US 20080279754A1

(19) **United States**

(12) **Patent Application Publication**

(10) **Pub. No.: US 2008/0279754 A1**

(43) **Pub. Date: Nov. 13, 2008**

Allara et al.

(54) **INDUCED ELECTRICAL PROPERTY CHANGES IN SINGLE WALLED CARBON NANOTUBES BY ELECTROMAGNETIC RADIATION**

(75) Inventors: **David Allara**, State College, PA (US); **Min Chen**, Arlington, MA (US); **Don Henley**, Denton, TX (US); **Timothy James Imholt**, Carrollton, TX (US); **James Andrew Roberts**, Krum, TX (US)

Correspondence Address:
JACKSON WALKER LLP
901 MAIN STREET, SUITE 6000
DALLAS, TX 75202-3797 (US)

(73) Assignees: **Penn State Research Foundation**; **University of North Texas**

(21) Appl. No.: **11/712,686**

(22) Filed: **Mar. 1, 2007**

Related U.S. Application Data

(62) Division of application No. 10/936,007, filed on Sep. 7, 2004, now abandoned.

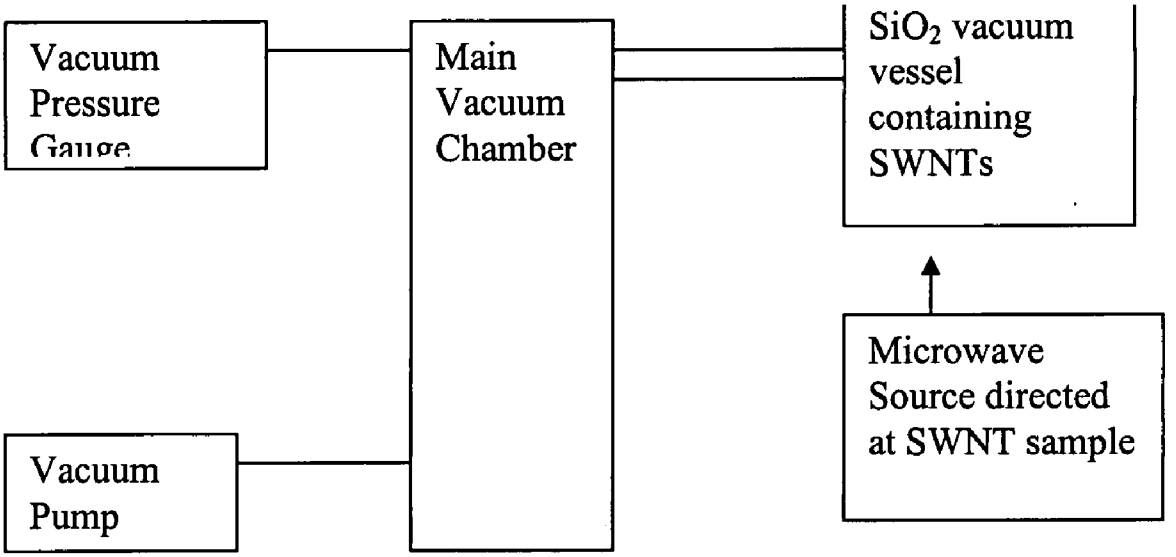
Publication Classification

(51) **Int. Cl.**
D01F 9/12 (2006.01)

(52) **U.S. Cl.** **423/447.2**; 423/447.1; 977/742

(57) **ABSTRACT**

In the apparatus and process of the present invention, it is possible to fabricate CNTs with specific diameters and morphologies. The morphology selection can yield samples of pre-selected diameter configurations making it possible to take a sample of SWNTs produced by any synthesis technique and induce a morphology change that causes the sample to be either all conductive, all narrow band gap semiconductive or wide band gap semiconductive, within a given nanotube rope.



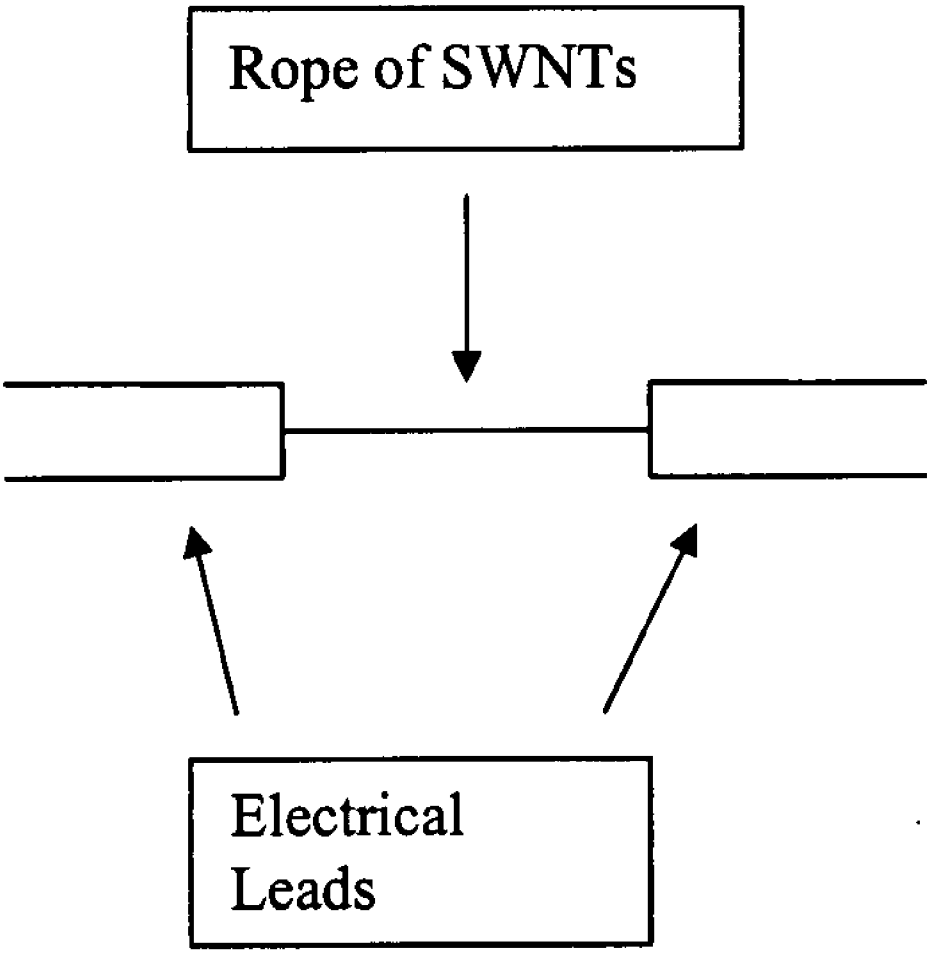


FIGURE 1

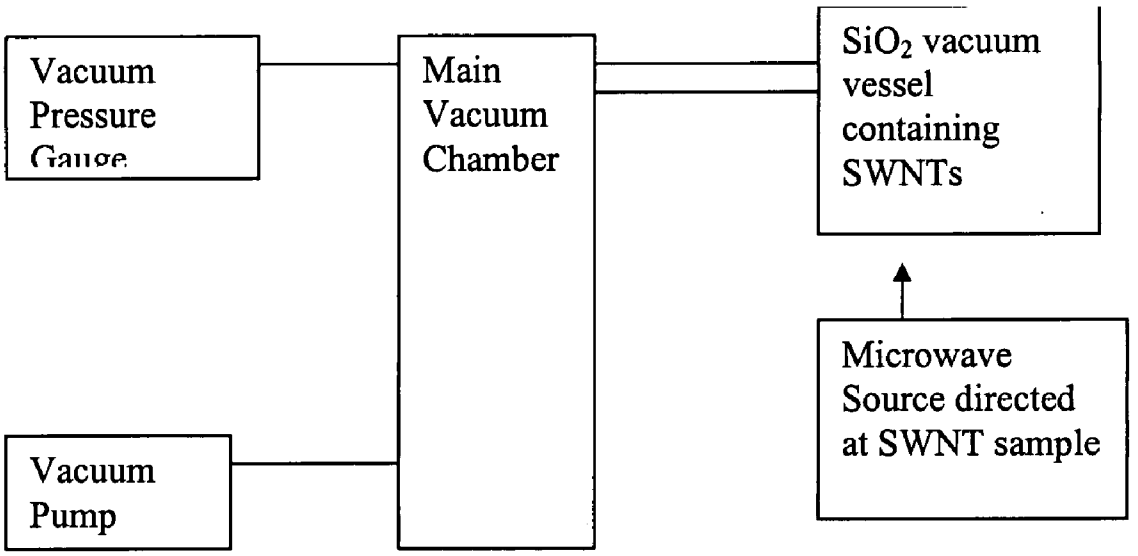

Vacuum Pressure Gauge
Main Vacuum Chamber
SiO_2 vacuum vessel containing SWNTs
Microwave Source directed at SWNT sample
Vacuum Pump

FIGURE 2

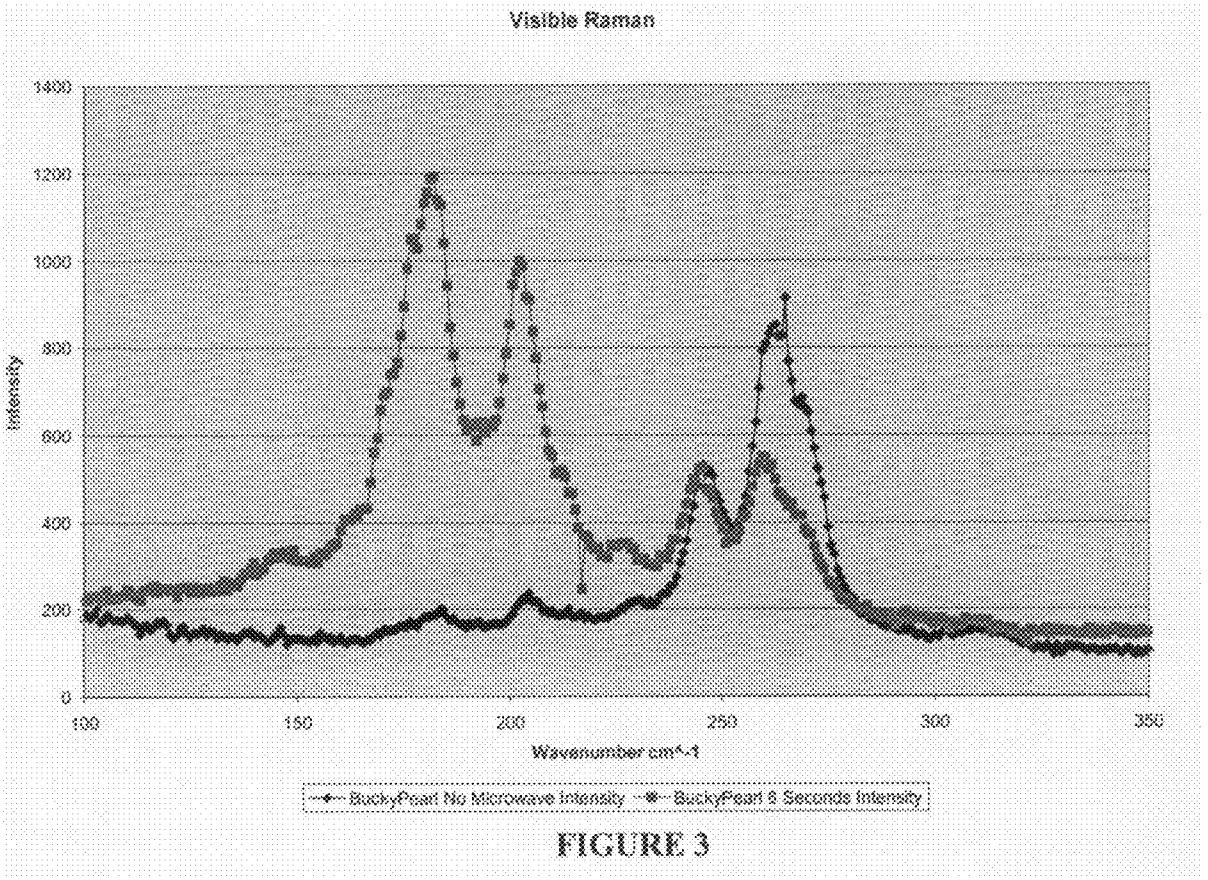

Visible Raman
1400
1200
1000
800
600
400
200
0
Intensity
100
150
200
250
300
350
Wavenumber cm^-1
BuckyPearl No Microwave Intensity
BuckyPearl 5 Seconds Intensity

FIGURE 3

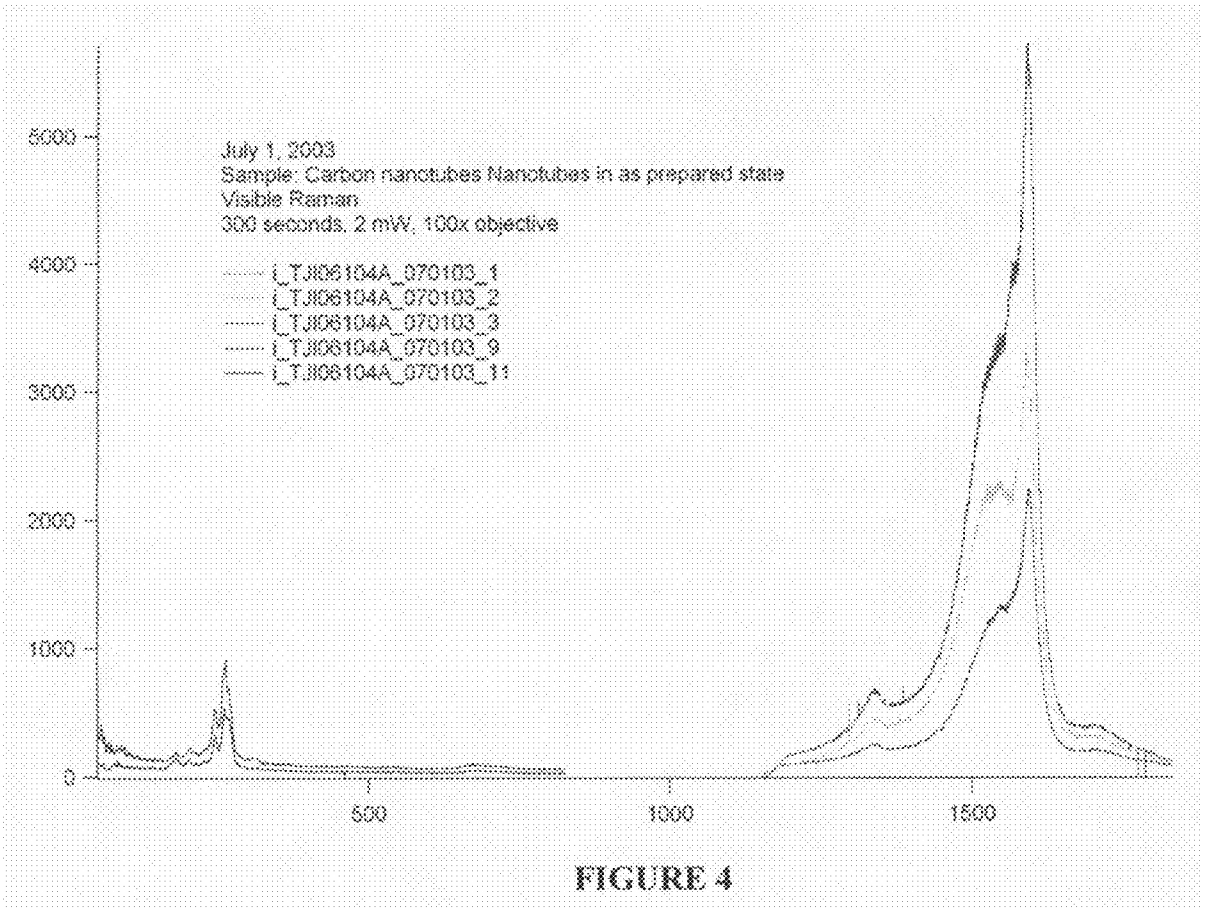

July 1, 2003
Sample: Carbon nanotubes Nanotubes in as prepared state
Visible Raman
300 seconds, 2 mW, 100x objective
I_TJI06104A_070103_1
I_TJI06104A_070103_2
I_TJI06104A_070103_3
I_TJI06104A_070103_9
I_TJI06104A_070103_11
5000
4000
3000
2000
1000
0
500
1000
1500

FIGURE 4

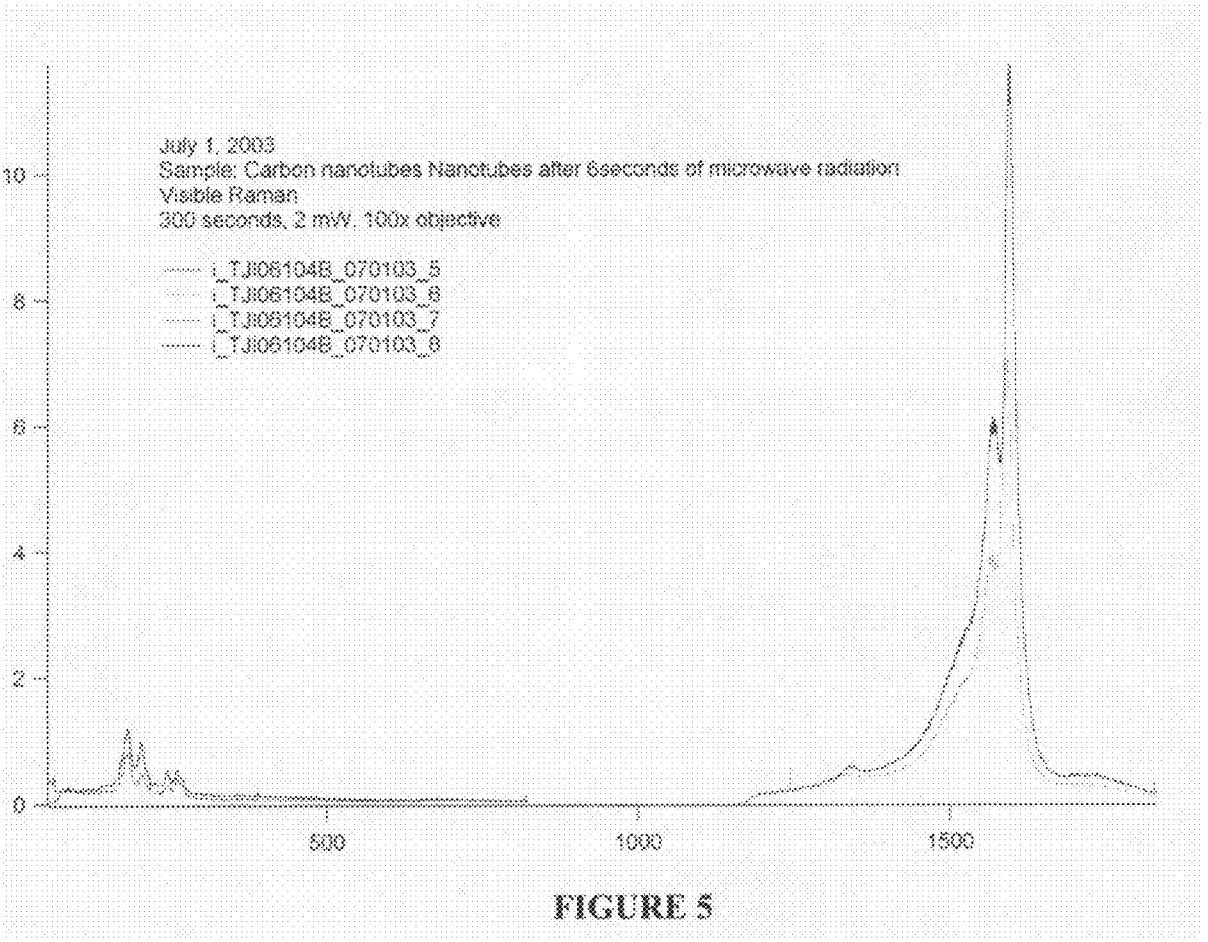

July 1, 2003
Sample: Carbon nanotubes Nanotubes after 6seconds of microwave radiation
Visible Raman
300 seconds, 2 mW, 100x objective
_TJI06104B_070103_5
_TJI06104B_070103_6
_TJI06104B_070103_7
_TJI06104B_070103_8
10
8
6
4
2
0
500
1000
1500

FIGURE 5

INDUCED ELECTRICAL PROPERTY CHANGES IN SINGLE WALLED CARBON NANOTUBES BY ELECTROMAGNETIC RADIATION

BACKGROUND OF THE INVENTION

[0001] Carbon nanotubes ("CNTs") were first observed in their multi-walled variety by Sumio Iijima at the NEC fundamental research laboratories. Multi-walled carbon nanotubes ("MWNT") can be thought of as a series of pipes within one another with anywhere from two to hundreds of layers. One of the many unique things about these carbon pipes is that their physical size is on the order of tens to hundreds of nanometers. MWNTs can be synthesized in a variety of methods such as arc discharge and laser ablation. Research on the properties of MWNTs and their synthesis eventually led to the observation of single-walled carbon nanotubes ("SWNTs"). SWNTs are pipes made of carbon on the scale of 0.5 nanometers to 5 nanometers. There are a number of different synthesis techniques to obtain SWNTs but the products of these processes and their properties remain very similar. While the structure of MWNTs are unique and interesting, SWNTs have received the majority of attention from researchers due to additional unique properties as compared to MWNTs.

[0002] The first observation of the SWNT was also recorded and published by Sumio Iijima and his coworkers at the NEC fundamental research laboratory. The discovery of SWNTs was made contemporaneously and independently in the United States. The structure of SWNTs is essentially that of a rolled up sheet of graphite which forms a very small, thin cylinder with no seam, and which is typically, although not always, closed at both ends. The lengths and diameters of SWNTs depend on a variety of conditions during the synthesis processes. The lengths of SWNTs are typically on the order of micrometers with diameters greater than 10 nanometers. SWNTs are therefore a novel pseudo one-dimensional material having many unique properties. During synthesis, SWNTs do not form as individual nanotubes but as "ropes" of nanotubes. These ropes appear just as normal ropes do in the macroscopic world, except that the strands are comprised of SWNTs and the overall diameter of the rope is typically less than 100 nanometers. Further, the ropes can be synthesized to be as small as 20 nanometers. These ropes are held together by an intermolecular Van der Waals force. Inside the ropes there are a plurality of different chirality and diameters of SWNTs. These different characteristics will cause the SWNTs to have various differing electrical properties such as semiconducting or conducting. A mixture of the two types within the rope will restrict the individual rope from being used as a semiconductor. If a rope comprises just one type of CNT (e.g., semiconducting), then it could be used as a semiconductor in an electronic device. The semiconductive nanotubes inside the ropes have electrical properties which allow them to be used in place of the more traditional silicon semiconductors. However, the ropes are very difficult to separate into their individual nanotube components. Separated nanotubes have only recently become available, although they are available in very small quantities. The scarcity and cost of the separated nanotubes has limited the ability of researchers to build nanotube components into electronics.

[0003] What is desired is an apparatus and process for fabricating CNT ropes that contain only semiconductive nanotubes that can be used as semiconductor devices in a variety of electronic devices and systems. Semiconductive nanotubes would have several advantages in addition to their semiconductive electrical properties. Semiconductive nanotubes have a reduced physical size over silicon devices and semiconductive nanotubes can handle much higher temperatures before breaking down. This makes them ideal for use in high performance devices.

BRIEF DESCRIPTION OF THE DRAWINGS

[0004] FIG. **1** is a schematic of a rope of SWNTs between two electrical leads in a device.

[0005] FIG. **2** is a schematic of the current apparatus of the present invention.

[0006] FIG. **3** is a plot of Raman Breathing Modes of SWNT before and after microwave irradiation using laser excitation at a frequency of 514 nm and power of 2 mW.

[0007] FIG. **4** is a plot of a SWNT sample Raman Spectra that has not been exposed to microwave radiation of any form.

[0008] FIG. **5** is a plot of a SWNT sample Raman Spectra that has been exposed to 6 seconds of microwave radiation at 2.45 GHz and 420 Watts of power.

SUMMARY OF THE INVENTION

[0009] It is generally known to those skilled in the art that to determine the nature of a particular individual nanotube as a conductor or a semiconductor, the diameter of the nanotube under consideration must be determined and then a comparison made with experimental results in known literature made. It is also generally known that if a sample of CNTs are sufficiently heated, their diameters will increase due to the coalescence of two neighboring nanotubes. Previously only exact doubling and tripling of CNT diameters was seen and reported in the literature.

[0010] In the present invention, the changes in diameter of CNTs are not doublings but are more selective diameter changes, indicating that, using the apparatus and process of the present invention, it is now possible to select specific CNT diameters or morphologies. The morphology selection can yield samples of pre-selected diameter configurations, making it possible to take a sample of SWNTs produced by any synthesis technique and induce a morphology change that causes the sample to be either all conductive, all narrow band gap semiconductive or wide band gap semiconductive, within a given nanotube rope. This novel apparatus and process of selectively which changes the diameter and morphology of a CNT rope is described in detail herein.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The interest in the CNTs was originally sparked by their physical size. The dimension at which CNTs exist is essentially a crossover point between the scale typically seen in consumer electronic devices and the molecular and atomic world. The small size of CNTs has attracted a great deal of interest in their electronic properties. It has been shown that the various diameters of SWNTs behave as both conductors and semiconductors. This fact, coupled with the additional fact that their thermal conductivity is high as compared to many other materials, suggests that if CNTs are used in electronic devices the lifespan of the devices could be greatly increased. The semiconductive type of CNT has been shown in some cases to perform in a manner similar to a silicon semiconductor. Advantageously, the similarity and behavior of CNTs to semiconductor devices, coupled with their much

smaller size, suggest an increase in overall processing speed of the associated electronics. This has been demonstrated with a single molecule sized transistor.

[0012] However, many difficulties have been encountered in connection with CNT device fabrication. One difficulty with CNT device construction is that a single nanotube must be disentangled from a rope of nanotubes. Further, the removed nanotube must be of the desired type of semiconductive nanotube. Then, this semiconductive nanotube must be placed in the correct location on the device to achieve the desired result. Because of the scale of these structures, these steps are difficult and time consuming.

[0013] Much research has been undertaken into the synthesis process of SWNTs in hope of fabricating a nanotube of just one type, semiconducting or conducting. Even if such a synthesis process develops, it may not be commercially viable due to low production yields typical of these processes. However, it is possible to fabricate CNT ropes in patterns and in chosen locations on a substrate. Thus, what is desired is a process and apparatus to change the CNT ropes, once grown, to contain CNTs of only one type. In such case, a molecular device could be fabricated. The present invention comprises an apparatus and process for achieving this objective. Using this invention, a semiconductor device can be fabricated by growing a CNT rope between two leads and then forcing the CNTs to be only of one type CNT. This method of devising a semiconductor device is shown in FIG. **1**. FIG. **1** is an illustration of a rope of SWNTs between two electrical leads in a device.

Typical Apparatus and Technique.

[0014] The apparatus for implementing the process of the present invention comprises a vacuum system capable of reaching 10-5 torr or lower pressures (the lower the pressure the more optimal the result as extensive oxidation of the sample is prevented), and a microwave source capable of generating a frequency of 2.45 GHz, at 400 Watts power, although a range of frequencies from 2 GHz to 90 GHz with power levels from 1 Watt to several thousand Watts can be used to achieve the objectives of the present invention. In this apparatus, the CNTs are exposed to a controlled amount of time, power and frequency of microwave radiation which causes a dramatic rise in temperature. Depending on the exposure time to this microwave source, the diameters of the nanotubes will change to become larger than in the original sample. By adjusting the frequency, power level and length of time, any sample of SWNTs can be shifted to having semiconductor properties or conductive properties. FIG. **2** provides a graphical description of one embodiment of the apparatus employed to achieve the objectives of the present invention. Numerous other embodiments can be used so long as they comprise, in general, a vacuum system and a microwave source. The actual configuration that causes this morphology can vary as described above. As seen in FIG. **2**, the microwave source is depicted external to the vacuum system. It is not a requirement that the microwave source be external to the vacuum system. The microwave source, along with the SWNTs, may both be internal to the main vacuum chamber. Further, the nanotube samples can also be placed in a microwave resonant cavity increasing the efficiency of the process.

Previous Diameter Effects Seen

[0015] Coalescence of carbon nanotubes in general is not a new phenomena, however, the type of coalescence obtained by the process of the present invention is novel. This effect was observed prior to 1991. The prior work involved fullerene molecules, which are the building blocks of nanotubes, coalescing into larger molecules. This phenomena was later seen in carbon nanotubes. In 1997, a mechanism was offered for these previous observations. It was observed that if a nanotube sample is heated in a controlled environment to 1400° C. for several hours, a small portion of the sample will exactly double in diameter and an even smaller portion of the sample will triple in diameter. If the experiment is performed in a hydrogen environment, the yield of diameter doubled nanotubes can be increased, indicating that a type of free radical chemistry is the mechanism for the phenomena. Nonetheless, the effect of diameter doubling still takes several hours, regardless of whether the heating is performed in a vacuum or in a hydrogen environment.

[0016] The work performed in 1997 suggests two explanations for the susceptibility of narrow diameter nanotubes to undergo a diameter change. The first is that the reactivity of a curved grapheme sheet increases as the tube diameter becomes smaller. This is because the curvature introduces more of an s-orbital effect into the π orbitals of the carbon atoms. The second is the coalescence of smaller diameter nanotubes is an exothermic reaction due to a release of strain energy.

Current Effects

[0017] In the process of the present invention, when a sample of carbon nanotubes is exposed to an appropriate frequency and power level of microwave radiation, a diameter increase accompanied (although not as a diameter doubling) by a chirality shift is observed. FIG. **3** shows the Raman breathing modes of SWNT before and after microwave irradiation using laser excitation at a frequency of 514 nanometers and a power of 2 milliwatts. In FIG. **3** the Raman spectra breathing modes can be seen for nanotubes not exposed to microwave irradiation and Raman breathing modes for nanotubes that have been exposed to only 6 seconds of microwave irradiation. This exposure is much shorter than what was required previously. If these breathing modes are compared with the results of well known techniques, it can be seen that the diameter change is not a doubling effect but rather a diameter change from an average of 1.0 nanometer to 1.5 nanometer (in the present case), although this is not the only diameter and chirality shift observed. This diameter increase is associated with a chirality shift, causing the nanotubes to consist of a much larger number of semiconducting nanotubes than existed prior to the exposure to the microwave field. This can be used to produce samples that are completely semiconductors or purely conductors.

[0018] FIGS. **4** and **5** show further Raman evidence for this shift in morphology and electrical properties. In FIG. **4** a plot of the Raman spectra of a SWNT sample produced by the HiPco process in a purified form, known as buckypearl, is shown. This sample has not been exposed to microwave radiation of any form. In FIG. **5** a plot of a Raman spectra of a SWNT sample produced by the HiPco process in purified

form, known as buckypearls, is also shown. Unlike the results of FIG. **4**, the sample of FIG. **5** has been exposed to 6 seconds of microwave radiation at 2.45 GHz and 420 Watts of power. Frequencies from 2 GHz to 100 GHz can be used to produce this effect.

[0019] The overall speed and efficiency of diameter changes can be greatly increased with the microwave process. Through selection of appropriate frequency and power levels of microwave radiation, in addition to environmental conditions, the resulting morphology of the CNT sample can be selected to whatever state is desired, e.g., narrow band gap semiconductor, wide band gap semiconductor or conductor. The advantage of the present invention is that it provides overall speed and selection capabilities improvements over other types of heating techniques.

[0020] The innovative teachings of the present invention are described with particular reference to the apparatus and process of selectively changing the diameter and morphology of a CNT rope using specific microwave frequencies and power settings. It should be understood and appreciated by those skilled in the art that the selective change in diameter and morphology described herein in order to obtain a semiconducting CNT provides only one example of the many advantageous uses and innovative teachings herein. Various alterations, modifications and substitutions can be made to the apparatus and process of the disclosed invention without departing in any way from the spirit and scope of the invention.

REFERENCES

[0021] Sumio Iijima, *Nature,* 354, 56-58, (1991).
[0022] C. H. Kiang, et al., *Carbon,* 33, 903 (1995).
[0023] J. M. Lambert, et al., *Chem. Phys. Lett.,* 215, 509, (1994).
[0024] T. Guo, et al., *Chem. Phys. Lett.,* 243, 49, (1995).
[0025] M. Yudasaka, et al., *Chem. Phys. Lett.,* 278, 102 (1997).
[0026] H. M. Cheng, et al., *Appl. Phys. Lett.,* 72, 3282, (1998).
[0027] S. Seraphin, *J. Electrochem. Soc.,* 142, 290 (1995).
[0028] X. Zhao, et al., *Carbon,* 35, 775 (1997).
[0029] Sumio Iijima, and Toshinari Ichihashi, *Nature,* 363, 603-605, (1993).
[0030] K. Tanaka, H. Kobayashi, M. Okada, M. Kobashi, and T. Yamabe, *Intern. J. Quantum Chem.,* 42, 45, (1992).
[0031] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer, and R. E. Smalley, *Science,* 273, 483, (1996).
[0032] J. W. G. Wildoer, *Nature,* 391, 59, (1998).
[0033] T. G. Dietz, et al., *Journal of Chemical Physics,* 74, 6511-6512 (1995).
[0034] M. S. Dresselhaus, *Physics World,* 18, (1996).
[0035] M. S. Dresselhaus, G. Dresselhaus, A. Jorio, A. G. Souza Filho, R. Saito, *Carbon,* 40 (2002) 2043-2061.
[0036] Y. Chai, et al., *J. Phys. Chem.,* 95 (1991) 7564.
[0037] C. Yeretzian, K. Hansen, F. Diederich, and R. L. Whetten, Nature 359 (1992) 44.
[0038] P. Nikolaev, A. Thess, A. G. Rinzler, D. T. Colbert, R. E. Smalley, *Chemical Physics Letters,* 266 (1997) 422-426.
[0039] M. S. Dresselhaus, G. Dresselhaus, A. Jorio, A. G. Souza Filho, and R. Saito, *Carbon,* 40, (2002) 2043-2061.

1-2. (canceled)

3. A process for selectively changing the diameter and morphology of a carbon nanotube, comprising:
placing a carbon nanotube in a vacuum area;
creating a vacuum in the vacuum area; and
directing a microwave at a selected frequency and power setting at the carbon nanotube.

4. The process of claim **3**, further comprising being adapted for fabricating carbon nanotube semiconducting devices.

5. The process of claim **3**, wherein the vacuum is at a pressure of about 10^{-4} to 10^{-9} torr.

6. The process of claim **3**, wherein the vacuum is at a pressure of about 10^{-5} torr.

7. The process of claim **3**, wherein the microwave has a field of about 1.01×10^{-5} eV.

8. The process of claim **3**, wherein the microwave emits microwave radiation with a frequency of between 0.1 GHz and 100 GHz with a power output of between 0.001 Watt and 1,500 Watts.

9. The process of claim **23**, wherein the microwave emits microwave radiation with a frequency of about 2.45 GHz at about 400 Watts.

10. The carbon nanotube produced by the method of claim **3**.

11. A process for selectively changing the diameter and morphology of a carbon nanotube, comprising:
placing a carbon nanotube in a vacuum area;
creating a vacuum with a pressure of about 10^{-4} to 10^{-9} torr in the vacuum area; and
directing a microwave frequency of between 0.1 GHz and 100 GHz and a power output of between 0.001 Watt and 1,500 Watts at the carbon nanotube.

12. The carbon nanotube produced by the method of claim **11**.

* * * * *