垂直配向単層カーボンナノチューブ膜の合成と応用

Production and applications of vertically aligned single-walled carbon nanotubes

伝正　*Erik Einarsson　（東大院学）　伝正　村上　陽一　（東大院）
門脇　政幸　（東大院学）　Hai M. Duong　（東大院）
伝正　井上　満　（東大院）　伝正　丸山　茂夫　（東大院）

Erik Einarsson, Yoichi Murakami, Masayuki Kadowaki, Hai M. Duong,
Mitsuru Inoue, Shigeo Maruyama
Dept. of Mech. Eng., The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Synthesis of vertically aligned single-walled carbon nanotube (VA-SWNT) thin films by alcohol catalytic chemical vapor deposition has been clarified using an *in situ* optical absorbance measurement technique, which makes it possible to control the final film thickness. These VA-SWNT films can be detached from the substrates on which they are grown and reattached onto arbitrary solid surfaces by a simple water-assisted process. This will allow many new areas of SWNT applications to be investigated.

Key Words : single-walled carbon nanotubes, vertically aligned, CVD

1. INTRODUCTION

One of the difficulties in developing practical nanotube-based devices is the large-scale production of aligned carbon nanotubes (CNTs). Due to their novel electronic and thermal properties[(1)], single-walled nanotubes (SWNTs) in particular show great potential for use in a variety of applications[(2)], as well as exploring fundamental properties of SWNTs, such as polarization-dependent optical absorption properties[(3)]. After our group first reported[(4)] growth of vertically aligned single-walled carbon nanotubes (VA-SWNTs), several other groups have also shown the ability to synthesize VA-SWNT films[(5-8)]. However, all of these synthesis methods are based on chemical vapor deposition (CVD), where SWNT growth requires temperatures above 600 °C. This high temperature environment places a major restriction on the possible substrates on which VA-SWNTs can be grown, thus restricting many interesting applications (i.e. VA-SWNT films on polymer substrates). In this study, we report recent advances in VA-SWNT film growth that not only allow accurate control of the film thickness, but the ability to transfer the film onto another surface after CVD growth without disturbing the vertical alignment.

2. EXPERIMENT

Films of VA-SWNTs were grown as described in previous studies[(9,10)] by the alcohol catalytic CVD (ACCVD) process[(11,12)]. Nanotube growth was catalyzed by Mo/Co bimetal nanoparticles, which were affixed to quartz substrates by a liquid-based dip-coat method[(13,14)]. Prior to growth the substrate was positioned such that a laser (λ = 488 nm) was incident normal to the substrate through a small opening in the bottom of the CVD chamber. The transmitted laser passed through another small opening in the top of the CVD chamber and incident onto a detector, where the intensity was measured. This allowed for *in situ* determination of the VA-SWNT film thickness based on the optical absorbance[(15)]. Details can be found in References 10 and 14. After growth, the samples were characterized by Raman spectroscopy as well as by field-emission scanning electron microscopy (FE-SEM).

3. RESULTS AND DISCUSSION

Characterization by resonance Raman spectroscopy (Fig. 1a) of as-grown VA-SWNT films is used to quickly confirm the presence of graphitic carbon, based on the presence of the G-band peak at 1593 cm^{-1} and the D-band peak around 1345 cm^{-1}, while the radial breathing mode peaks between 100 and 400 cm^{-1} confirm the presence of SWNTs[(1)]. A high ratio between G and D band peak intensities (approx. 25:1) indicates high-purity SWNTs. Additionally, the sharp peak at 180 cm^{-1} and relatively weaker peaks at 164 and 203 cm^{-1} are indicative of vertical alignment[(16)]. This vertical alignment is confirmed by FE-SEM observations, as shown in Fig. 1b. By monitoring the optical absorbance during CVD growth, a VA-SWNT film of desired thickness can be synthesized by cutting off the carbon source (in this case ethanol vapor) after reaching the desired film thickness. However, this technique is limited to VA-SWNT films less than ~30 μm thick, as almost no light is transmitted through films of this thickness.

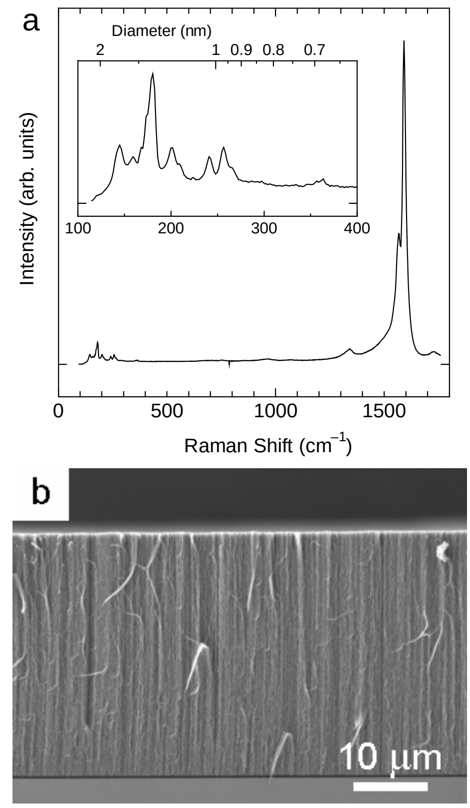

Fig. 1: (a) a resonance Raman spectrum indicating the presence of VA-SWNTs (see text) and (b) a corresponding FE-SEM image confirming vertical alignment. The film shown here is ~30 μm thick, and was synthesized by the ACCVD method.

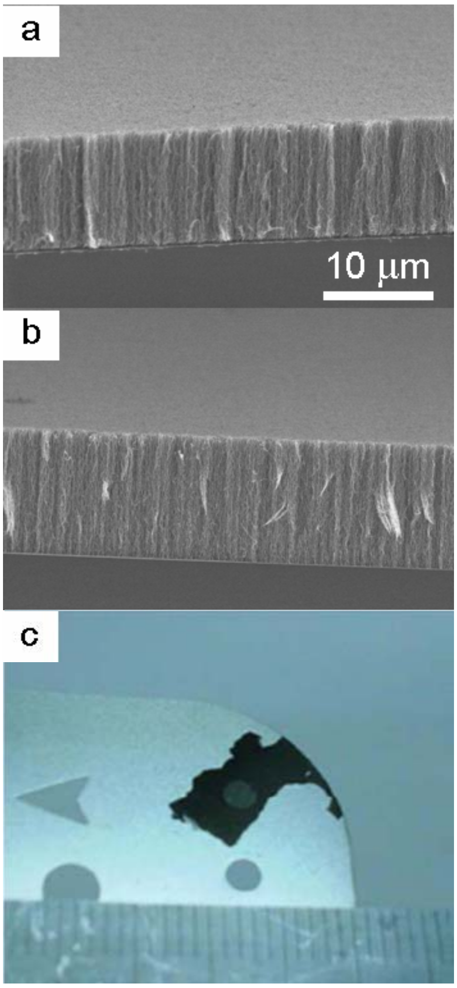

Fig. 2: (a) FE-SEM image of an as-grown VA-SWNT film on a quartz substrate, and (b) the same film after being transferred onto a silicon substrate by the water-assisted technique (see text). The scale bar applies to both FE-SEM images. (c) A VA-SWNT film placed over a ϕ = 2.5 mm hole in a drawing stencil, showing unsupported films are mechanically sound.

A VA-SWNT film produced on a quartz substrate (as described above) is shown in Fig. 2a. This film was then removed from the substrate by the method described in Reference 17. In brief, the sample (VA-SWNT film + quartz substrate) was slowly dipped into a bath of distilled water heated to 60 °C, where the sample was oriented vertically with respect to the surface of the water. When inserted into the hot water, VA-SWNT film peels away from the quartz substrate, and remains floating on the surface of the water. The VA-SWNT film can then be attached to a different surface by inserting the new substrate (such as silicon, metal, etc.) into the water bath and gently lifting it out in such a way that it contacts the floating VA-SWNT film as the substrate leaves the water. The new sample (e.g. silicon substrate + VA-SWNT film) is subsequently dried under a flowing Ar/H_2 mixture (3% H_2) at 200 °C for approximately 30 minutes. Removal and reattachment of VA-SWNT films by this technique conserves the vertical alignment of the film, as confirmed by FE-SEM observation shown in Fig. 2b. Raman spectra (not shown) are unchanged by the reattachment process(17), indicating no change in the film morphology.

After dozens of trials, it was found that the critical condition for water-assisted removal is that the temperature *difference* between the sample (VA-SWNT film and substrate) and the water be ≥ 40 °C(17). Based on this result, it is thought the VA-SWNT film removal from the substrate is related to the thermocapillary effect(18), where a thin liquid film climbs up the quartz substrate (driven by the temperature gradient along the substrate) as the sample is inserted into the heated water. The hydrophobic VA-SWNT film is repelled by this water film, thus peels away from the substrate(17) and remains floating on the surface.

4. SUMMARY

This report addresses recent advances in the synthesis and applications of vertically aligned single-walled carbon nanotubes (VA-SWNTs). Not only can an *in situ* optical absorbance technique be employed to grow VA-SWNT thin films to a desired thickness, the films can then be transferred onto arbitrary surfaces after CVD growth by a simple water-assisted process. The reattached films retain their vertically aligned morphology, which makes possible the investigation of many new areas of nanotube-based applications, such as VA-SWNT-polymer composites capable of withstanding high temperatures, flexible nanotube-based photovoltaic cells, or integration into other optical applications.

5. REFERENCES

1. R. Saito, G. Dresselhaus, and M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, London, 1998.
2. M.S. Dresselhaus, G. Dresselhaus, P. Avouris (Eds.), *Carbon Nanotubes*, Springer, Berlin, 2001.
3. Y. Murakami, E. Einarsson, T. Edamura, S. Maruyama, Phys. Rev. Lett. **94** (2005) 087402.
4. Y. Murakami *et al.,* Chem. Phys. Lett. **385** (2004) 298.
5. K. Hata *et al.,* Science **306** (2004) 1362.
6. G. Zhong *et al.,* Chem. Vap. Deposition **11** (2005) 127.
7. S. Noda *et al.,* Carbon, in press
8. G. Zhang *et al.,* cond-mat/0511035.
9. Y. Murakami, E. Einarsson, T. Edamura, S. Maruyama, Carbon **43** (2005) 2664.
10. S. Maruyama, E. Einarsson, Y. Murakami, T. Edamura, Chem. Phys. Lett. **403** (2005) 320.
11. S. Maruyama *et al.*, Chem. Phys. Lett. **360** (2002) 229.
12. Y. Murakami, Y. Miyauchi, S. Chiashi, S. Maruyama, Chem. Phys. Lett. **374** (2003) 53.
13. Y. Murakami, Y. Miyauchi, S. Chiashi, S. Maruyama, Chem. Phys. Lett. **377** (2003) 49.
14. Y. Murakami, S. Chiashi, Y. Miyauchi, S. Maruyama, Jpn. J. Appl. Phys. **43** (2004) 1221.
15. E. Einarsson, Y. Murakami, M. Kadowaki, S. Maruyama, to be submitted.
16. Y. Murakami, S. Chiashi, E. Einarsson, S. Maruyama, Phys. Rev. B **71** (2005) 085403.
17. Y. Murakami and S. Maruyama, Chem. Phys. Lett., in press.
18. V. Ludviksson, E.N. Lightfoot, AIChE J. **17** (1971) 1166.