Carbon Nanotubes:
CVD Reactor Deign and Growth of Multi-Walled Carbon Nanotubes

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Abstract-- Carbon Nanotubes are researched to develop for new technology of transporting electrons in one dimension and have commercial potential as nanoscale transistors. Carbon Nanotubes need to be made by using chemical vapor deposition (CVD). This CVD technique is used to deposit thin film on substrates. As the gas decomposes, it frees up carbon atoms, which can recombine in the form of nanotubes. The conditions for the controlled and directed CVD growth of Nanotubes are planed being established with the use of thin film metal catalyst by using RIT's CVD Reactor. This CVD reactor was designed and made for growing the specific, high yield, possibly phase pure, and multi-wall carbon nanotubes in RIT.

1. INTRODUCTION

Carbon Nanotube was found by Sumio Iijima, at NEC Fundamental Research Laboratory in Tsukuba, Japan, nearly 10 years ago. Sumio Iijima was studying the material deposited on the cathode during the arc-evaporation synthesis of fullerences. He found that the central core of graphitic structures including nanoparticles and nanotubes. Carbon nanotubes are fullerene-related structure. These structures consist of graphene cylinders closed at either end with caps containing pentagonal rings, figure 1. Also, the carbon nanotubes are made of pure carbon as regular and symmetric as crystals. These are very tiny tubes about 10,000 times thinner than a human hair.

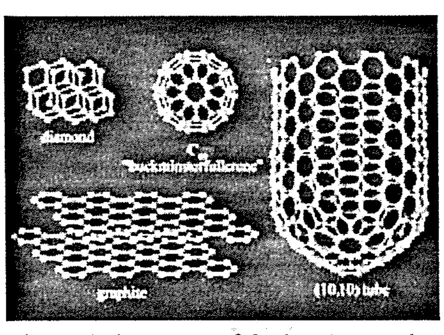
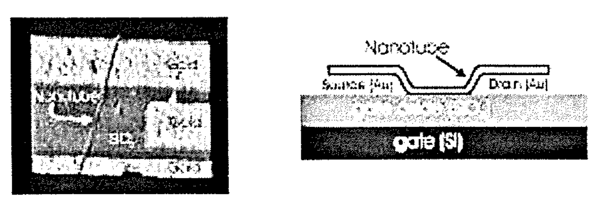


Figure 1: Structure of Carbon Nanotubes

There are two kinds of carbon nanotubes, single- and multi-wall carbon nanotubes. The multi-walled carbon nanotubes, MWCNT, contains a number of hollow cylinders of carbon atoms nested inside one another. This MWCNT was found first by Iijima. Later IBM researchers include Sumio Iijima found single-walled carbon nanotubes, SWCNT. This SWCNT are made of just one layer of carbon atoms.

For the microelectronic industry, these carbon nanotubes are new conduction and insulation materials for devices. The conduction or insulation behavior of carbon nanotubes are depending on how the graphene sheets rolled into a nanotube. The geometry of nanotubes limits electros to select few silices of graphite's energy state. If they are rolled as straight nanotubes, this makes two thirds of the nanotubes metallic. If they are rolled as twisted nanotubes, the slices of allowed energy state for electrons are similarly cut at an angle, with that results about two thirds of twisted tubes miss the Fermi point and are semiconductors.

Because of the speed, density and efficiency of microelectronic devices all raise rapidly as the minimum feature size decreases, the materials for the devices are getting closed to limit. By many researchers, like IBM, FETs use single semiconduction nanotubes as a channel. Because of its tiny size, the nanotube FET should switch reliably using much less power than a silicon-based device. Theorists predict that a truly nanoscale switch could run at clock speeds of one terahertz of more than 1000 times as fast a processors available today.



(a) (b)

Figure 2: Nanotube Field-effect Transistor from IBM.
(a) actual nanotube FET
(b) closed section of the nanotube FET

There are three ways to grow nanotubes, "zap", "bake" and "blast". In my research, the way of bake, we called chemical vapor deposition (CVD), will be used to grow the nanotubes. This CVD was used to make nanotubes for the first time in Japan. Duke University recently invented a porous catalyst that they claim can convert almost all the carbon in a feed gas to nanotubes. Stan Ford University have been able to control where the tubes from and have been working to combine this controlled growth with standard silicon technology. The growth temperature is typically in the rage 500-700°C. At these temperatures the carbon atoms dissolve in the metal nanoparticles that eventually become saturated. The carbon then precipitates to form solid carbon tubes, the diameters of which are determined by the size of the metal particles in the catalyst.

The problem of this project is that we don't have any experience to grow carbon nanotubes at RIT. We don't have any special equipment for only growing carbon nanotubes. Therefore, we are going to make our own CVD equipment for carbon nanotube growing system.

A CVD reactor is a chamber in which gasses at high temperature and controlled pressure undergo chemical reactions that result in growing a thin film on a solid surface (called the substrate) inside the reactor. this CVD reactor can be divided by 3 sections, the gas distribution system, reactor zone, and exhaust system, Figure 3. The major difficulties of CVD research have to do with understanding the complex brew of chemical reactions that occur as the source gasses diffuse toward the substrate. The gasses decompose into fragment molecules, which in turn react with each other and with the unreacted source gas. Some of the fragments stick to the surface, where they recombine to produce a film.

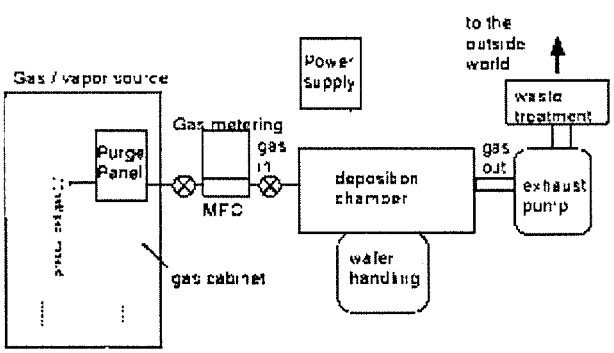


Figure 3: Basic Structure of CVD Reactor

Most Gases and vapors in CVD are for practical purposes "ideal".

$$PV = NRT \qquad (1)$$

P is pressure in Pascal, V is volume in m3, N is number of moles in gram, R is universal gas constant (=8.3 Joules/mole K), and T is absolute temperature in K. Gas flows are usually measured and reported as standard liters per minute (SLPM) or standard cubic centimeters per minute (SCCM). Both measure gas volume at 0 °C, and 1 atmosphere, these are measures of MOLAR flow. In most CVD applications absolute temperature varies modestly (factors of 2 to 3) whereas pressure varies tremendously large volume expansions occur that is a few cubic centimeters of input gas at atmospheric pressure can become many liters of gas at chamber operating pressure.
If we know the geometry, gas flows and composition, and the speed of the reactions at the surface, we can make simple estimates of what is happening inside, using the assumption of a "Zero-dimensional" reactor (simplest non-trivial transport analysis). Concentrations are the same everywhere in the reactor, no gradients.

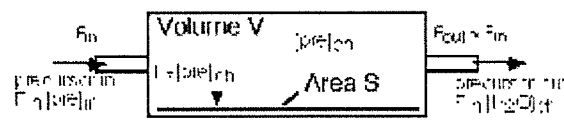


Figure 4: Zero-dimensional theory

From Figure 4, "pre" is precursor chemical for deposition, "[pre]" is concentration (moles/cm3, moles/m3, moles/liter, as convenient), "F" is volume flow (e.g. m3/second), "Ks" is surface reaction rate constant (units of velocity, e.g. cm/second or m/second), "ch" is concentration in chamber, and "in" is inlet concentration. Therefore, the utilization (X) equation can be as equation (2).

$$X = \frac{Moles(pre)_{in} - Moles(pre)_{out}}{Moles(pre)_{in}} \qquad (2)$$

When X is approached to zero, it becomes " differential" reactor that concentration is same as inlet concentration. When X is approached to one, it becomes "Starved" reactor that has large gradients in concentration.

Viscous flow equation, equation (3), can be used to calculate effective speed of roughing chamber where the C_1 is volume of chamber and C_2 is the volume of roughing line.

$$\frac{1}{S_{eff}} = \frac{1}{Sp(MP)} + \left(\frac{1}{C_1} + \frac{1}{C_2}\right) \qquad (3)$$

Also, the molecular flow equation, equation (4), can be used to calculate effective speed of high-vac pumping

$$\frac{1}{S_{eff}} = \frac{1}{Sp(HVP)} + \left(\frac{1}{C_1}\right) \qquad (4)$$

2. Chemical Vapor Deposition (CVD) Reactor

By the supports of department of Chemistry and Physics of Rochester Institute of Technology, CVD reactor can be built in the Physics Research Laboratory in the Gosnell Building (RIT building #8). Parts from the used but cleaned and equipments from chemistry department of RIT were used and supported during designing and building CVD reactor.

A. Design

CVD reactor was designed that followed by some specification, table 1 and figure 5.

Table 1: Specification of CVD reactor

Mechanical Pump Speed		2.2 m^3/hr
Roughing Chamber	Diameter	1.5”
	Length	35.43”
Roughing Line	Diameter	0.5”
	Length	24”
Gas	Argon	Max 1 l/min
	Methane	Max 1 l/min

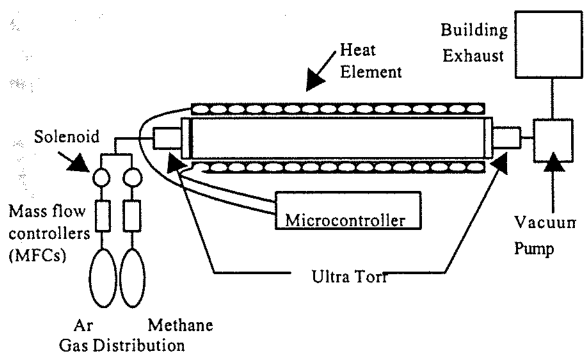
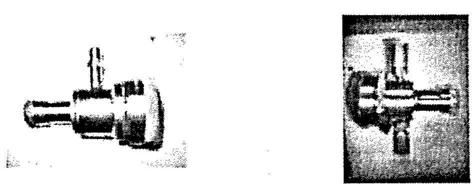


Figure 5: Diagram of CVD Reactor

End caps were designed first. This end caps are called “Ultra Torr”, Figure 6, which can make tube easily in vacuum. Also, the tube was designed to fit this end caps.



(a) Front (b) back

Figure 6: End Caps (Ultra Torr)

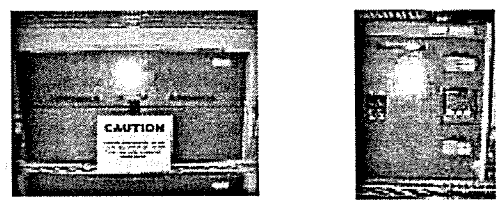
These end caps have 1.5 inches diameter of tube contact and 0.5 inches diameter of input of front and output of back end caps. Therefore, 1.5 inches diameter tube and 0.5 inches line tubes for input and output of gas into the chamber were designed.

The volume of Roughing Chamber can be calculated as equation (5). C1 is the volume of chamber and C2 is the volume of roughing line.

$$C = \pi * \frac{Diameter}{2} * Length \quad (5)$$

Therefore, C1 is 250.44 in3, and C2 is 4.7 in3. The effective pumping speed (S_{eff}) can be calculated as equation (3) is 4.3 in3/min that is .0043 m3/hr.

The chamber tube is located inside of container, Figure7, that has heater elements and thermocouples. This container was designed to have 3 zones, Load, center, and source. These thermocouples at each zone connected to the microcontroller, Figure 7, that can control the heater of each zone.



(a) Container of heater element (b) Microcontroller

Figure 7: Heater control equipments

In the gas distribution area, all gases were connected with mass flow controllers (MFC) and solenoids, figure 8. These MFC were designed to control the gas rate in l/min. The purpose of using solenoid is that can protect from back flow from tube and make sure that all unnecessary gases are blocked.

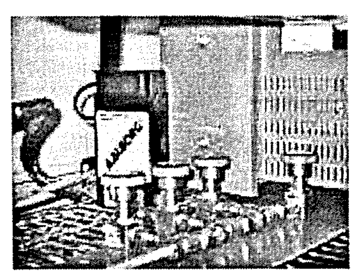


Figure 8: Mass Flow Controller and Solenoids

Due to slow gas pumping was needed, the slow mechanical pump was used, figure 9, with 2.2 m^3/hr speed. This mechanical pump is dry pump not oil pump because

the methane was used to flow through this pump that can make some hazardous acting with oil.

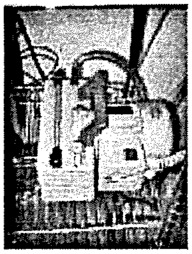


Figure 9: Mechanical Pump

This mechanical pump is connected to the building exhaust system, figure 10. The building Exhaust system is already built in this Lab. Therefore, just connect line from the pump to this system is just needed. This system was designed to exhaust all output gases to outside building.

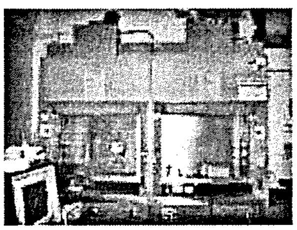


Figure 10: Building Exhaust System

B. Results and Observation

All equipments were assembled and tested as CVD Reactor for growing nanotubes, figure11. The actual size of tube was different from design because design was by scale of inches but tube distributors used metrics; therefore, the designed-tube cannot be found. The diameter of actual tube was 3 inches and length of tube was 60.43 inches. The volume of tube is 284.77 cubic inches. The effective speed is change to 17.53 cubic inches per minutes that is four times faster than designed speed, but it is still slow speed that CVD reactor needs.

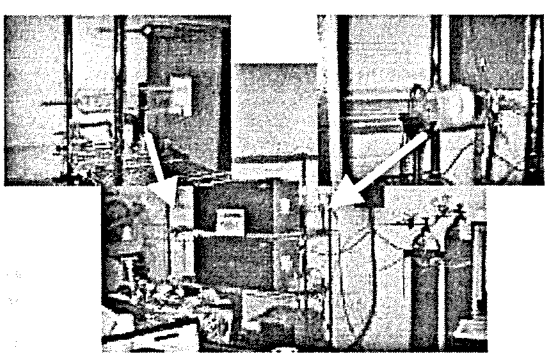


Figure 11: Actual CVD Reactor

The ramping up temperature rate was observed as Figure 11. The rates of ramping up temperature were shown as table 2.

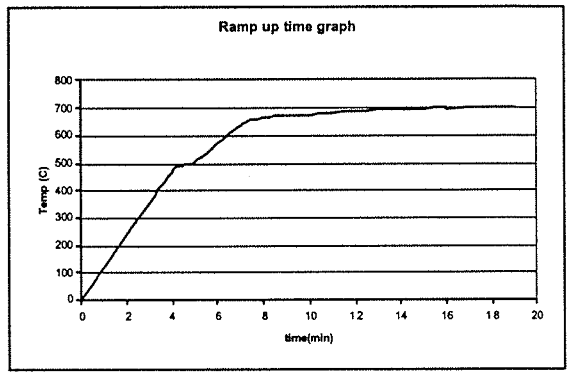


Figure 12: Temperature vs. Time Graph

Table 2: Ramp Up Time Rate Chart

Temperature Rage(°C)	Ramp Up Rate(°C/min)
0-500	125
500-650	21
650-700	3.85

Temperature was ramped up very fast as 125 °C per minutes, but it slowed down when temperature reached at 500 °C. For 8 minutes of ramp up time, temperature was already reached to 650 °C; therefore, approximately 10 minutes of ramp up time was needed to reach up to 700 °C.

3. GROWING THE SAMPLE OF CARBON NANOTUBES

10 sccm of Methane and 90 sccm of Argon flow at 700°C for 20 min were used for recipe of growing sample of carbon nanotubes. Two runs were performed for this project. At this time multi-Walled Carbon Nanotubes or garphene structure was expected being grown on top of the catalytic film.

A. Results and Observation

From the first run, there were only catalyst metal, figure13, that suppose form carbon nanotubes or graphene structure, grew on the silicon. This film was observed as defect from moisture in the lab because these films' adhesion was not well and color was dark gray. The suggestion was using longer dehydrate time without ramp temperature up; therefore, gases were flew for around one hour with out ramping temperature up that may get rid of moisture inside of chamber tube.

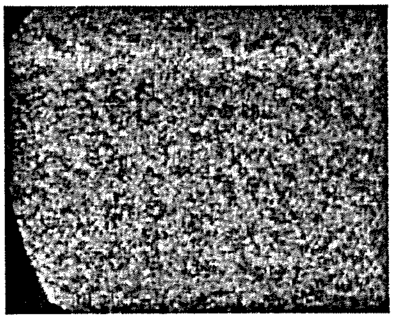
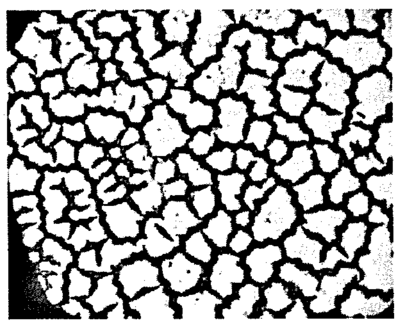
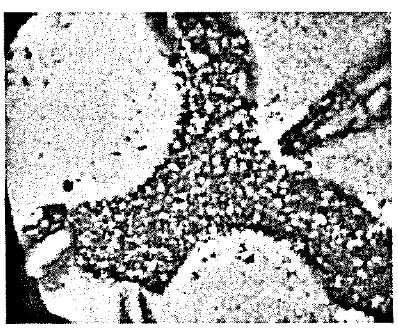


Figure 13: The result film deposition from first run

After second run, the same film as the first run was observed on the top of the silicon, but at the end of the silicon, there were curl structure of catalyst metal were observed. From the microscopic observation, the graphene structure were grew under this catalyst metal, figure 14. From my research, the graphene structure can grow on the catalyst film, but this case showed that if there were gaps between silicon and catalyst film, graphene can grows under the catalyst film.



(a) Curl catalyst film



(b) graphene structure

Figure 14: The result film deposition from second run

4. CONCLUSION

CVD Reactor for growing Carbon Nanotubes was designed and built in RIT. This CVD Reactor was not built as designed because of the chamber tube, but it worked and got expected result. This CVD Reactor proved that it could grow carbon nanotubes because it already made graphene structure. But there will be some improvement process needed for forming carbon nanotubes from this graphene structure or catalytic film. In the future, the specific, high yield, possibly phase pure, single and multi-wall carbon Nanotubes can be grown, and nano-electronic devices can be fabricated in RIT.

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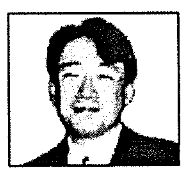

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