Dynamics of Nanotube Synthesis

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Introduction

Carbon nanotubes are potential candidates for use in many functional devices such as field emitters and for use in nanoelectronics.[1] The synthesis of aligned nanotube bundles is of great importance in this area, [1] that is the goal of this experimentation. Carbon nanotubes are the world's smallest solid-state light emitters, and the first electrically controlled, single molecule emitter.[2] Nanotube transistors have been "successfully fabricated and tested using individual multi-wall or single-wall as the channel of a field-effect transistor."[2]

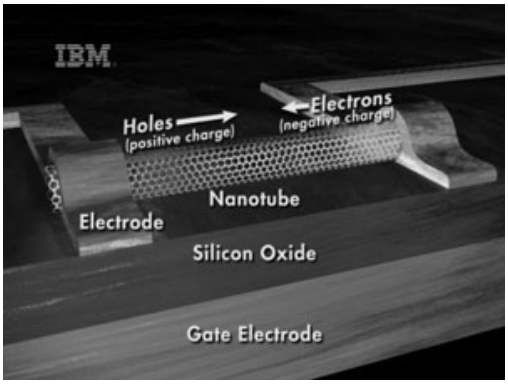


Figure 1. IBM scientists simultaneously inject positive and negative charges into a carbon nanotube through the source and drain electrodes at its two ends.[2]

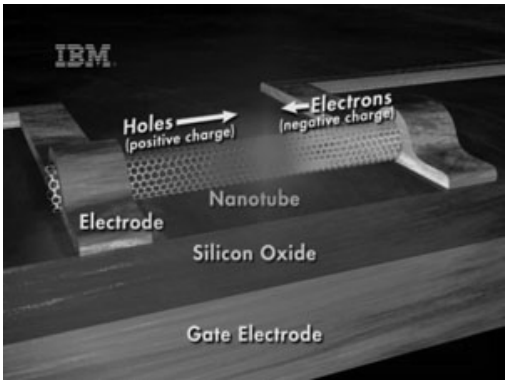
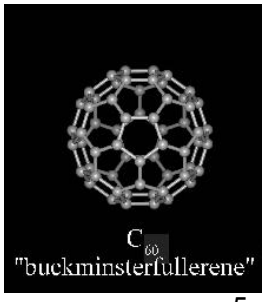


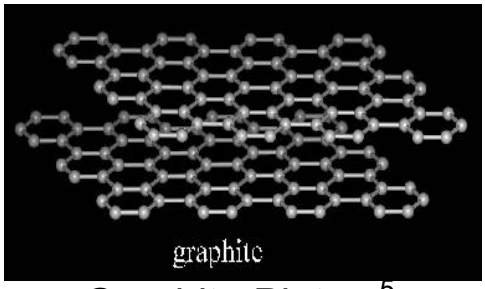
Figure 2. When the electrons and holes meet in the nanotube, they neutralize each other and generate light.[2]

Carbon nanotubes may be defined as greatly elongated fullerenes with exactly twelve pentagons and millions of hexagons, while a fullerene is a closed shell all carbon molecules with an even number of carbon atoms.[3] An alternate definition is that carbon nanotubes are graphite sheets wrapped into a cylinder and capped by fullerene-like structures[4] (See Figure 3).

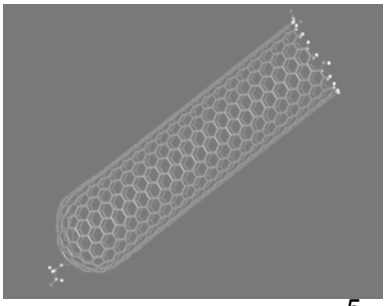
Figure 3. A fullerene, graphite plates, and carbon nanotube to better aid in the description



A fullerene.[5]



Graphite Plates.[5]



Carbon nanotube.[5]

There are two forms of carbon nanotubes: multi- and single-walled. Multi-walled carbon nanotubes (MWNT) are comprised of concentric cylinders formed around a common central hollow with spacing between the layers close to that of the interlayer spacing of graphite (0.34 nm).[3] Single-walled carbon nanotubes (SWNT) differ from multi-walled nanotubes in the fact that they are composed of a single graphite sheet.[3]

MWNTs were initially discovered by Iijima in 1991 via arc-evaporation of graphite rods in an inert atmosphere inside the cathodic deposit.[6,7] This led to an explosion of nanotube research being conducted. SWNTs were first synthesized in 1993 in an arc discharge apparatus.[8] In this experiment; the method of ferrocene pyrolysis was used to obtain bundles of aligned MWNTs.

Experiment

Via the method of injection chemical vapor deposition (CVD), "aligned nanotube films were obtained from temperatures of 550 °C and above"[7]. Using that same method, the length of the nanotubes increased until reaching a temperature of 680 °C, and then proceeded to decrease in length. However, in this experiment, using ferrocene pyrolysis, a mixture of 80% argon (Ar) and 20% hydrogen (H_2) is used as the carrier gas, and the carbon source is acetylene. All of the nanotubes in these experiments are synthesized at 700 °C on a quartz plate, both orthogonal and parallel to the gas flow, while placed inside a quartz boat.

Prior to heating, the Ar:H_2 mixture is flowed into the furnace. The ferrocene is heated at a constant rate in the first stage of the furnace, until it has sublimed, using a temperature controller. This heating takes place before the acetylene begins to flow through the reaction tube. There were various temperature settings for the heating of the ferrocene in the first stage. The temperature settings for the heating of ferrocene varied per sample. However, the starting temperature was always room temperature (approximately 23 °C), and the final temperature ranged between 160 and 170 °C.

For Sample 1, the heating rate of the ferrocene was: from starting temperature to 90 °C in the first 20 minutes, 90 °C to 130 °C in 5 minutes, 130 °C to 150 °C in five minutes, 150 °C to 160 °C in 5 minutes, and held constant at 160 °C for 15 minutes. The

flow rates of Ar, H_2, and acetylene, for this sample, are 150 sccm (standard cubic centimeters), 37.5 sccm, and 8 sccm respectively. The mass of ferrocene used was 200 mg.

For Sample 2, the heating rate of the ferrocene was: from starting temperature to 60 °C in the first 15 minutes, 60 °C to 90 °C in 5 minutes, 90 °C to 170 °C in 15 minutes, and held constant at 170 °C for 15 minutes. The flow rates of Ar, H_2, and acetylene, for this sample, are the same as those for Sample 1. The mass of ferrocene used was 300 mg.

For Sample 3, the heating rate of the ferrocene was: from starting temperature to 60 °C in the first 15 minutes, 60 °C to 120 °C in 5 minutes, 120 °C to 170 °C in 10 minutes, and held constant at 170 °C for 50 minutes. The flow rates of Ar, H_2, and acetylene, for this sample, are 210 sccm, 52.5 sccm, and ~6 sccm respectively. The mass of ferrocene used was 400 mg.

At the same time, the second stage of the furnace heats at a constant rate until it reaches 700 °C (during the first 20 minutes of the experiment), which is the temperature chosen to grow the aligned MWNT bundles. Once the temperature of 700 °C is attained, after 20 minutes, the acetylene flow begins, and the temperature is held constant at approximately 700 °C for 30 to 60 minutes. Once the process is completed, the furnace and nanotubes are allowed to cool until they are both at room temperature. The products were then characterized with a Hitachi S3000-H scanning electron microscope.

Results/Discussion

The temperature controller used for the experimentation was not very accurate. Therefore, for each sample, the actual temperatures of ferrocene after each time interval were observed. The actual heating rate for Sample 1 was: 18.7 °C to 87.5 °C in the first 20 minutes, 87.5 °C to 125.5 °C in 5 minutes, 125.5 °C to 147.3 °C in five minutes, 147.3 °C to 158.3 °C in 5 minutes, and held constant at approximately 160 °C for 15 minutes.

The actual heating rate for Sample 2 was: 20 °C to 58.8 °C in the first 15 minutes, 58.8 °C to 86.9 °C in 5 minutes, 86.9 °C to 166.5 °C in 15 minutes, and held constant at approximately 170 °C for 15 minutes.

The actual heating rate for Sample 3 was: 22.1 °C to 59.8 °C in the first 15 minutes, 59.8 °C to 115.8 °C in 5 minutes, 115.8 °C to 166.5 °C in 10 minutes, and held constant at approximately 170 °C for 50 minutes.

Effects of Ferrocene Mass

For Sample 1, 200 mg of ferrocene was used. This experiment yielded short, aligned nanotubes that were about 30 microns (μm) in length. These nanotubes proved to be the most aligned nanotubes that were synthesized in the series of experiments, and they can be seen in Figure 4. For Sample 2, 300 mg of ferrocene was used, and the results were aligned nanotubes, but they were shorter than and not quite as aligned as those found in Sample 1. The nanotubes from this sample had a length of 12 μm. However, the far edge of the plate, furthest away from the ferrocene source, showed nanotubes with the length of 22 μm. For Sample 3, 400 mg of ferrocene was used. The only material remaining on the quartz support was a very thin layer of carbon nanotubes.

Effects of plate positioning

The concentration of ferrocene was assumed higher near the top of the reaction tube than it is at the bottom. To confirm or disprove this theory, there were two positions in which the quartz plate was placed: parallel and perpendicular to the flow of the gases. When the plate is placed parallel to the gas flow, there is a low rate of aligned nanotube synthesis. However, when the plate is placed perpendicular to the gas flow, the rate of successful aligned nanotube synthesis is high in comparison to the plate being placed parallel to the gas flow. Samples 1 and 3 were both synthesized with the plate perpendicular to the flow of gases. However, in Sample 2, the plate was placed parallel to the gas flow.

Figure 4. SEM images of the MWNTs from Sample 1

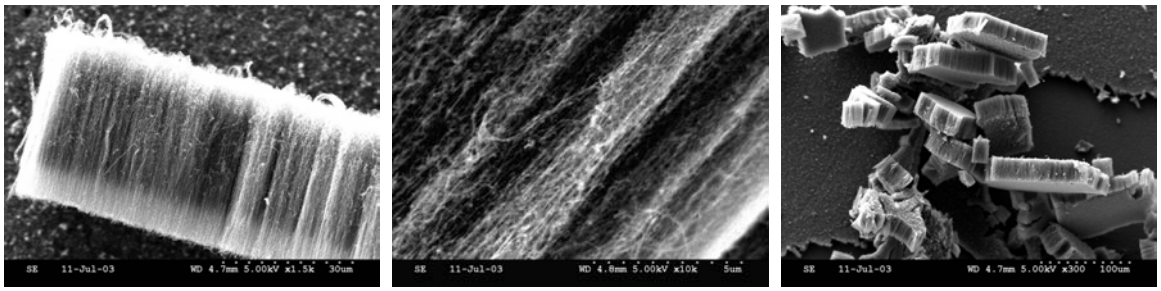
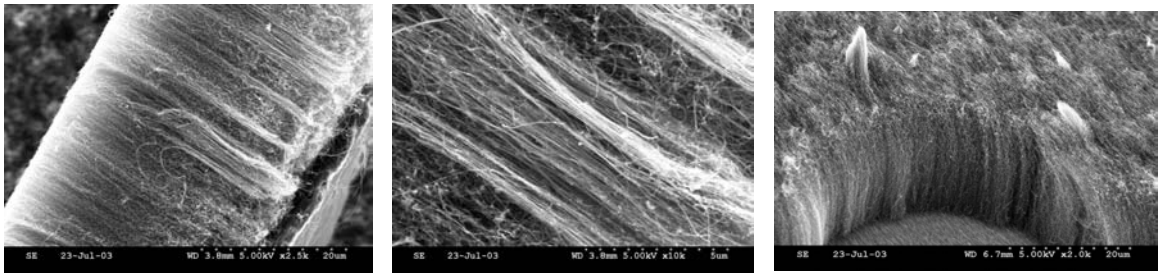


Figure 5. SEM images of the MWNTs from Sample 4



Conclusions

The mass of ferrocene was varied between 200 and 400 milligrams (mg). The experimentation concluded that 200 to 300 mg was sufficient for the growth of nanotubes. However, 400 mg was a little too much. Therefore, aligned nanotubes will form almost consistently when using between 200 and 300 mg of ferrocene as the catalyst. However, when attempts were made to synthesize nanotubes with 400 mg of ferrocene, the results showed that there was a possibility that nanotubes formed, but they were too short to be characterized by the SEM.

The nanotubes also form rather consistently when the quartz support is perpendicular to the flow of gases as opposed to parallel. It is assumed that this has to do with the concentration of ferrocene at different levels of quartz tube. It is believed that the concentration of ferrocene will be higher near the top of the reaction tube, in

comparison to the concentration near the bottom, where the nanotubes are being grown. In addition, it appears as though when the support is parallel to the flow, generally any nanotubes formed blown off the quartz support into the tube.

Acknowledgements

I would like to thank NSF, the McNair Scholars Program staff who put me in the position to conduct this research, Dr. Henry Foley and his research group, and my family for their constant support.

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