the direction of the applied electric field on the substrates. The density and length of these SiNTs vary with the dc bias voltages on the substrates, and the techniques of supplying the Cu catalysts. Cu vapor is usually supplied by the *in situ* sputtering of the Cu plasma wire that connecting the RF-power generator and the substrate holder (1 in figure 1(a)). SiNTs grown at −350 V have lower density and shorter length (figure 1(b)) while those grown at higher

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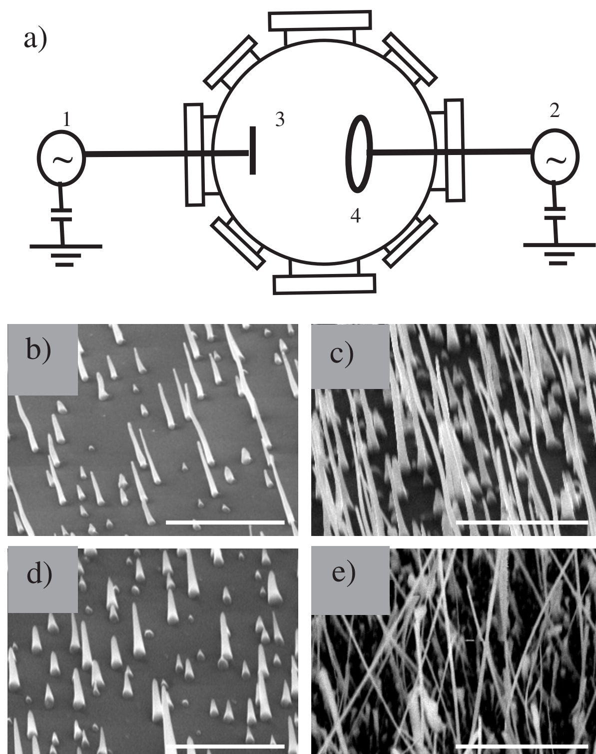

Figure 1. (a) Schematic drawing of the experimental setup for growing SiNTs. SEM images of SiNTs grown by substrate bias voltage of (b) −350 V, (c) −450 V with exposed Cu plasma wires. SiNTs can be grown without Cu plasma wire but with Cu coated substrates (d). Longer and denser SiNTs can be grown by using a Cu ring electrode (e). The scale bars of the SEM images are 3 μm.

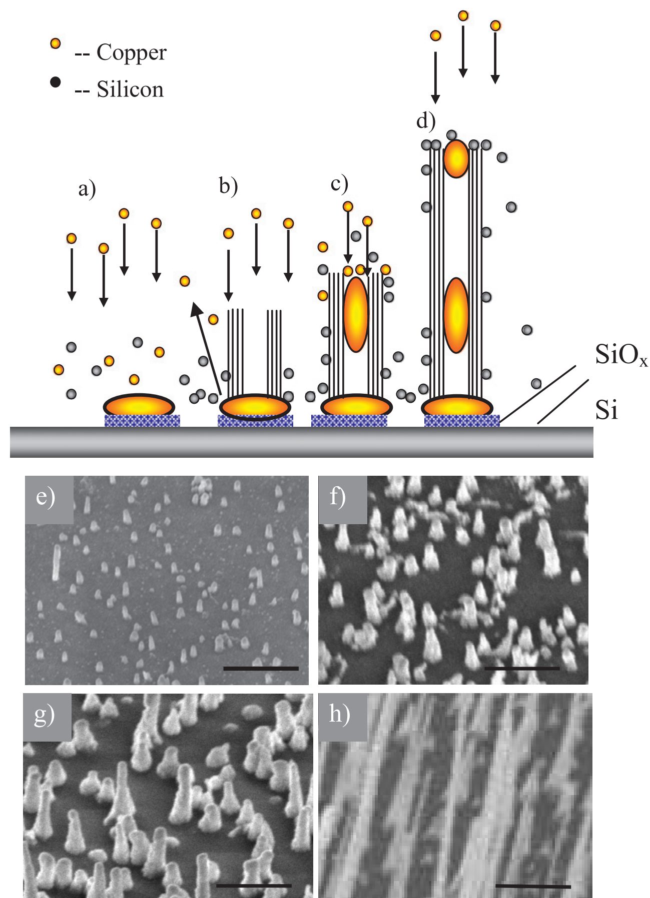

Figure 2. Schematic drawing for the self-assembly of SiNTs from an oxidized Si substrate with activated Si and Cu vapors (a)–(d). SEM images of samples grown for (e) one hour, (f) two hours, (g) three hours, and (h) four hours. The scale bars of the SEM images are 1 μm.

magnitudes of biasing (for example −450 V) demonstrate higher densities and longer lengths (up to 8 μm in figure 1(c)). SiNTs cannot be grown at biasing between 0 and −250 V. These results indicate that the growth of SiNTs depends on the magnitude of the substrate bias voltages.

The growth of SiNTs is also affected by the way the Cu vapor is supplied. When the Cu wire is covered by using ceramic beads, SiNTs cannot be grown on bare substrates but can be synthesized on substrates coated with 25 nm thick Cu films (figure 1(d)). As shown, these SiNTs are shorter than those grown at similar condition with Cu plasma wire (figure 1(c)). In addition, when the molybdenum ring electrode wire (4 in figure 1(a)) is replaced by a copper wire, longer SiNTs with smaller diameters can be formed, as shown in figure 1(e). This is due to the additional supply of Cu vapor from the ring electrode. These SiNTs are as long as 20 μm but sometimes are decorated with Cu clusters on the growth surfaces. These results indicate that the growth rates of SiNTs can be controlled by the method of supplying the Cu catalysts.

We propose a modified vapor–liquid–solid (VLS) growth model for these self-assembled SiNTs, as illustrated in figure 2. First, Cu particles will be formed on the oxidized Si substrate, either from the Cu thin films or from the condensation of the surrounding Cu vapor. The Si oxide layer and the Cu particles will both be subject to physical sputtering as induced by negative dc bias voltages that were initiated by the RF nitrogen plasma. This is due to the high kinetic energy of accelerating ions (N^{2+}) in the plasma (∼350–450 eV). Some Cu particles will survive from the sputtering and remain on the substrates with the oxide layer shielded under the nanoparticles. This oxide layer will work as the diffusion barrier that prevents the diffusion of Cu into the Si substrates. Some oxide surfaces will be exposed if the Cu condensates are totally removed by sputtering. At these areas, sputtering of the Si oxide will occur, followed by the sputtering of Si and the generation of Si vapor. Since Si has high solubility in Cu at the growth temperature [13], Si vapor from the substrate will be dissolved into the adjacent Cu particles. When Si inside the Cu particles reaches the supersaturation condition, Si will start to segregate as SiNTs, consistent with the VLS mechanism (figure 2(b)).

Our growth condition is a combination of physical sputtering and chemical VLS processes. We believe that the highly energetic growth species involved here is one of the reasons for the growth of SiNTs instead of SiNWs. Because of the presence of physical sputtering and plasma etching, the Cu catalyst on the SiNTs will be evaporated during the growth process and thus slow the growth rate, as described in figure 1(d). Thus continuously supply of Cu vapor from the sputtering of the Cu ring electrode could compensate the loss of Cu catalyst and lead to the enhanced growth rate and

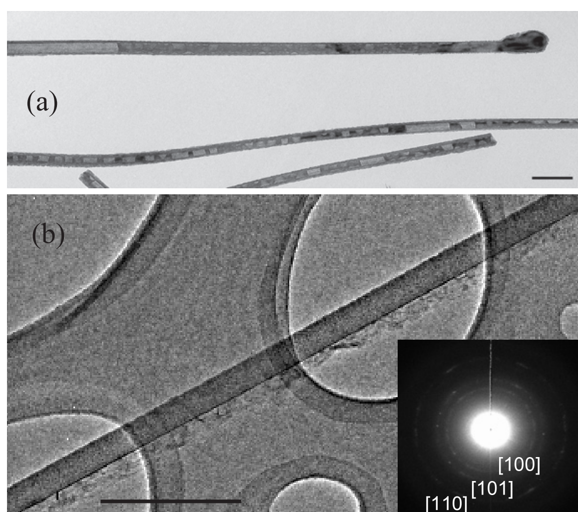

Figure 3. A TEM image of the (a) as-grown SiNTs partially filled with Cu. TEM images of (b) an etched SiNT. Diffraction pattern (inset) of the etched SiNTs. The scale bars for the TEM images are 200 nm.

growth density of the SiNTs shown in figure 1(e). This growth mechanism is supported by a time-dependent evolution of the growth morphology, as shown in figures 2(e)–(h). As shown, the growth rates of the SiNTs are slow in the first three hours due to the time needed to sputter away the Si oxide layer for the generation of Si vapor.

Transmission electron microscopy (TEM) images reveal the interior morphology of these SiNTs (figure 3(a)). These particular SiNTs have diameters ∼50–80 nm and are partially filled. The wall thicknesses of these SiNTs are ∼10–15 nm. The fillings inside these SiNTs are Cu and can be chemically etched by dipping the sample into copper etchant at room temperature for 1 h. This etchant is a mixture of 30% $FeCl_3$ + 3% HCl + 67% H_2O [14]. The reaction for etching of copper with ferric chloride is

$$Cu(s) + 2Fe^{3+} + 3Cl^{-} \rightarrow CuCl_3^{-} + 2Fe^{2+}.$$

The Fe^{3+} ions are reduced to Fe^{2+}, which remain in solution, while the copper metal is oxidized to Cu^{2+}. HCl assists in the dissolution of the ferric chloride, and also etches copper. After etching, the samples were dipped into deionized water for another hour. Figure 3(b) shows a typical hollow structure of these SiNTs after etching. Electron diffraction patterns of the etched samples (inset) indicated the formation of oxidized Si during the etching process.

We have characterized the element distribution of the as-grown SiNTs by x-ray mapping [15]. SiNTs were first suspended in ethanol and then transferred onto graphite substrates. Figure 4(a) is the SEM image of a thick SiNT, which clearly shows the filled and hollow segments, consistent with the TEM images. As shown in figure 4(b), Si signals (dots) are homogeneously distributed along the SiNT. Some traces of Si signals are detected from the substrate (background in figure 4(b)) due to the scratched Si powders on the graphite substrate. The Cu mapping in figure 3(c) shows that Cu

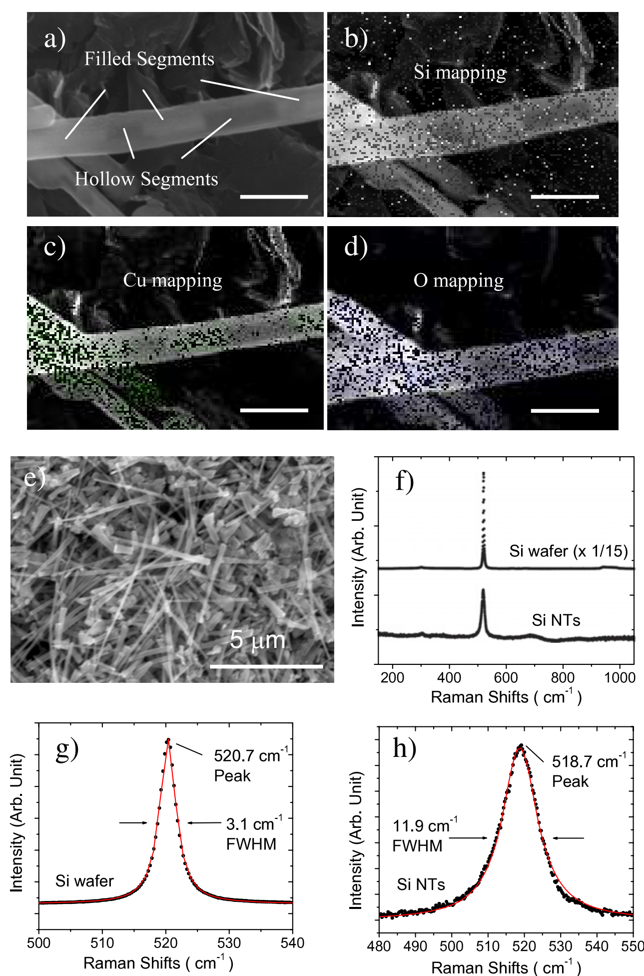

Figure 4. SEM images (a) and x-ray mapping for (b) Si, (c) Cu, and (d) oxygen are shown for comparison. The scale bars for SEM images and x-ray mapping are 300 nm. (e) Dispersed SiNTs on a graphite substrate and the related Raman spectra for the (f) SiNTs and a clean Si substrate. Raman spectra for (g) a Si substrate and (h) SiNTs fitted with Lorentzian line shapes.

appears mainly on the filled segments. We also found that O is homogeneously coexistent along the whole tube with Si (figure 4(d)). We believe that these signals are from the native oxide at the surfaces of these SiNTs, as commonly detected in SiNWs [16–18]. These oxides were coated on the shells of the crystallized SiNTs as confirmed by high-resolution transmission electron microscopy (HRTEM, not shown here).

The SiNTs were also characterized by Raman spectroscopy. These SiNTs are coated on a graphite substrate from their suspension in ethanol (figure 4(e)). Raman spectra were collected from a bare Si substrate and the SiNTs (figure 4(f)) using a He–Ne laser (632.8 nm, 1.96 eV). Raman shifts from the Si substrate are centered at $\sim 520.7\ cm^{-1}$. The spectra detected from SiNTs are red shifted to $\sim 518.7\ cm^{-1}$. This is expected due to the phonon confinement effect of nanoscopic materials, which is also commonly observed from SiNWs [16–18]. The bandwidth of the Raman signal for single-crystalline Si substrates is narrower (figure 4(g), $3.1\ cm^{-1}$) than that detected from the SiNTs (figure 4(h), $11.9\ cm^{-1}$) according to the fitting by Lorentzian line

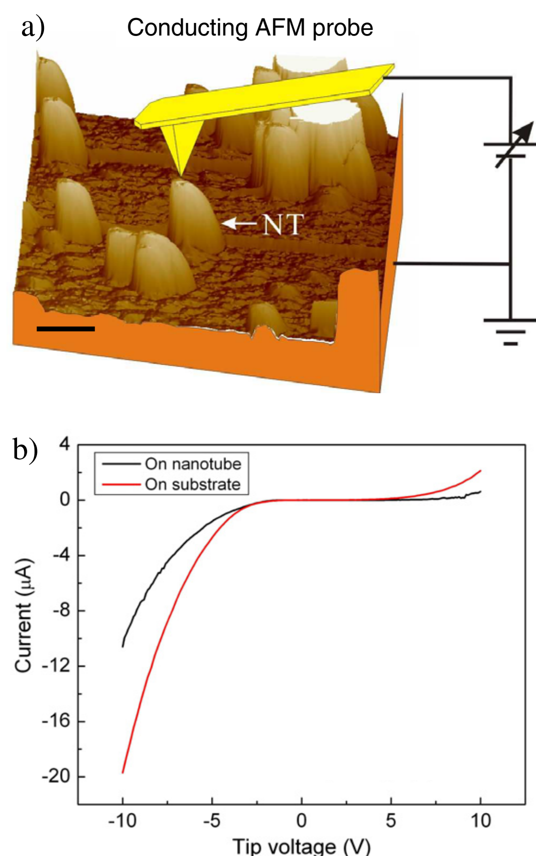

Figure 5. (a) Schematic of I–V measurement circuit with a 3D AFM image showing the vertical grown SiNTs (scale bar: 1 μm). The actual measurements were conducted on longer SiNTs at room temperatures. (b) Typical I–V characteristic obtained from an individual SiNT and the substrate.

shapes. The spectra broadening effect is also quite common for SiNWs, with typical reported values ranging from 10 to 20 cm^{-1} [17, 18]. The detected Raman spectra also suggested that our SiNTs have face-centered cubic structures like conventional Si substrates and SiNWs.

We have investigated the electronic properties of the as-grown vertically aligned SiNTs by using conductive atomic force microscopy (AFM) in conjunction with an external data acquisition system. Figure 5(a) shows the schematic measurement circuit with a 3D contact mode AFM image of SiNTs (the actual measurements were conducted on longer SiNTs at room temperatures). Conductive AFM probes coated with thin Ti–Pt film were used for these measurements. Figure 5(b) shows the I–V curve obtained from one of these individual SiNTs. As shown, current flows are detected at negative bias voltages on the AFM tip. As a comparison, the I–V curve measured on the p-type substrate was also acquired, which demonstrates slightly larger conductance. The high current level obtained from the substrate indicates that the oxide layer of the originally oxidized Si substrate has been etched away by the plasma, consistent with our growth model and our previous report on the growth of boron nitride nanotubes [19]. In addition, the asymmetry of the I–V curve from the SiNT resembles that from substrate. This characteristic reveals the p-type nature of the as grown SiNTs. This I–V curve also demonstrates the opposite feature to that acquired from n-type vertical nanowires with the same measurement setup [20].

In summary, we have demonstrated a new technique to transform bulk substrates into one-dimensional nanostructures. Specifically, we have converted p-type Si substrates into p-type Si nanotubes (SiNTs). We have shown that these Si nanotubes remained as conventional Si crystalline structures, instead of structures predicted by theories. The reported approach could be useful for creating one-dimensional nanostructures with predictable transport properties.

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