

## Self-assembly of Silicon Nanotubes

Ming Xie, Jiesheng Wang, Chee Huei Lee, and Yoke Khin Yap

Department of Physics, Michigan Technological University, 118 Fisher Hall, 1400 Townsend Drive, Houghton, MI, 49931

### ABSTRACT

The growth of silicon nanotubes (SiNTs) by a dual-RF-plasma treatment technique is reported here. These SiNTs are vertically aligned and self-assembled from Si substrates at 500 °C by the use of Cu catalysts. Their diameters are ~50 to 80 nm with tubular wall thickness of ~10-15nm. Cu vapors were found partially filled inside the SiNTs. This is a novel technique that can convert bulk materials into their nanostructures.

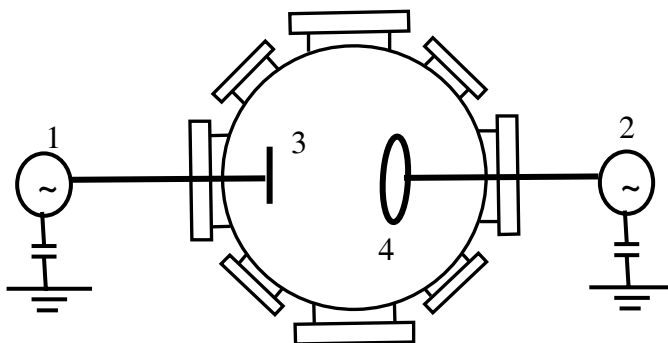
### INTRODUCTION

Silicon nanowires (SiNWs) [1, 2] are one of the most attractive nanomaterials because of their compatibility to the state-of-the-art integrated circuit technology. Different techniques have been used to synthesize SiNWs, such as laser ablation [1, 2], chemical vapor deposition [3]. Recently, Silicon nanotubes (SiNTs) have attracted attentions because of their intrigue tubular structures and properties that could enhance the uses of SiNTs for applications. Theoretically, many research groups have investigated the possible existence of SiNTs [4-9], but not many experiments were reported. There are several reports on the growth of SiNTs by using templates. Sha et al. [10] grew SiNTs using a nanochannel Al<sub>2</sub>O<sub>3</sub> substrates by chemical vapor deposition (CVD). Jeong et al. [11] synthesized SiNTs on the alumina template by molecular beam epitaxy (MBE). Li et al. [12] reported fabrication of SiNTs by anodic aluminium oxide (AAO) templates. Recently, Tang et al. [13] synthesized self-assembled SiNTs under supercritically hydrothermal conditions. However, all of these techniques are low in yields. Here we report the growth of self-assembled SiNTs by a simple dual RF-plasma treatment. This technique is compatible to vacuum technology without involving templates, or dangerous precursors. Furthermore, these SiNTs are vertically aligned on substrates and can be easily extracted for applications.

### EXPERIMENT

The growth of SiNTs was conducted in a stainless steel vacuum chamber as shown in Figure 1. This chamber has a base pressure as low as  $\sim 5 \times 10^{-7}$  mbar. A *p*-type Si (100) substrate is used as the source materials as well as the substrate. This substrate has a nominal thermal oxide layer of ~100 nm. This substrate is heated up to 500°C on a ceramic heater after the chamber was back filled with nitrogen gas of  $5 \times 10^{-2}$  mbar. Two RF plasma generators (1 and 2 in Figure 1) are used for the growth of these SiNTs. Generator 1 is connected to the substrate steel holder (3 in Figure 1) by a copper wire. This plasma will generate dc bias voltages on the substrates. Generator 2 was connected to a molybdenum ring electrode ~ 3 cm in front of the substrate (4 in Figure 1) with a forward power of ~25 W (dc bias voltage -400V). 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 the plasma wires and the substrates. These SiNTs were examined by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), x-ray mapping, and micro-Raman spectroscopy.



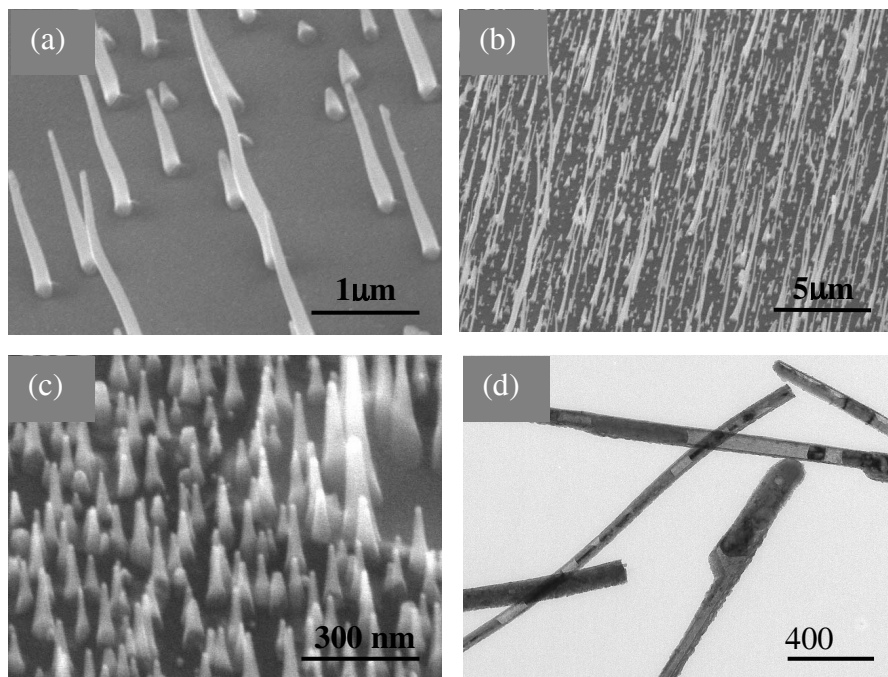
**Figure 1.** Schematic drawing of the experimental setup for growing SiNTs by a dual RF-plasma treatment.

## DISCUSSION

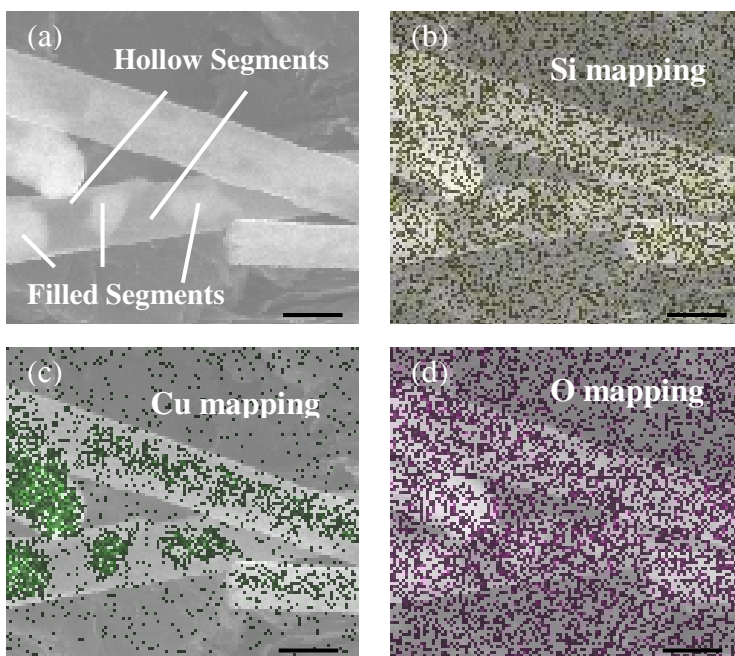
Figure 2 shows a set of images obtained by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of the as grown SiNTs arrays. These SiNTs are vertically-aligned on the substrates. The density and length of SiNTs vary with the bias voltages on the substrates. SiNTs grown at  $-350V$  are having lower density and shorter length ( $< 3 \mu m$ ) as shown in Figure 2a. The diameters of these SiNTs are  $\sim 60-120$  nm at the tips. At higher bias voltages (for example  $-450V$ ), SiNTs can be grown at higher densities and longer lengths (up to  $10 \mu m$ ) as shown in Figure 2b. The diameters of these SiNTs are  $\sim 40-100$  nm at the tips. SiNTs can not be grown at bias voltages lower than  $-300V$ . Obviously, the density and length of these SiNTs depend on the substrate bias voltages. On the other hand, SiNTs can also be grown by Cu film coated substrates instead of using a Cu plasma wire (1 in Figure 1). For example, when the Cu wire is covered by using ceramic beads, SiNTs can not be grown on bare substrates but can be synthesized on substrates coated with  $25nm$  thick Cu films as shown in Figure 1c. As shown, these SiNTs are shorter than those grown at similar condition with Cu plasma wire (Figure 1b). TEM images reveal the interior morphology of these SiNTs as shown in Figure 2d. As shown, these particular SiNTs are having diameters  $\sim 50$  to  $80$  nm and are partially filled. The wall thicknesses of these SiNTs are  $\sim 10-15$  nm.

We have then characterized the element distribution of these SiNTs by a combined energy dispersive X-ray spectroscopy (EDS) and digital imaging technique (i.e. X-ray mapping) in a FESEM [14]. For these experiments, SiNTs were first scratched from the as grown samples and suspended in ethanol and then transferred on a graphite substrate. Figure 3a is the SEM image of some SiNTs which clearly shows the filled and hollow segments as consistent with the TEM images. As shown in Figure 3b, Si signals (dots) are homogeneously distributed along the SiNT. Some trace Si signals is detected from the substrate (background in Figure 3b) due to the scratched Si powders on the graphite substrate. Cu mapping in Figure 3c shown that Cu appears

mainly on the filled segments. We also found that oxygen is homogeneously coexistent along the whole tube with Si (Figure 3d). We believed that these signals are from the native oxide at the surfaces of these SiNTs.

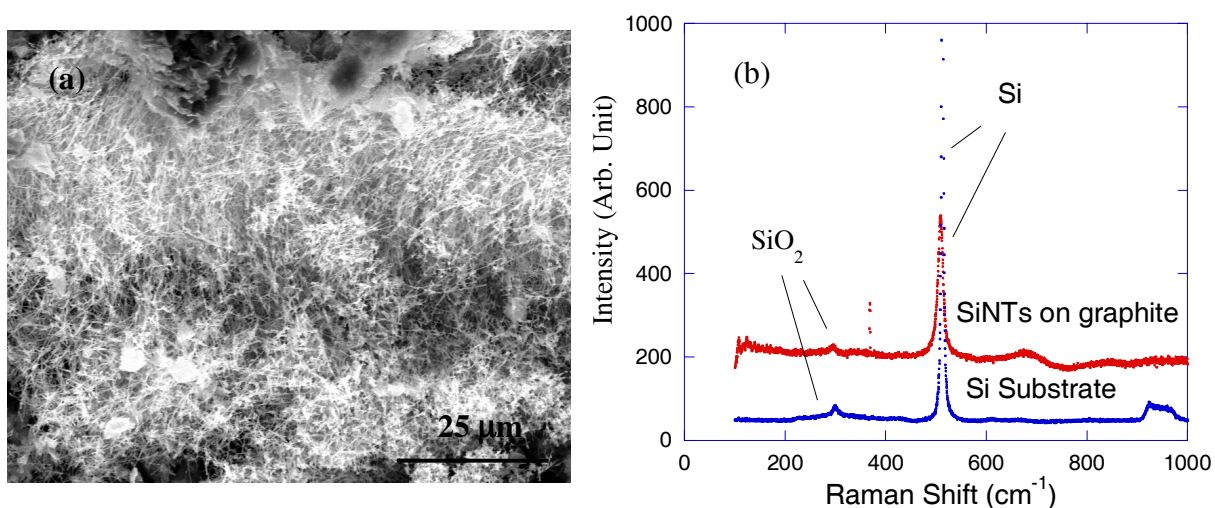


**Figure 2.** SEM images of SiNTs grown by substrate bias voltage of (a) -350V, (b) -450V with exposed Cu plasma wires. SiNTs can be grown without Cu plasma wire but with Cu coated substrates (c). The TEM image (d) indicates that these SiNTs are partially filled.



**Figure 3.** Images of SEM (a) and X-ray mapping for (b) Si, (c) Cu, and (d) oxygen are shown for comparison. Scale bars for SEM and X-ray mapping are 300 nm.

To supplement the X-ray mapping analysis, these SiNTs were characterized by Raman spectroscopy. In this case, a thick layer of SiNTs are coated on a graphite substrate from their suspension in ethanol. As shown in Figure 4a, these SiNTs are thick enough to cover the graphite surface underneath to suppress the strong graphitic peak from the substrate. Raman spectra were collected using a He-Ne excitation laser (632.8 nm, 1.96 eV) from a bare Si substrate and the SiNTs as shown in Figure 4b. As shown, the Raman shift detected from the Si substrate is shown with a strong sharp peak centered at  $\sim 520.7 \text{ cm}^{-1}$ , and our SiNT has a peak at  $518.7 \text{ cm}^{-1}$ , which has its frequency down-shifted by  $2 \text{ cm}^{-1}$ . This is expected due to the phonon confinement effect of nanoscopic materials, which is also commonly observed from SiNWs [15-17]. Thus our Raman spectra confirmed that our samples are SiNTs.



**Figure 4** (a) SiNTs dispersed on a graphite substrate. (b) Raman Spectrum of SiNTs on the graphite substrate in comparison with the spectrum obtained from a plain Si substrate.

## CONCLUSIONS

In summary, we have transformed Si substrates into vertically-aligned SiNTs by using a simple dual-RF-plasma treatment technique at 500 °C. SEM, TEM, X-ray mapping, and Raman spectroscopy are used to characterize the structures and physical properties of these SiNTs. As discussed, our approach can convert bulk Si substrates into SiNTs by Cu catalysts introduced either by Cu films or Cu vapors generated by RF plasma sputtering. We think that this approach could be useful for transforming other bulk materials into nanotubes or nanowires.

## ACKNOWLEDGMENTS

This work is supported National Science Foundation CAREER awards (Award No. 0447555, Division of Materials Research). The authors thank Yong Ding and Zhong Lin Wang at Georgia Institute of Technology for the TEM analysis.

## REFERENCES

1. A.M. Morales, C.M. Lieber, *Science* **279**, 208 (1998).
2. D.P. Yu, C.S. Lee, I. Bello, G.W. Zhou, Z.G. Bai, *Solid State Commun.* **105**, 403 (1998).
3. F. Zhang, Y. H. Tang, H. Y. Peng, N. Wang, C. S. Lee, I. Bello, S. T. Lee, *Appl. Phys. Lett.* **75**, 1842 (1999).
4. S.B. Fagan, R.J. Baierle, R. Mota, A.J.R. da Silva, A. Fazzio, *Phys. Rev. B* **61**, 9994 (2000).
5. G. Seifert, T. Kohler, H.M. Urbassek, E. Hernandez, T. Frauenheim, *Phys. Rev. B* **63**, 193409 (2001).
6. R.Q. Zhang, S.T. Lee, C.K. Law, W.K. Li, B.K. Teo, *Chem. Phys. Lett.* **364**, 251 (2002).
7. V.V. Ivanovskaya, A.A. Sofronov, A.L. Ivanosvkii, *Phys. Lett. A* **297**, 436 (2002).
8. M. Zhang, Y.H. Kan, Q.J. Zang, Z.M. Su, R.S. Wang, *Chem. Phys. Lett.* **379**, 81 (2003).
9. V. Kumar, Y. Kawazoe, *Phys. Rev. Lett.* **90**, 55502 (2003).
10. J. Sha, J.J. Niu, X.Y. Ma, J. Xu, X.B. Zhang, Q. Yang, D. Yang, *Adv. Mater.* **14**, 1219 (2002).
11. S.Y. Jeong, J.Y. Kim, H.D. Yang, B.N. Yoon, S.H. Choi, H.K. Kang, C.W. Yang, Y.H. Lee, *Adv. Mater.* **15**, 1172 (2003).
12. C. Li, Z.T. Liu, C. Gu, X. Xu, Y. Yang, *Adv. Mater.* **18**, 228 (2006).
13. Y.H. Tang, L.Z. Pei, Y.W. Chen, C. Guo, *Phys. Rev. Lett.* **95**, 116102 (2005).
14. Y. K. Yap, M. Yoshimura, Y. Mori, T. Sasaki, *J. Chem. Phys.* **116**, 6286 (2002).
15. S. Bhattacharyya, S. Samui, *Appl. Phys. Lett.* **84**, 1564 (2004).
16. S. Piscanec, M. Cantoro, A.C. Ferrari, J.A. Zapien, Y. Lifshitz, S.T. Lee, S. Hofmann, J. Robertson, *Phys. Rev. B* **68**, 241312 (R) (2003).
17. J.D. Struthers, *J. Appl. Phys.* **27**, 1560 (1956).