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GROWTH PROCESS OF VERTICALLY ALIGNED SINGLE-WALLED CARBON NANOTUBES

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1. INTRODUCTION

The recent boom in nanoscience and nanotechnology research is largely due to the novel electronic, thermal, and mechanical properties [1,2] of single-walled carbon nanotubes (SWNTs). The ability to exploit these unique properties could lead to various new applications [1-3], however producing sufficient amounts of SWNTs with controlled morphologies has proved to be a significant hurdle in making such applications a reality. The most promising production method to date is catalytic chemical vapor deposition (CCVD). An alcohol-based CCVD process [4] has been used to produce vertically aligned films of SWNTs up to 5 μm thick [5] on quartz substrates. The present study investigates the growth process of these SWNT films.

2. EXPERIMENT

Cobalt catalyst was supported on a quartz substrate by dipping the substrate into a Co-Mo acetate solution (both 0.01 wt% in ethanol), and then slowly withdrawing the substrate (at 6 cm/min). The catalyst was then oxidized by heating the dip-coated substrate in air at 400 ºC, and then reduced in a flowing Ar/H_2 mixture (3% H_2) during heating of the CCVD chamber. Catalyst prepared by this method resists agglomeration at the growth temperature (800 ºC), resulting in densely deposited (~10^{17} m^{-2}), mono-dispersed catalyst particles with diameters of 1-2 nm [6]. When the CCVD chamber reached the growth temperature of 800 ºC, the Ar/H_2 mixture was stopped, and ethanol vapor was introduced at a pressure of 10 Torr to initiate SWNT growth. Although it is common practice to add hydrogen as a catalyst activator during the growth stage, it was found that SWNTs grown without the addition of hydrogen were better aligned and in higher yield than those grown in the presence of added hydrogen.

3. RESULTS AND DISCUSSION

A series of time-progressive scanning electron microscope (SEM) images of the produced SWNT films are shown in Fig. 1. Vertical growth of bundles occurs early on, causing alignment of the SWNT film. After 10 minutes (Fig. 1 (d)) the film thickness exceeds 4 μm, but the thickness decreases after longer reaction times. The burning temperature of SWNTs in air is ~450 °C [7], but since the SWNTs are grown in vacuum at a temperature of 800 °C, a likely explanation for the apparent decrease is oxidation of the film by trace present in the CCVD chamber during growth. This can be thought of as a negative growth rate,

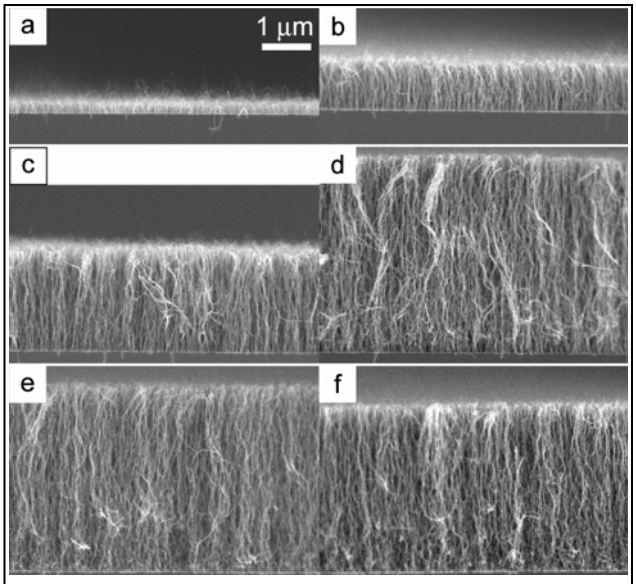

Fig. 1. Growth of aligned SWNT films after (a) 15 seconds, (b) 1 min, (c) 3 min, (d) 10 min, (e) 30 min, and (f) 100 min. The scale bar applies to all images.

but is insignificant if the catalyst activity is high. However, if the growth chamber seal is poor, oxygen can enter the chamber and re-oxidize the catalyst particles. This is known as catalyst poisoning. We observed in our experiments that this decrease in SWNT thickness is suppressed if the background vacuum of the CCVD chamber is good (i.e. the leak rate is low). This illustrates the importance of thorough catalyst reduction, and preserving catalyst activity, in the production of SWNTs. The presence of hydrogen helps counter this oxidation, but is unnecessary if the background vacuum is good.

The SWNT film was further characterized by resonance Raman spectroscopy (Fig. 2). The peak at ~1590 cm^{-1} (G-band) is characteristic of graphitic materials, while the series of peaks between 100 and 400 cm^{-1} confirms the existence of SWNTs [8]. The high ratio between the G-band and the weak D-band peak near 1350 cm^{-1}, which is caused by impurities and defects in the sample, shows the SWNTs to be very high purity. The diameters of the SWNTs in the sample range from ~0.8 nm to ~2.0 nm, as determined from the positions of the RBM peaks [8]. There is no appreciable difference in the RBM, indicating the tube diameter is independent of growth time.

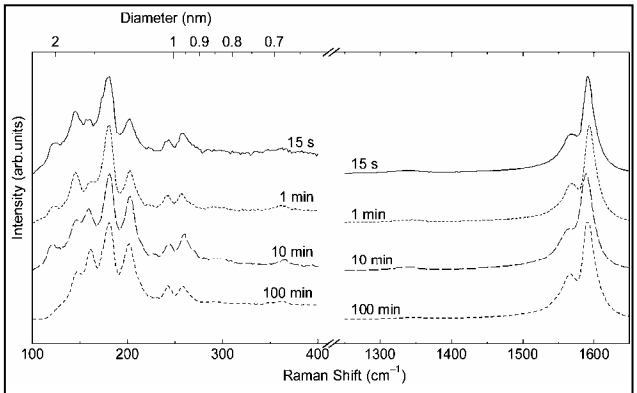

Fig. 2. Resonance Raman spectra corresponding to (a), (b), (d), and (f) in Fig. 1. The RBM signal does not change with CCVD time, indicating the initial catalyst activity is very high.

The contributing factors to the growth rate are shown qualitatively in the inset in Fig. 3. The dashed upper line represents the catalyst activity and the dotted lower line represents the destructive effects of oxygen. The solid line shows the net growth rate, which can eventually become negative if oxidation is significant enough. This is a simplified model, however, as the details are not yet well known.

Using the optical absorption properties of SWNTs [9], we measured the absorption of 488 nm laser light by the SWNT films shown in Fig. 1, and compared the absorbance to the film thickness determined by the above images. The results are also shown in Fig. 3. There is a clear relationship between the film thickness and the measured absorbance, indicating a simple optical measurement may be used to determine the film thickness.

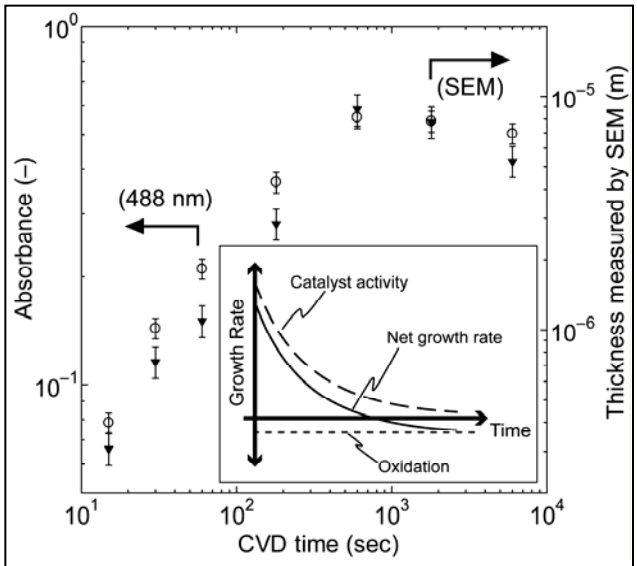

Fig. 3. A plot showing the optical absorbance at 488 nm (left axis) and film thickness measured by SEM (right axis) as a function of growth time.

4. CONCLUSIONS

In this report, vertically aligned SWNT films were grown using an alcohol catalyzed chemical vapor deposition method. The SWNTs characterized by resonance Raman spectroscopy and scanning electron microscopy. Analysis of the results show the SWNT film follows a non-linear growth rate, where the thickness is observed to decrease after reaction times in excess of 10 minutes. This decrease is attributed to a combination of a decrease in the catalyst activity and oxidation of the SWNTs due to excessive oxygen in the CCVD chamber, and can be suppressed by enhancing the quality of the chamber vacuum.

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