

Selective Growth of Vertically Aligned Carbon Nanotubes on Nickel Oxide Nanostructures Created by Atomic Force Microscope Nano-Oxidation

Yu-Hsien Chang¹, Jung-Hsien Yen², Ming-Hung Huang^{1*}, Ju-Hung Hsu¹, Ing-Chi Leu²,
Heh-Nan Lin¹ and Ming-Hsiung Hon²

¹*Department of Materials Science and Engineering,
National Tsing Hua University*

²*Department of Materials Science and Engineering,
National Cheng Kung University*

We report the selective growth of carbon nanotubes (CNTs) on nickel oxide catalytic templates created by atomic force microscope nano-oxidation. By applying a negative bias to the tip, nickel oxide patterns are first produced on a nickel film by the process of nano-oxidation. In a subsequent wet etching, the unoxidized nickel is etched away whereas the nickel oxide is preserved. Nickel oxide nanostructures with sizes down to 40 nm are successfully fabricated. Vertically aligned multi-wall CNTs are then selectively grown on the oxide nanostructures by inductively coupled plasma chemical vapor deposition. The growth of single CNTs with variable diameters on oxide nanodots has also been realized.

Introduction

Since their discovery, carbon nanotubes (CNTs) have been the focus of extensive research activities due to their extraordinary properties.¹ In many applications, selective growth of CNTs is an essential issue. Photolithography,² e-beam lithography,^{3,4} micro-contact printing,⁵ shadow masking,⁶ etc. have been utilized to create catalytic templates that can be used for the desired selective growth. Among these techniques, electron beam lithography is used most often to generate catalytic patterns of sizes from sub-micron down to several tens of nanometer scales. In this paper, we report an alternative approach for this purpose. The catalytic templates are made of nickel oxide created by atomic force microscope (AFM) nano-oxidation.^{7,8} Successful growth of vertically aligned CNTs on the nickel oxide templates has been realized by inductively coupled plasma chemical vapor deposition (ICP-CVD).⁹

Experiment

A schematic diagram of the whole process is shown in Fig.1. A nickel film with a thickness of 10 nm was prepared by e-beam evaporation onto a silicon substrate with a 1- μm silicon dioxide buffer layer. The nano-oxidation was performed in a commercial AFM (Smena-A, NT-MDT, Russia) under ambient conditions. The sample was then dipped into a nitric acid solution to remove the nickel. On the other hand, the created nickel oxide patterns were not affected by the wet etching.

The nickel oxide patterns were put in the reaction chamber with a vacuum of 5×10^{-3} Torr. H_2 was then introduced into the chamber and substrate was heated to 660 °C. The reactor pressure was adjusted to 3 Torr and the sample was pre-treatment by plasma about 10 min for the reduction of nickel oxide. Methane (CH_4) flow was induced to growth CNT for 40 min. After the CNT growth, the reactor was allowed to cool (<100 °C) in H_2 atmosphere before

exposure to air.

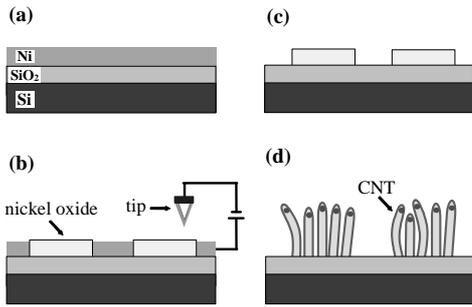


Fig. 1. Schematic diagram of the experimental procedure.

Results and Discussion

With a tip bias of -8 V , a nickel oxide square with a size of $4 \times 4\ \mu\text{m}^2$ was generated and the image after the wet etching is shown in Fig. 2. To verify if the nickel was completely removed by the etching process, auger electron spectroscopy measurements were performed on the pattern and the surrounding region. The results indicated a successful removal of the nickel without affecting the oxide pattern.

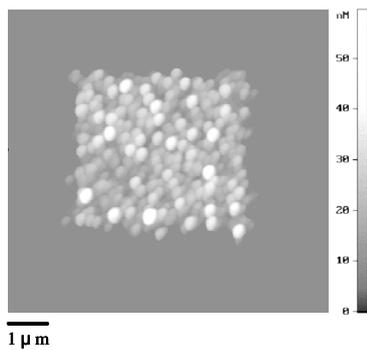


Fig. 2. A $4 \times 4\ \mu\text{m}^2$ nickel oxide square.

A 4×4 nickel oxide nanodot array generated with the application of -9 V , 0.7 ms pulses is shown in Fig. 3. The average height and width are around 8 and 50 nm , respectively, as determined from cross section analysis.

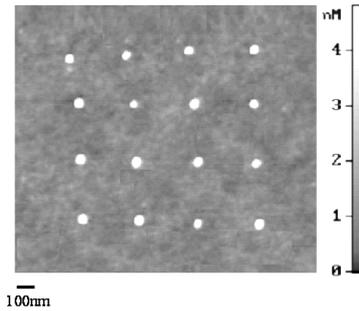


Fig. 3. A 4×4 nickel oxide nanodot array.

Vertically aligned CNTs were then successfully grown on the nickel oxide, and the resultant scanning electron microscope (SEM) image is shown in Fig. 4. As can be seen clearly, the CNTs have the nickel catalysts at their tops. The tip growth mode is therefore preferred over the base growth mode.

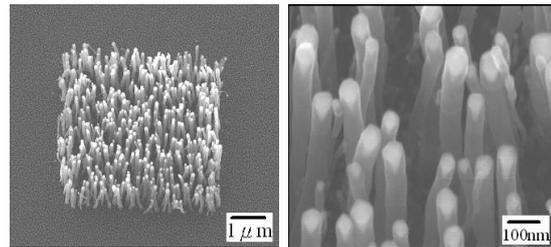


Fig. 4. SEM image of vertically aligned CNTs grown on a nickel oxide square.

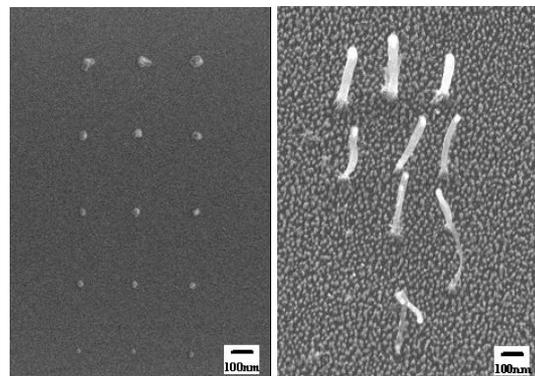


Fig. 5. SEM images of nickel oxide nanodots and the vertically aligned single CNTs grown on them.

Single CNTs were then successfully grown on a nanodot array and the result is shown in Fig. 5. The nanodots have sizes of 81, 77, 65, 51, and 37 nm from top to bottom. The diameters of the CNTs range from 77 to 35 nm. For the nanodots with sizes below 60 nm, the growth was not always successful as can be seen. However, it is obvious that the diameter can be effectively controlled by the size of the nanodot. The present method can be potentially valuable for the construction of CNT based nanodevices

References

1. H. Dai, *Surf. Sci.* **500**, 218 (2002).
2. Y. Yang, S. Huang, H. He, A. W. H. Mau, and L. Dai, *J. Am. Chem. Soc.* **121**, 10832 (1999).
3. Z. F. Ren, Z. P. Huang, D. Z. Wang, J. G. Wen, J. W. Xu, J. H. Wang, L. E. Calvet, J. Chen, J. F. Klemic, and M. A. Reed, *Appl. Phys. Lett.* **75**, 1086 (1999).
4. K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga, W. I. Milne, D. G. Hasko, G. Pirio, P. Legagneux, F. Wyczisk, and D. Pribat, *Appl. Phys. Lett.* **79**, 1534 (2001).
5. H. Kind, J.-M. Bonard, C. Emmenegger, L.-O. Nilsson, K. Hernadi, E. Maillard-Schaller, L. Schlapbach, L. Forró, and K. Kern, *Adv. Mater.* **11**, 1285 (1999).
6. S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell, and H. Dai, *Science* **283**, 512 (1999).
7. Ph. Avouris, T. Hertel, and R. Martel, *Appl. Phys. Lett.* **71**, 285 (1997).
8. J.-H. Hsu, H.-W. Lai, H.-N. Lin, C.-C. Chuang, and J.-H. Huang, *J. Vac. Sci. Technol. B* **21**, 2599 (2003).
9. J. H. Yen, I. C. Leu, C. C. Lin, and M. H. Hon, *Appl. Phys. A.*, in press.

* e-mail: g923598@oz.nthu.edu.tw.