

# Thermal CVD growth of vertically aligned single-walled carbon nanotube films on substrates and their optical/microscopical characterizations

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**Keywords :** Carbon nanotubes, SWNTs, vertical alignment, CVD, alcohol CCVD

## ABSTRACT

We report optical and microscopical characteristics of our recently developed vertically aligned single-walled carbon nanotube (SWNT) film. This film is grown from Co catalyst supported on quartz substrate with the use of alcohol catalytic CVD (ACCVD) method at 800 °C, having the thickness of approximately 5 μm. Its optical anisotropy due to the alignment is shown by polarized optical absorption spectroscopy. The growth process along with CVD time is investigated both by SEM and optical absorption, from which the alignment process unique to current SWNTs, which is different from the known case of multi-walled carbon nanotubes (MWNTs), is described.

## 1. INTRODUCTION

In order to best utilize unique properties of carbon nanotubes, their morphologically controlled growth has been sought. So far, growth of SWNTs parallel to substrate surfaces and vertical growth of MWNTs have been reported. The difficulties in attempting to align SWNTs vertically on substrates had lied in their flexibility and necessity of preparing small catalyst particles having diameter similar to that of SWNTs (1 ~ 2 nm). This year, we reported that a vertically aligned film of SWNTs with a thickness of a few μm could be synthesized on quartz substrates (Murakami, 2004a). Here we perform the optical and microscopical characterizations of thereby obtained SWNT film and report its unique growth process.

## 2. EXPERIMENT

### 2.1 Procedure for catalyst support and CVD

We use the alcohol catalytic CVD (ACCVD) method (Maruyama, 2002) (Murakami, 2003a) for SWNT growth. Detailed procedure for catalyst supporting process is described in Refs. (Murakami, 2003b) (Murakami, 2004b). In short, Co catalyst are supported on substrates by dip-coating of bimetallic Co-Mo acetates dissolved in Ethanol so that their metal concentrations were 0.01 wt%, followed by calcination and reduction. With this procedure, highly mono-dispersed Co catalytic particles (density  $\approx 1 \times 10^{17} \text{ m}^{-2}$ ) with diameters of 1.0 ~ 2.0 nm was formed densely on the surface of quartz substrate. Detailed catalyst formation process and dispersion mechanism of Co have been elucidated our previous reports by XPS and TEM analyses (Hu, 2004). Descriptions for our CVD apparatus shall be referred to Murakami, 2004b.

### 2.2 Characterizations with SEM and Raman scattering

Figure 1 shows the SEM image of vertically aligned SWNT films after direct growth on a quartz substrate, taken at the fractured

edge of the substrate from tilted angle. Each string seen in Fig. 1 corresponds to a bundle of SWNTs and average diameter of the bundle is 15 nm. Estimated density of SWNTs determined by SEM and TEM are almost equal to that of Co catalyst (i.e.  $\approx 1 \times 10^{17} \text{ m}^{-2}$ ). High quality of obtained SWNTs has been confirmed by Raman spectroscopy shown in Fig. 2 and TEM (Murakami, 2004c).

### 2.3 Absorption anisotropy toward polarized light

Figure 3 shows optical absorption spectrum for s- and

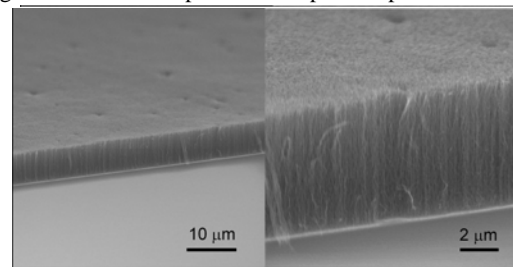


Fig. 1. FE-SEM image of vertically aligned SWNT film directly grown on a quartz substrate.

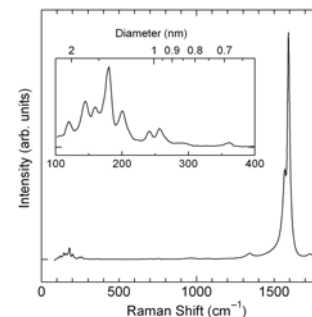


Fig. 2. Raman scattering spectrum taken by 488 nm laser light incident from top of the film. Inset magnifies lower frequency region to show the radial breathing mode peaks.

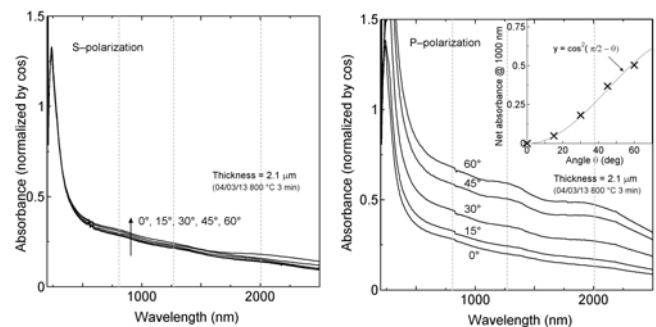


Fig. 3. Optical absorption spectrum of the film measured with s- (left) and p- (right) polarization at different tilt angle. Inset shows the net absorption of p-polarized light at 1000 nm.

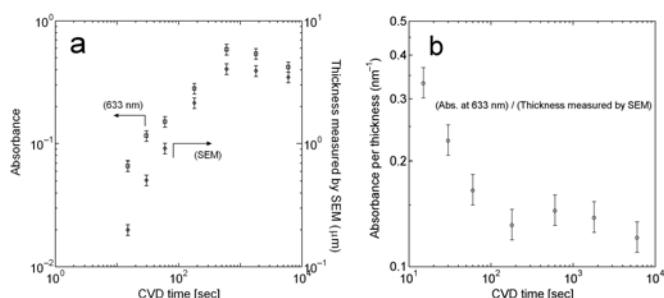


Fig. 4. (a) Change of optical absorption and thickness of the film determined by SEM toward CVD time. (b) Ratio of absorbance at 633 nm and film thickness vs. CVD time.

p-polarized light absorption at several incident angle of the light (See definition of polarization for Murakami, 2004a). While the absorption is independent of the angle for s-case, the absorption is drastically increased with the angle when p-case according to  $\cos^2\theta$ , as shown in the inset. This indicates the absorption has an anisotropy characteristic to 1-D aligned tube. Three vertical dotted lines in the right figure indicate the corresponding wavelengths of  $E_{11}^S$ ,  $E_{22}^S$ , and  $E_{11}^M$  inter sub-band transitions of current SWNTs ( $d_{av} = 2.0$  nm,  $\sigma = 0.4$  nm) (Murakami, 2004c).

### 3. DISCUSSION AND SUMMARY

Figure 4a shows the change of absorbance at 633 nm and thickness measured by SEM of the film according to CVD time. At current CVD condition, growth is ceased within several tens of minutes and the thickness start to decrease due to burning by presumably invading oxygen molecules into CVD chamber. The cease of the growth is attributed to the catalyst poisoning by such oxidizing molecules; however, the detailed mechanism is currently under investigation. For detailed growth process, refer to Maruyama, 2004. When the ratio of optical absorption to film thickness is taken (Fig. 4b), it is noticed that optical absorption per unit film thickness is higher at initial growth stage. It is deduced that, by considering the result of Fig. 3, the alignment of SWNTs here are formed gradually from the initial random growth followed by mutual sustaining among high density bundles only allowing them to grow away from substrate with lifting up this initial random layer. We conclude that the alignment of highly flexible SWNTs observed here are due to the extremely high density growth SWNTs resulting from efficient use of the densely monodispersed Co catalytic particles supported by the dip-coating method.

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