Direct Observations of the Growth of Carbon Nanotubes using \textit{in situ} Transmission Electron Microscopy$^*$

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Nucleation and growth of carbon nanotubes, formed during chemical vapor deposition, was observed using an environmental transmission electron microscope (ETEM). Carbon nanotubes formed readily when acetylene ($\text{C}_2\text{H}_2$) was leaked into the sample area of the ETEM containing Ni/SiO$_2$ catalyst at 470-700$^\circ\text{C}$. Carbon nanotubes were observed to nucleate and grow in a sequential manner, i.e. one or two tubes nucleating and growing before new tubes were nucleated. Straight single wall tubes were observed to grow with no catalyst at the tip at 475$^\circ\text{C}$ at very low $\text{C}_2\text{H}_2$ gas pressures ($<$ 10 mTorr). We observe that the growth rate and growth mechanism are directly controlled by the temperature and pressure. [DOI: 10.1380/ejssnt.2006.460]

Keywords: environmental transmission electron microscope; carbon nanotubes

I. INTRODUCTION

Carbon nanotubes (CNTs) have attracted much attention since their discovery because of their remarkable properties [1–3]. Their synthesis has been a subject of research for quite some time and a number of different processes have been perfected to improve the yield of CNTs. Currently there are three main processes used for large scale synthesis; 1) arc discharge between carbon electrodes, 2) laser ablation, and 3) chemical vapor deposition (CVD). Currently, CVD is most favored due to its low cost and potential for better quality control of the CNTs. However, the selective synthesis of nanotubes with a desired structure and properties is still a challenge. The product often contains a mixture of various forms of carbon, amorphous, graphitic, onion rings, fullerenes, and carbon nanotubes with varying inner and outer diameter and wall thickness. Chemical methods have been developed and successfully employed to purify single-wall carbon nanotubes from this mixture [4, 5]. Researchers have also been able to qualitatively select the catalyst compositions and reaction conditions that produce single-wall carbon nanotubes with high yield [6, 7]. For some applications, such as field emitters, they need to be synthesized directly as part of the device and more stringent control of the synthesis conditions is required.

In order to determine the best synthesis conditions for a certain type of CNT, it is important to understand the relationship between the synthesis conditions (temperature and pressure) and their structure. Although CVD is a very straightforward synthesis process, temperature, pressure, the choice of carbon precursor, the choice of catalyst, and the size of catalyst particles, all control the structure and properties of CNTs. A number of hypotheses have been proposed to explain the effect of synthesis conditions on the structure of CNTs (e.g. [8–11]). Similarly, a growth mechanism has been proposed for the growth of carbon nanofibres [12]. We have also recently reported that the growth rates and growth mechanisms are controlled by the synthesis conditions [13, 14].

In order to understand the effect of synthesis conditions on growth mechanisms we have employed in situ transmission electron microscopy (TEM) observations of the nucleation and growth of CNTs as they are formed.

II. EXPERIMENTAL

We have used a specially modified transmission electron microscope, the Tecnai F20ETEM, operated at 200 kV, equipped with a Gatan imaging filter (GIF) and a Gatan annular dark field (ADF) detector for in situ observations.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{High resolution image of Ni particles recorded at 470$^\circ\text{C}$ in 6 Torr of N$_2$.}
\end{figure}

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This microscope permits samples to be observed in a controlled gaseous environment at pressures up to 8 Torr and temperatures up to 900°C, while maintaining near atomic resolution imaging capability [15]. The Ni/SiO$_2$ catalyst with a very narrow particle size distribution (1.5-3.0 nm), and a surface area of 1.75 m$^2$/g was obtained by the co-precipitation method described elsewhere [16]. The catalyst powder, dry loaded on 400 mesh Ni grids, was first heated to 450-480°C for 30-60 minutes in the microscope column in a vacuum of $\sim$10$^{-6}$ Torr, in H$_2$ or in N$_2$ to ensure the reduction of any nickel oxide that might be present in the sample. Then 0.08-100 mTorr of acetylene (C$_2$H$_2$) was slowly leaked into the sample region at the reaction temperature. Bright field images were recorded on a CCD camera and a digital TV rate camera. Videos were recorded at intermediate magnification, to monitor a large area and increase the probability of directly observing CNT formation. High resolution images were recorded before and after the reaction using a 1024 × 1024 CCD camera. Growth rates and growth mechanisms were obtained by studying sequential video frames.

The sample was surveyed by high resolution electron microscopy (HREM) after stopping the gas flow and evacuating the sample area ($\sim$10$^{-6}$ Torr) to characterize the types of CNTs formed after the in situ observations. Similar nanotubes also formed in the areas not irradiated by the electron beam, indicating that the electron beam radiation had no significant effect on the nucleation and growth process under typical imaging doses.

III. RESULTS AND DISCUSSION

Figure 1 shows a high resolution image of Ni particles recorded at 470°C in 6 Torr of N$_2$. The measured lattice parameters (0.20 and 0.22 nm) confirm that the catalyst particles are metallic under these conditions with no oxide layer. Similar results were obtained for samples heated in H$_2$ and in vacuum.

Figure 2 shows a set of images recorded using the CCD camera at 475°C in 10 mTorr of C$_2$H$_2$. The Ni catalyst particles were homogeneously distributed on the support (Fig. 2a) at the reaction temperature. CNTs were observed to form immediately after the introduction of C$_2$H$_2$ at temperatures between 470-670°C.

At low pressures (below 10 mTorr), single wall carbon nanotubes formed at temperatures as low as 470°C. Figure 2b, recorded after 1 minute of exposure to 10 mTorr of C$_2$H$_2$ at 475°C shows that a number of nanotubes have formed within this short time interval. The CNTs were often observed to form as bridges between two catalyst particles (Fig. 2b). An HREM image of the area shows the formation of predominantly single-walled carbon nanotubes (SWCNTs) with small diameters (marked A in Fig. 2c). SWCNTs could be observed as isolated tubes and as bundles (marked A and B respectively).

Bright field images were also recorded, using a digital video recorder, as acetylene was slowly leaked into the sample region at the reaction temperatures in order to record the dynamic growth process in situ. Individual frames were extracted from the video sequences with a time resolution of 1/30 sec. Careful analysis of each frame was used to reveal the growth mechanisms and growth rates at different temperatures and pressures. CNTs nucleated and grew out of the substrate (catalyst/support) in a sequential manner. One or two tubes nucleated and grew in the region under observation, and this was followed by the nucleation of new tubes. For example, Fig. 3 shows digitized images of the growth sequence of an isolated CNT at 480°C in 18 mTorr of C$_2$H$_2$. Under these conditions most of the tubes were observed to be anchored at both ends to the substrate. One of the ends detached after growing for a few seconds [14]. Sometimes, tubes were observed to grow straight out of the substrate (Figs. 3a-c). The tip of the tube had a hollow round structure (Figs. 3b-3c) indicating the absence of a Ni particle at the tip. HREM images confirmed that the tip in this case was in the form of an onion ring type structure and did not contain a catalyst particle. Although it was difficult to image the root of the tube, the absence of a catalyst particle at the tip indicated that a root growth mechanism was most likely [10, 11]. We have observed CNTs to grow with or without the catalyst at the tip depending upon the reaction conditions. Although we have observed
FIG. 3: Three frames from a digital video sequence showing the growth of a CNT, labeled A. The CNT labeled B grew before A.

FIG. 4: Length and growth rate of CNT labeled A.

both single and multi-walled tubes growing without a catalyst at the tip, we have not yet observed a single-walled CNT with a catalyst particle at the growing (moving) tip during or after the growth period.

CNT growth profiles under different reaction conditions were examined and the incremental change in projected length during each frame (1/30 sec) was used to estimate instantaneous length for each frame, shown in Fig. 4. The measured growth rate of this nanotube (estimated from the slope of this curve) was broadly distributed, indicating discontinuous growth. It varied from zero, to growth rates of up to 45 nm/sec. Not all of the growth rate discontinuities can be explained by simple image projection artifacts. The average growth rate for this particular tube (5.0 nm/sec) is in good agreement with growth rates measured for other tubes formed under the same conditions [14]. Although nanotubes have been observed to grow as fast as 100 nm/sec at pressures above 20 mTorr. Our data show that the growth rates, duration of growth, structure and length of the CNTs, are all controlled by the synthesis conditions. For example, the total growth time of individual CNTs after nucleation was observed to be 15-45 sec at gas pressures below 20 mTorr compared to 3-5 sec at higher pressures. At gas pressures above 20 mTorr, nanotubes grew up to 340 nm in length, in a serpentine manner, while straight single wall carbon nanotubes grew at low pressures (~10 mTorr) with an average length of ~50 nm.

IV. CONCLUSIONS

Our observations show that the growth rate, the growth mechanism, and the structure of the CNTs formed depend on the reaction temperature and pressure. The CNTs grow in a sequential manner, probably due to subtle differences in the reactivity of various catalyst particles. Another possibility is the depletion of reactant gases in the vicinity of the growing tube, temporarily inhibiting the growth of neighboring tubes. The instantaneous growth rates observed were broadly distributed as reported earlier, but unlike previous observations, straight walled CNTs were observed to form. It is possible that such tubes were first anchored at both ends and then one of the ends becomes detached and continues to grow. Our observations confirm that CNTs can grow by more than one mechanism, and the growth mechanism is dependent upon temperature and pressure. The reactivity of various catalyst surfaces appears to play a significant role, and is currently under investigation.

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