Journal of Undergraduate Research in Physics
August 27, 2010

Effects of Hydrogen Flow Rate on Carbon Nanotube Growth

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Integrated Optics for Undergraduates *(IOU)*
an NSF-ERC sponsored Research Experience for Undergraduates (REU) Program

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Abstract

This article presents the synthesis and characterization of carbon nanotubes (CNTs) on silicon substrates by chemical vapor deposition (CVD) at 900ºC using methane and hydrogen flow rates. The variation of H_2 gas concentration and a set growth time of 15 minutes have a significant effect on distribution, morphology, internal structure, and electronic properties of the nanotubes. The transmission electron microscope (TEM) and state-of-the-art scanning electron microscope (SEM), equipped with Raman spectrometer, allowed us to obtain critical information on the morphology and chemical and electronic structures of the CNTs. The results revealed substantial quantity trends as hydrogen flow rate increased from 100 to 700 standard cubic centimeter per minute (sccm). At a constant CH_4 flow rate of 700 sccm and varied H_2 of 100 and 200 sccm, we observed that few CNTs were produced. Between H_2 flow rates of 300 and 400

sccm, the highest density of CNTs were grown; therefore, suggesting optimum growth conditions within that range. Increasing H_2 to 700 sccm, the amount of CNTs decreased. The results from this study will guide a production process to obtain high quantity and quality CNTs with desired properties.

Key Words: **Carbon nanotubes (CNTs); chemical vapor deposition (CVD); hydrogen; methane; substrates; silicon**

1. Introduction

Carbon nanotubes (CNTs) have become a forefront topic in research because of their unique electrical properties, chemically stable nature, and excellent mechanical strength. In addition, because of their efficient conductivity of electricity and heat, they are potentially useful in a wide variety of applications. A few of these applications include the making of solar cells, diodes, transistors, small electronic devices, high efficiency energy conversion fuel cells, smart materials, high performance sensors, and structural materials under extreme environment [4]. In order to fulfill the potential applications, extensive research must be carried out to ensure proper characteristics of these CNTs. This research is devoted to investigate the effects of hydrogen gas flow on the quantity and quality of CNTs.

In 1991, Sumio Iijima, a Japanese physicist, was credited for discovering CNTs [1]. Throughout research, there have been found to be three common variations of CNTs: single-walled (SWCNTs) double-walled (DWCNTs) and

multi-walled (MWCNTs). Single-walled CNTs can be described as a one-atom thick planar sheet of bonded carbon atoms (graphene) that are densely packed in a honeycomb crystal lattice. They can be categorized based upon their chiral vector or indices, (*n, m*). If the pair of indices is (*n, 0*), the structure is zigzag. If it is (*n, n*), the structure is known to be armchair. All other combinations are chiral [6]. When CNTs have two layers of the planar sheets, they are called double-walled CNTS and more than two layers of graphene, multi-walled CNTs.

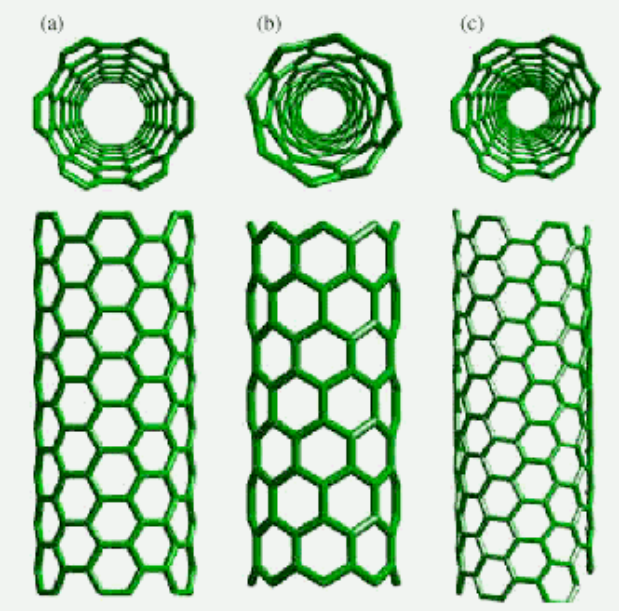

Figure 1 . (a) armchair, (b) zigzag, (c) chiral

Carbon nanotubes are grown using various methods. Some of these methods include chemical vapor deposition (CVD), arc discharge, and laser vaporization [5]. For this experiment, the CVD method is used mainly because it readily

allows a reproduction of trials, a large-scale nanotube production in a single trial, and an ease of process control.

Once the samples are grown, they are characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. From these characterization methods, details such as density, electrical properties, inner diameter, common variation (SW, DW, or MW-CNTs), and overall quality are determined.

2. Experimental Procedure

Carbon nanotubes were synthesized on silicon wafers using the chemical vapor deposition (CVD) system with gas flows of H_2, CH_4, and Ar. The parameters held constant for the experiment were: flow rates of 700 sccm (CH_4), 1000 sccm (Ar), baking time of 15 minutes, and furnace temperature of 900^0C. The testing parameter was H_2 at 100, 200, 300, 400, 500, and 700 standard cubic centimeter per minute (sccm). A 0.1 mL sonicated catalyst solution of bis(acetylacetonato)-dioxomolybdenum (VI) [$(C_5H_8O_2)_2$ MoO_2], iron nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$], aluminum oxide [Al_2O_3], and methanol was deposited on the wafers before being placed in the CVD gas flow system.

The established method for deposition of the catalyst solution was determined by comparing the outcomes of what we called the blow-drying and spinning methods. The first method consisted of dropping 0.1 mL of the solution onto the wafers, blow-drying the solution, and baking at 150°C for fifteen minutes. The

second method involved a spinner system in a clean room. The silicon wafer was placed on the chuck; 0.1 mL of the solution was deposited, and allowed to spin at different speeds for thirty seconds. The wafers/substrates were then ready to be used in the CVD system. The spinner method was first assumed to distribute the catalyst solution more evenly over the wafer compared to the first (blow-dry) method, but in testing, there was no major difference of catalyst dispersion seen between the two methods. The blow-drying method was therefore chosen to be used.

The operation of the CVD system started with Ar being released into the system until the furnace reached 900°C. H_2 and CH_4 were then allowed to flow simultaneously for fifteen minutes. Ar was opened again as the furnace was turned off to cool. The flow of Ar while cooling prevents the CNTs from being burned at such high temperatures. When the cooling was complete, the samples were ready to be removed for analysis. A total of four samples per condition were run in trial. Not all samples gave similar results so additional trials were run as needed.

Hitachi SEM S-4800, SEM S-4500, Hitachi TEM, and our state-of-the-art Renishaw Raman Spectroscopy, equipped on a Hitachi SEM S-3400 were the instruments used for analysis. To prepare the sample for TEM, the substrate must be submerged in isopropanol (IPA), scraped and bath-sonicated for approximately 30 minutes. The solution is then extracted using a syringe and placed on a copper

grid specifically designed for the TEM. The grids are left to air-dry. No additional preparation, such as coating, is needed for the SEM and Raman analysis.

3. Results and Discussion

All four samples from H_2 at 100 sccm showed very few CNTs as shown in Figure 2(a). Amorphous carbon was present on two of the four samples. The high CH_4 content decomposed to excessive amount of C atoms, which coated around the catalysts. This increased the activation energy of the CNT growth process, resulting in low density of CNTs. Three of the four samples for H_2 at 200 sccm showed little CNT growth (not shown in Figure 2). The fourth sample was highly inhomogeneous; some locations on the substrate possessed an abundance of CNTs while other areas had little CNT growth. All four samples for H_2: 300 sccm had an abundance of CNTs. These CNTs however had short branches and smaller outer diameters seen from SEM image in Figure 2(b). An abundance of CNTs was produced at H_2: 400 sccm on three of five samples. Around 300 and 400 sccm, the optimum growth condition is in close proximity to allow abundant production of CNTs. For H_2: 500 sccm, a small amount of CNTs was seen on the samples. Amorphous C was present also (not shown). Similar to H_2: 300 sccm, the CNTs had short branches. For all four samples at H_2: 700 sccm, low density of CNT was present. The CNTs also had short branches. As

the flow rate approached 700 sccm, the excessive presence of H atoms to C atoms produced few CNTs.

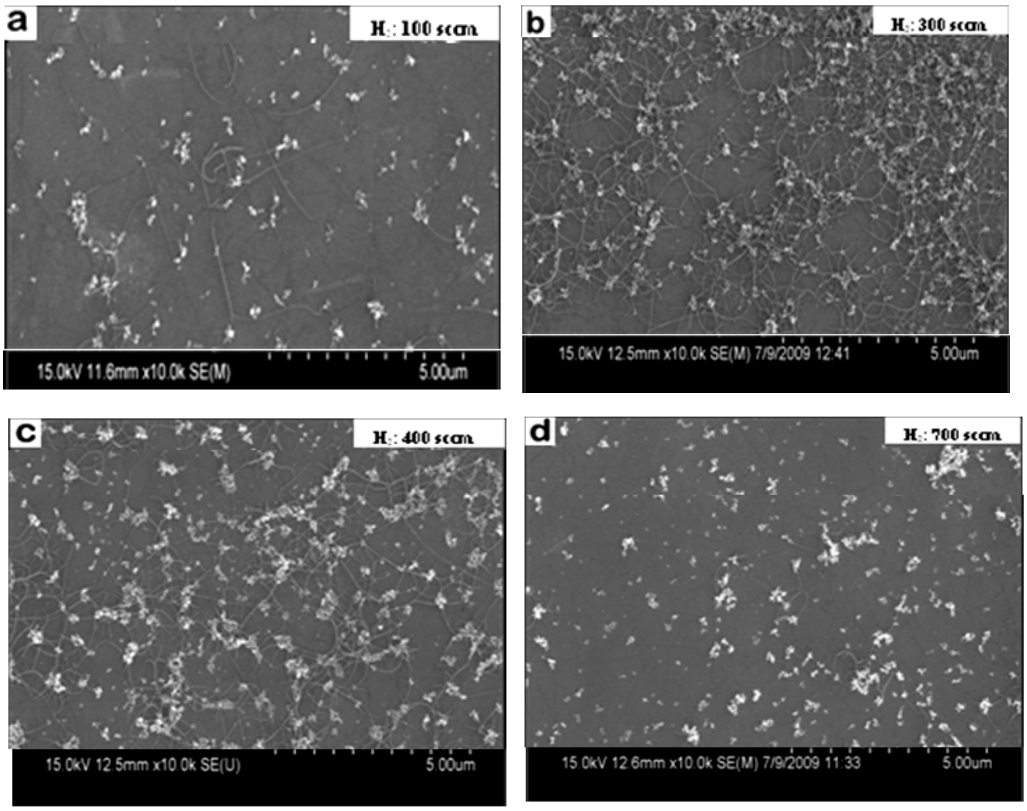

Figure 2. SEM images of CNTs grown at hydrogen flow rate of: (a) 100 sccm; (b) 300 sccm; (c) 400 sccm; (d) 700 sccm.

Figure 3 depicts TEM images of (a) graphite structure; (b) double-walled CNT; (c) multi-walled CNT. When images such as Fig. 3(a) are seen, the density of the CNTs is low. The graphitic structures are undesirable in our research. We prefer to have DWCNTs and MWCNTs as shown in (b) and (c).

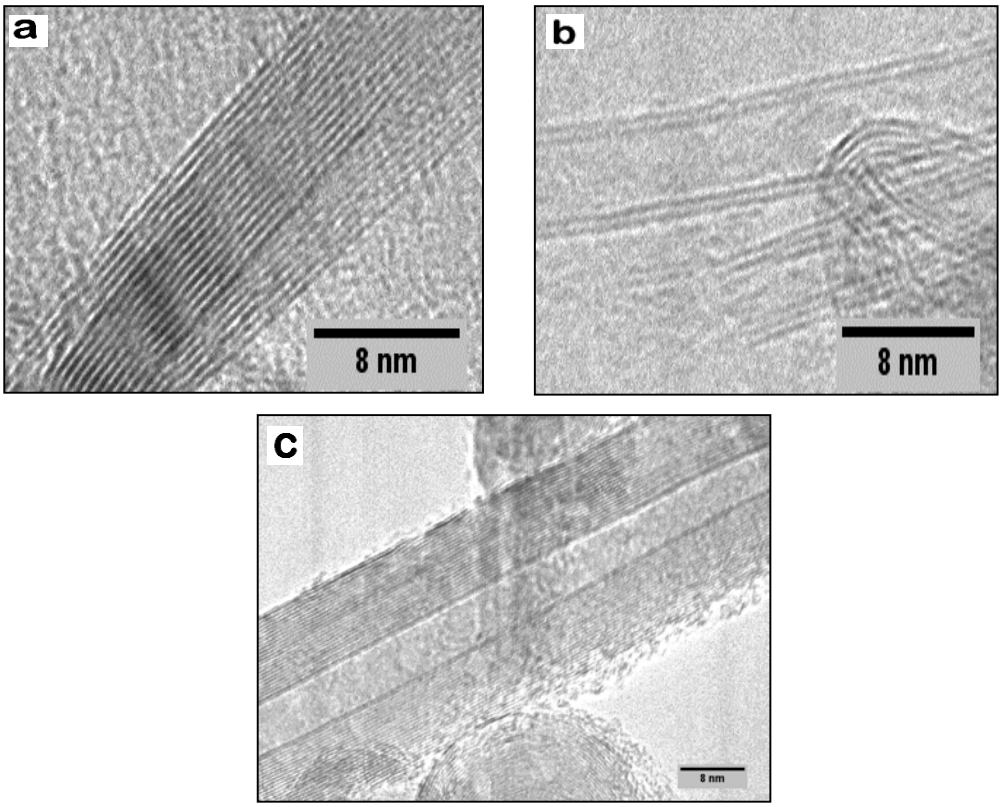

Figure 3 TEM images of: *(a)*: Graphitic structure obtained from H_2 @ 300 sccm; *(b)*: Double-walled CNT obtained from H_2 @ 200 sccm; *(c)*: Multi-walled CNT obtained from H_2 @ 100 sccm

Raman spectroscopy was used to analyze the H_2: 200 sccm sample as shown in Figure 4. Using the Radial Breathing Mode (RBM) and its equation [5]:

$$\omega_{RBM} = \alpha / d_t$$

where ω is the RBM peak frequency, α is a constant equaling 248 nm•cm^{-1}, the inner diameter (d_t) of the CNTs of this corresponding location was calculated. Calculating the diameter at all five extreme RBM peaks and taking the average, the average diameter equals 1.40 nm. The term D/G ratio commonly is used to represent the overall quality of the CNTs; quality as in the alignment and bonding regularity of the honeycomb crystal lattice. If less this D/G ratio is than two

percent, then the CNTs of that spectrum are of high quality. It was found that the D/G ratio of the spectrum shown in Figure 4, (2500/67500) equals 3.7 percent. Therefore, it was deduced that the CNTs grown at this location are low quality CNTs. The G-band indicates the electrical properties of the CNTs. Its specific shape infers that these CNTs are semi-conducting.

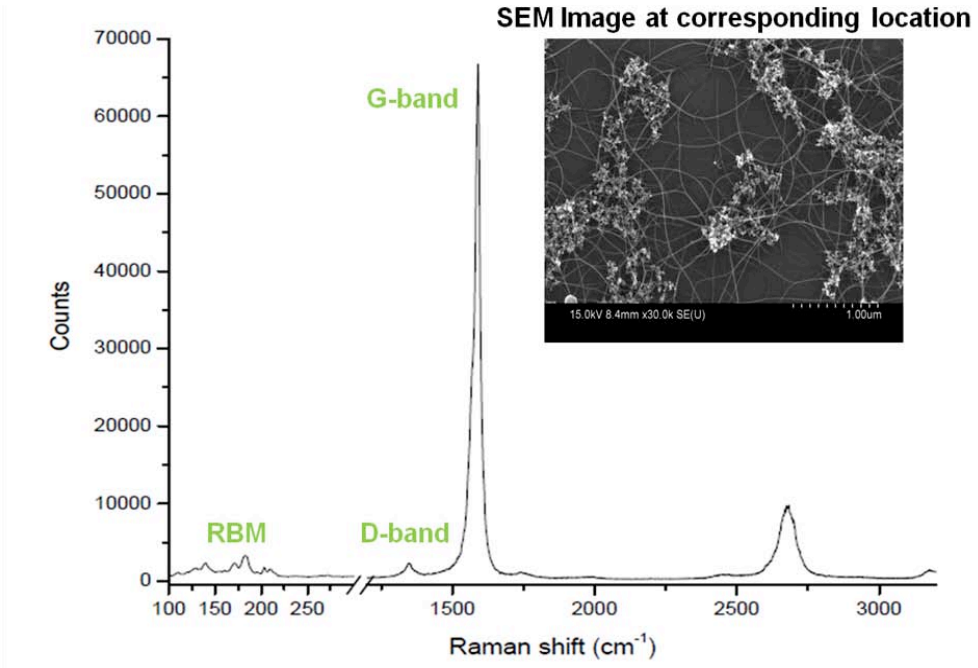

Figure 4. Raman Spectrum of H_2: 200 sccm sample, acquired at the center spot of the SEM image (inset).

4. Conclusion

Our results show that as H_2 flow rate increases from 100-300 sccm, the amount of CNTs increases to a peak density when H_2 flow rate is between 300-400 sccm.

However, the CNTs seem to grow less at higher H_2 flow rates such as 500 and 700 sccm.

5. Future Work

Studies are planned to continue to testing this thesis. Testing H_2 flow rates at smaller intervals between 300 and 400 sccm should result in a more defined optimum condition.

6. Acknowledgements

The authors would like to thank NSF-ERC grant number EEC-0812072, Dr. Brian Leroy, Jiamin Xue, UA Physics Dept., Lu Wang, Phil Anderson, and University Spectroscopy and Imaging Facilities (USIF) for their contributions towards this research project.

7. References

[1] S. Ijima, "Helical microtubules of graphitic carbon," Nature 354, 56 (1991).

[2] Y.C. Choi, W. Choi, Carbon 43 (2005), 2737-2741.

[3] N. R. Franklin, Y. Li, R. J. Chen, A. Javey, H. Dai, Applied Physics Letters, Vol. 79, No. 27, (December 2001), 4571-4573.

[4] W. Choi, D. Kim, Y. C. Choi, J.Haung, Nanomaterials for Electronic Applications, JOM (March 2007), 44-49.

[5] B. Duong, Y. Peng, M. Ellis, S. Seraphin, H. Xin, "Combined Raman Spectroscopy and SEM Analysis of CVD Grown Carbon Nanotubes," Proc. Microscopy and Microanalysis (2008), 14:1130-1131CD.

[6] "Carbon Nanotubes & Buckyballs," University of Wisconsin Madison Material Research Science and Engineering Center, The Board of Regents of the University of Wisconsin System, [2008]. http://mrsec.wisc.edu/Edetc/nanoquest/carbon/index.html [Accessed: 25 August 2010].