

A Growth Mechanism for Vertically Aligned Single-Walled Carbon Nanotubes

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Key Words: Carbon Nanotube, Alcohol CVD, Vertically Aligned, SEM, Raman Scattering

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) show great potential for use a variety of applications^(2,3). The alignment of SWNTs has been reported, but only parallel to the substrate in the presence of strong electric or magnetic fields⁽⁴⁻⁶⁾. However, the use of alcohol in a simple chemical vapor deposition (CVD) method developed by our group⁽⁷⁾ has shown to produce dense mats of vertically aligned SWNTs⁽⁸⁾. In this study we investigate the growth mechanism leading to this vertical alignment.

Vertically aligned SWNTs were grown at 800 °C and 10 torr using an alcohol CVD process⁽⁸⁾. The CVD reaction was catalyzed by Mo/Co bimetal nanoparticles, which were affixed to quartz substrates by a dip-coat method (0.01 wt% Mo/Co acetate). Subsequent annealing in air at 400 °C oxidized the nanoparticles, preventing catalyst agglomeration in the high-temperature CVD environment. Flowing Ar/H₂ (3% H₂) during preheating of the reaction chamber reduced the catalyst in order to retrieve catalyst activity before the growth stage. When the CVD chamber reached 800 °C, the Ar/H₂ flow was stopped, followed by the introduction of ethanol vapor. The reaction time was varied in order to observe samples at different stages of growth. The samples were characterized with a Hitachi S-4700 field-emission scanning electron microscope (FE-SEM). Figure 1 shows a thick mat of aligned SWNTs on a quartz substrate surface. Further characterization was done by micro-Raman spectroscopy (Fig 2). The G-band peak around 1590 cm⁻¹ and the D-band peak near 1350 cm⁻¹ confirm there

is carbon, while the radial breathing mode (RBM) near 200 cm⁻¹ is unique to SWNTs⁽¹⁾. A high ratio between the G and D band peak intensities (here approx. 30:1) indicates high-purity of SWNTs⁽⁹⁾. Additionally, the sharp peak at 180 cm⁻¹, indicative of vertical alignment, is clearly present, although the origin of this peak is not yet well understood. The location of the RBM peaks is related to the tube diameters⁽¹⁰⁾, which fall primarily between 1 and 2 nm. The diameter distribution is not affected by growth time.

Aligned growth begins with bundling of individual SWNTs, which initially grow randomly. Figure 3a shows this early stage of alignment, occurring after only 30 seconds of growth. At this stage the SWNT mat is uneven and not well aligned, with long bundles extending far above the top of the mat. After 3 minutes of growth, (Fig. 3b), the SWNT mat has become thicker and more uniform, and is now aligned perpendicular to the substrate surface. The mat thickness at this stage is well over 1 μm. Introducing ethanol for 10 minutes (Fig. 3c) results in a mat of aligned SWNTs that is quite thick (more than 2 μm) and well aligned. The thickness continues to increase as the growth time is extended, being more than 3 μm thick after 30 minutes. However, after 1 hour of growth (Fig. 3d), the mat thickness had decreased to approximately 500 nm. The thickness at this stage is uniform across the substrate, but the bundles are not well aligned. The above results can be explained by the following growth mechanism. It is believed that individual SWNTs are produced by a base-growth mechanism, where the reaction between the carbon source flowing through the chamber and the catalyst particles occurs at the substrate surface. The growth direction is

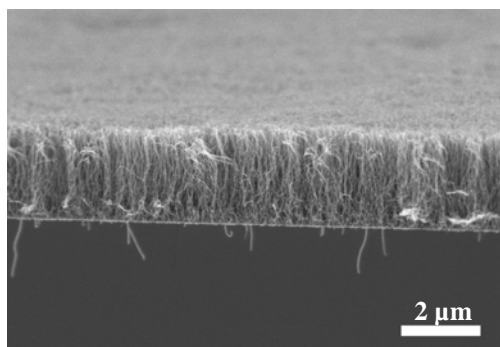


Fig.1: A mat of aligned SWNTs after 30 min of growth.

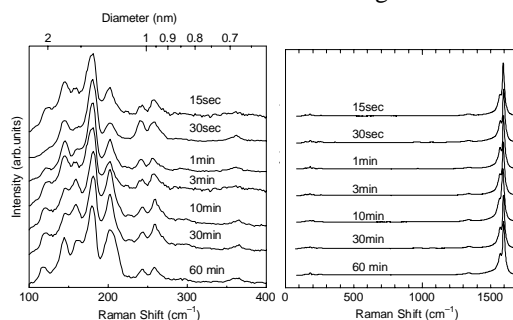


Fig.2: Raman spectra of SWNT samples (rt), and detailed view of corresponding RBM signals (left).

* Received: July 8, 2004, Editor: Shigenao MARUYAMA

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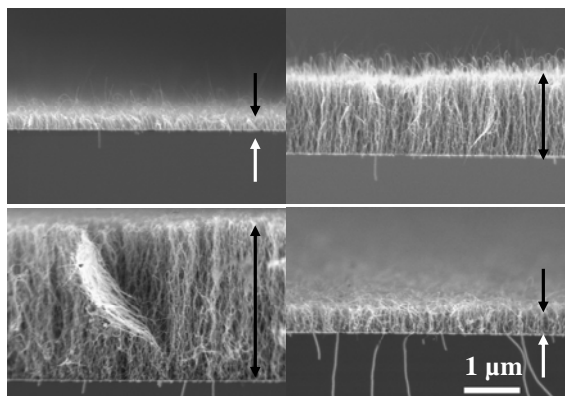


Fig.3: Growth stages of aligned SWNTs after (a) 30 seconds (b) 3 min (c) 10 min, and (d) 60 min.

random, with SWNTs forming bundles with neighboring tubes. If the density of SWNTs is high, the bundles essentially crowd each other, blocking growth in all directions parallel to the substrate. The only direction in which SWNTs are free to grow is perpendicular to the substrate, resulting in vertical alignment. The thickness of the self-supporting mat is demonstrated in Fig. 4, where the mat has been peeled away from the substrate surface, yet maintains its overall structure. However, since the catalyst is on the surface, the increasing thickness of this dense mat begins to act as a barrier, cutting off the supply of ethanol to the catalyst below. This results in a growth rate that decreases as the thickness of the mat increases. If the mat is not uniform, growth will be faster in the thinner regions, leading to nearly uniform growth overall. For longer reaction times (more than 30 minutes) however, our results show that the final mat thickness decreases (Fig 5). The cause of this is not yet clear, but we attribute this to the presence of excess oxygen in the CVD chamber, due to an insufficient vacuum. The presence of oxygen not only inhibits growth by reducing the catalyst activity, but can also oxidize the topmost portion of the mat. If both processes are competing, then growth will proceed as long as the catalyst is active and the growth rate is faster than the decay. When the catalyst activity decreases, and the carbon supply has been reduced by the thickness of the mat, oxidation will reduce the length of the tubes. Based on this growth process, the length of the aligned SWNTs

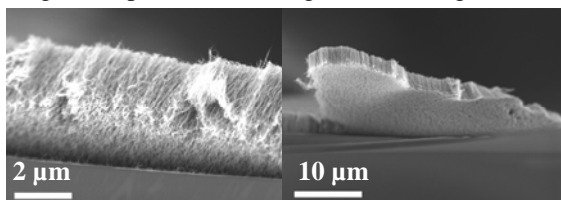


Fig.4: The aligned mat peeled away from the substrate in (a), and overhanging the edge in (b).

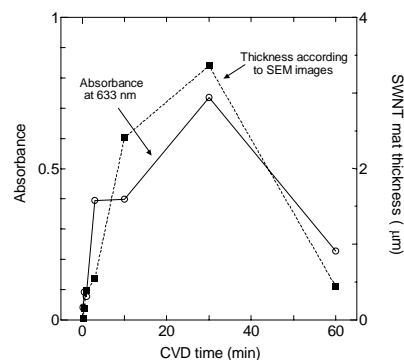


Fig.5: A plot of the relationship between growth time, mat thickness, and optical absorbance.

can be controlled by controlling the CVD reaction time. The relationship between the mat thickness and optical absorption is also shown in Fig. 5. This correlation could be used to estimate the mat thickness over larger regions, and may have optical applications.

This report shows vertical alignment of SWNTs is caused when high tube density impedes growth in all directions parallel to the substrate surface. The growth time can be adjusted to control the thickness of the aligned SWNT mat, but the growth rate decreases with increasing mat thickness. Excessive growth time leads to either no further growth or slow destruction of the upper portion of the SWNT mat, which is slowly burned away by interaction with oxygen present in the CVD chamber. A better understanding not only of the mechanism behind the growth of individual nanotubes, but also the production of large-scale arrangements such as vertically aligned films, is important for developing production methods for CNT-based applications.

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