# Internal Structure of Vertically Aligned Single-Walled Carbon Nanotube Arrays

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# 1. Introduction

Single-walled carbon nanotubes (SWNTs) are known for their unique physical properties, which arise from their one-dimensional structure [1-3]. Some of these properties, such as near-ballistic transport [4], anisotropic optical absorption [5-8], and high thermal conductivity [9-11] make SWNTs particularly well-suited for various advanced applications. In order to exploit these properties, however, it is necessary to have control over the location, size, and morphology of the SWNTs. Many advancements in these areas have been made in the past few years, particularly regarding the synthesis of vertically aligned (VA-)SWNTs [12-19].

Here we report recent observations of the internal structure of VA-SWNTs synthesized from alcohol [20]. It was found that the SWNTs within the array form into thin, aligned bundles, containing roughly ten SWNTs. Small bundle size is significant in that it results in reduced tube-tube interactions, thus retaining their 1D properties.

# 2. Synthesis of VA-SWNTs

The VA-SWNTs investigated in this study were synthesized by the alcohol catalytic chemical vapor deposition (ACCVD) method [20], where alcohol vapor reacts with metal catalyst nanoparticles inside a conventional CVD chamber to form SWNTs. The nanoparticles are supported by quartz or silicon substrates, and are loaded onto the substrates using a liquid-based dip-coat method [12]. An overview of the growth procedure will be presented here, but details regarding the growth conditions and procedure can be found elsewhere [12, 21].

The dip-coated substrate is heated to the growth temperature (typically 700 – 800 °C) under 40 kPa of flowing Ar/H<sub>2</sub> (3% H<sub>2</sub>, Ar balance, flow rate of 300 sccm). At the growth temperature, the Ar/H<sub>2</sub> flow is stopped, and alcohol (typically ethanol) is introduced into the chamber at a flow rate of 300 to 500 sccm and a pressure of approximately 1.4 kPa (10 Torr). This produces VA-SWNTs such as those shown in Fig. 1a. During CVD growth, the film thickness can be measured by an optical absorbance technique, [21, 22]. This makes it possible to control over the final film thickness by cutting off the alcohol flow when the VA-SWNT film has reached the desired thickness.

# 3. Results and Discussion

**Observation of Internal Structure** 

Electron microscopy techniques are extremely valuable in SWNT characterization, providing information on the overall morphology by scanning electron microscopy (SEM), and information on the individual SWNT scale, such as diameters estimation, by transmission electron microscopy (TEM). In the case of SWNT arrays, however, preparation for TEM observation destroys the original morphology, making it impossible to image the SWNTs in their aligned state. Recently, however, our group has succeeded in imaging SWNTs in their aligned state [23] by transferring the as-grown films onto a TEM grid via a hot-water assisted method [24] that preserves the SWNT alignment. In this study we use the same approach, but scan the focal plane, obtaining cross-sectional images at different depths into the VA-SWNT film.

Figure 1a shows a VA-SWNT film approximately 4 µm thick. Such a film was transferred onto a TEM grid, and imaged as described above. Figures 1b - 1d show three images of the VA-SWNT film obtained at 0, 600, and 900 nm into the SWNT film. The distance was determined by imaging the top of the film, (0 nm), and then adjusting the focal plane without moving the sample stage. The change over this distance is not significant, due to the alignment of the SWNTs. Some regions, however, are very obscure because of the thickness of the film ( $\sim 4 \mu m$ ). One thing that is clear, however, is that the SWNT bundles are very small, in agreement with previous TEM observations [23]. This small bundle size is believed to preserve the 1D optical properties of the SWNTs [23, 25], which would otherwise be altered by tube-tube interactions and more closely resemble bulk graphite.

### 4. Conclusions

Here we report observations of the internal structure of VA-SWNTs synthesized from alcohol. Cross-sectional TEM images were obtained at different depths into the aligned SWNT array. Observation of small SWNT bundles agrees with previous findings showing very little bundling of these aligned SWNTs. Since the degree of bundling affects the electrical and optical properties, this is believed to be significant regarding use in related devices.



Fig. 1 (a) SEM image of 4  $\mu$ m VA-SWNT film. (b), (c), (d) show cross-sectional TEM images at 0, 600, and 900 nm from the top.

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