Production and Applications of Vertically Aligned Single-Walled Carbon Nanotubes*

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Abstract

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 hot 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[15,16]. Details can be found in Refs. 10 and 14. After growth, the samples were characterized by Raman spectroscopy and scanning electron microscopy (SEM).

3. Results and Discussion

Characterization by resonance Raman spectroscopy (Fig. 1a) of VA-SWNT films confirms the presence of graphitic carbon, based on the presence of the G-band peak at 1593 cm^{-1}, while the radial breathing mode peaks between 100 and 400 cm^{-1} confirm the presence of SWNTs[1]. A weak D-band peak (~1345 cm^{-1}) indicates high-purity SWNTs. Additionally, a strong peak at 180 cm^{-1} and relatively weaker peaks at 164 and 203 cm^{-1} indicates vertical alignment[16], which was confirmed by SEM observation (Fig. 1b). The correlation between film thickness and optical absorbance (Fig. 1c) allows us to determine the thickness of the VA-SWNT film during growth by monitoring the absorbance *in situ.* These data are shown as circles in Fig. 1c, and are fit well by a growth model (red line) [15]. Using this technique, a

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VA-SWNT film of desired thickness can be synthesized by halting the growth 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 thicker films.

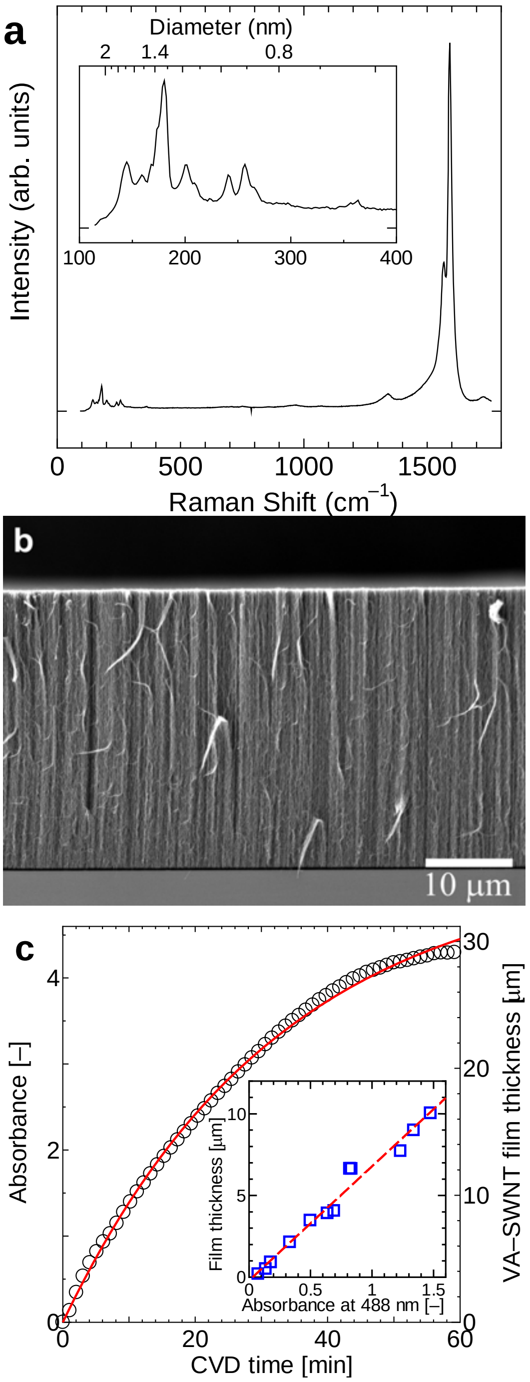

Fig. 1 (a) a Raman spectrum indicating the presence of VA-SWNTs (see text) and (b) a corresponding SEM image confirming vertical alignment. Film growth was recorded by an *in situ* optical absorbance measurement (c), which shows the growth up to the final thickness of ~30 μm. The linear relationship between absorbance and film thickness is shown in the insert.

An image of a VA-SWNT film produced on a quartz substrate is shown in Fig. 2a. This film was removed from the substrate by slowly submerging the sample (VA-SWNT film + quartz substrate) into a water bath with the sample oriented perpendicular to the water[17]. After removal from the substrate, the VA-SWNT film remains floating on the surface of the water. It can then be attached to a different surface by inserting the new substrate (here, silicon) into the hot water bath and gently lifting it out such that it contacts the floating film as the substrate leaves the water. After transfer, the VA-SWNT film was dried at 200 °C for 30 minutes under a flowing Ar/H_2 mixture (3% H_2). Removal and reattachment of VA-SWNT films by this technique conserves the vertical alignment of the film[17], as

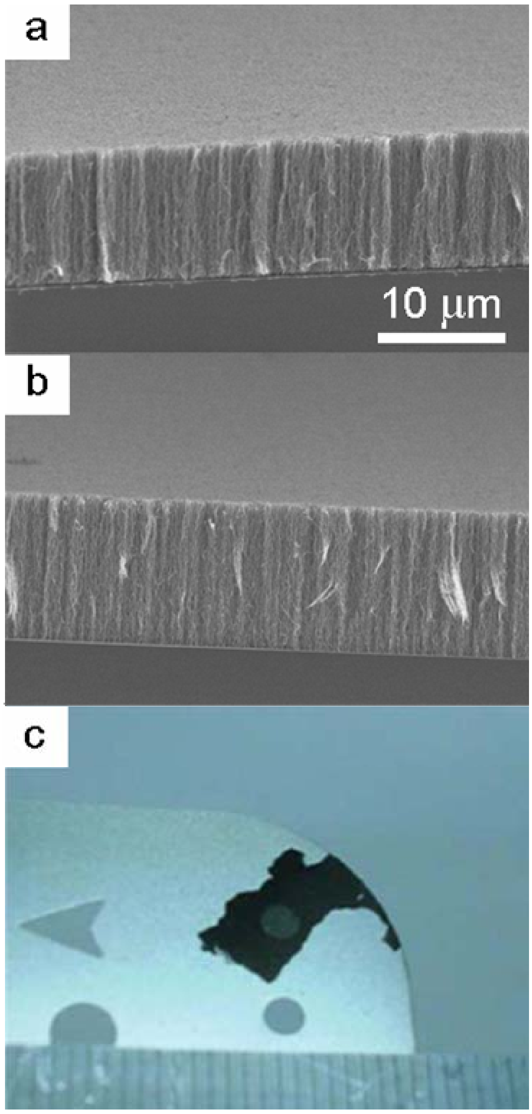

Fig. 2 (a) An as-grown VA-SWNT film on a quartz substrate, and (b) the same film after transfer onto a silicon substrate. The scale bar applies to both images. (c) A VA-SWNT film placed over a ϕ = 2.5 mm hole, showing unsupported films are still mechanically sound.

confirmed by SEM observation shown in Fig. 2b. Figure 2c shows the free-standing film is robust enough to remain intact even while spanning a 2.5 mm hole, indicating free-standing films may be used in applications.

After dozens of trials, it was found that the critical condition for successful removal is that the temperature of the water be approximately 40 °C higher than the temperature of the sample, e.g. if the sample is at room temperature, removal occurs if the water is heated to ~60 °C. The film is also removed if the water is at room temperature and the sample is chilled in the freezer (to about -20 °C). The importance of the temperature difference indicates VA-SWNT film removal is caused by the thermocapillary effect[17,18], where a thin liquid film climbs up the substrate (driven by a temperature gradient along the substrate) as the sample is inserted into the heated water. The hydrophilic quartz is wetted by the water, whereas the hydrophobic VA-SWNT film is repelled, thus is peeled away from the substrate. For slightly lower temperature differences (e.g. 30-35 °C), the VA-SWNT film is only partially removed[17].

4. Summary

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

5. References

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