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AN OVERVIEW ON CARBON NANOTUBES

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ABSTRACT:

In different fields like semiconductors, field emission, conductive plastics, energy storage, conductive adhesives and connectors, molecular electronics, thermal materials carbon nanotubes are applicable. Carbon nanotubes are generally produced by three main techniques: arc discharge, laser ablation, chemical vapour deposition. In arc discharge, a vapour is created by an arc discharge between two carbon electrodes with or without catalyst. Nanotubes self-assemble from the resulting carbon vapour. In the laser ablation technique, a high-power laser beam impinges on a volume of carbon –containing feedstock gas (methane or carbon monoxide). At the moment, laser ablation produces a small amount of clean nanotubes, whereas arc discharge methods generally produce large quantities of impure material. In general, chemical vapour deposition (CVD) results in Multi Walled Nanotubes or poor quality Single Walled Nanotubes. The SWNTs produced with CVD have a large diameter range, which can be poorly controlled. But on the other hand, this method is very easy to scale up, what favours commercial production.

Keywords: *arc-evaporation synthesis, semiconductors, arc discharge, laser ablation, chemical vapour deposition*

[I] INTRODUCTION

1.1 Carbon Nanotubes

Carbon nanotubes are applicable in the field of nanotechnology, having simple in chemical composition but have particularly various applications. Carbon nanotube which is nothing but a fullerene related arrangement. It consists of a graphite layer rolled into a cylinder and closed at the either ends.It is fullerene related arrangement consist of graphite layers rolled into cylinders closed at either ends with caps.

1.2 Classification of Carbon Nanotubes

1.2.1 Single Walled Nanotubes

Most single-walled nanotubes (SWNT) have a diameter of close to 1 nanometer, with a tube length that can be many millions of times longer. The structure of a SWNT can be conceptualised by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder. SWNTs are an important variety of carbon nanotube. Single-walled nanotubes are likely candidates for miniaturising electronics.

1.2.2 Multi Walled Nanotubes

Multi-walled nanotubes (MWNT) consist of multiple rolled layers (concentric tubes) of graphene. Its individual shells can be described as SWNTs, which can be metallic or semiconducting. Because of statistical probability and restrictions on the relative diameters of the individual tubes, one of the shells, and thus the whole MWNT, is usually a zero-gap metal.

Double-walled carbon nanotubes (DWNT) form a special class of nanotubes because their morphology and properties are similar to those of SWNT but their resistance to chemicals is significantly improved.

1.3 Growth Mechanism

The growth mechanism is a subject of controversy, and more than one mechanism might be operative during the formation of CNTs. These mechanisms consists of three steps. First a precursor to the formation of nanotubes and fullerenes, C_2, is formed on the surface of the metal catalyst particle. From this metastable carbide particle, a rod-like carbon is formed rapidly. Secondly there is a slow graphitisation of its wall. Postulates that metal catalyst particles are floating or are supported on graphite or another substrate [1].

[II] MATERIALS AND METHODS

2.1 Arc Discharge

The carbon arc discharge method, initially used for producing fullerenes, is the most common and perhaps easiest way to produce carbon nanotubes as it is rather simple to undertake. Recent investigations have shown that it is also possible to create nanotubes with the arc method in liquid nitrogen[2].The discharge vaporizes one of the carbon rods and forms a small rod shaped deposit on the other rod. Producing nanotubes in high yield depends on the uniformity of the plasma arc and the temperature of the deposit form on the carbon electrode [3].

These properties affect the speed with which the carbon and catalyst molecules diffuse and cool, affecting nanotube diameter in the arc process. This implies that single-layer tubules nucleate and grow on metal particles in different sizes depending on the quenching rate in the plasma and it suggests that temperature and carbon and metal catalyst densities affect the diameter distribution of nanotubes[3].

2.1.1 Synthesis of SWNT

If SWNTs are preferable, the anode has to be doped with metal catalyst, such as Fe, Co, Ni, Y or Mo. A lot of elements and mixtures of elements have been tested by various scientists[4] and it is noted that the results vary a lot, even though they use the same elements. This is not surprising as experimental conditions differ.

2.1.1.1 Inert Gas

The most common problems with SWNT synthesis are that the product contains a lot of metal catalyst, SWNTs have defects and purification is hard to perform. On the other hand, an advantage is that the diameter can slightly be controlled by changing thermal transfer and diffusion, and hence condensation of atomic carbon and metals between the plasma and the vicinity of the cathode can control nanotube diameter in the arc process. This was shown in an experiment in which different mixtures of inert gases were used.

2.1.1.2 Optical Plasma Control

A second way of control is plasma control by changing the anode to cathode distance (ACD). The ACD is adjusted in order to obtain strong visible vortices around the cathode. This enhances anode vaporisation, which improves nanotubes formation. Combined with controlling the argon-helium mixture, one can simultaneously control the macroscopic and microscopic parameters of the nanotubes formed [5].

2.1.1.3 Catalyst

Knowing that chemical vapour deposition (CVD) could give SWNTs with a diameter of 0.6-1.2 nm, researchers tried the same catalyst as used in CVD on arc discharge. Not all of the catalysts used appeared to result in nanotubes for both methods. But there seemed to be a correlation of diameter of SWNTs synthesized by CVD and arc discharge [4-6].

2.1.1.4 Improvement of Oxidation Resistance

A strong oxidation resistance is needed for the nanotubes if they have to be used for applications such as field emission displays. Recent research has indicated that a modified arc-discharge method using a bowl-like cathode (see Figure 4), decreases the defects and gives cleaner nanotubes, and thus improves the oxidation resistance [7].

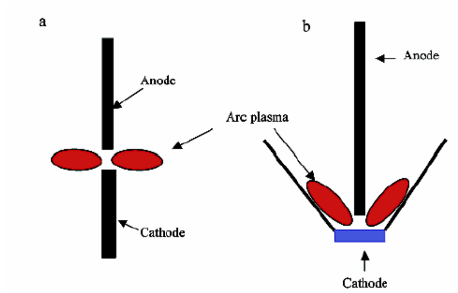

Fig. 1: Schematic drawings of the electrode set-ups for (a) The conventional and (b) The new arc discharge electrodes.

The Raman spectrum of the newly synthesised nanotubes shows that the nanotubes formed are cleaner and less defective compared with those synthesised by conventional methods.

2.1.1.5 Open Air Synthesis with Welding Arc Torch

Only a couple of years ago, researchers discovered that it was possible to form MWNTs in open air[8]. A welding arc torch was operated in open air and the process was shielded with an argon gas flow.

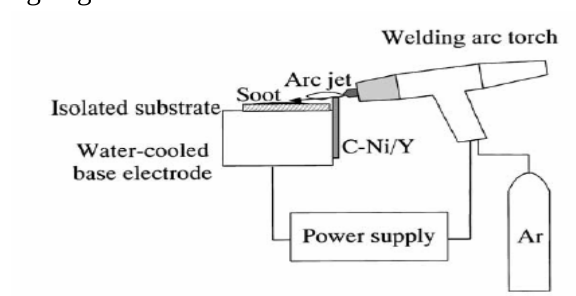

Fig. 2: Experimental set-up of the torch arc method in open air.

This method was modified for preparing SWNTs[9]. The torch arc aimed at the edge of the target and the soot was deposited on the substrate behind the target . There are two reasons for this fact. At first, because of the open air, the lighter soot will escape into the atmosphere. Secondly, the carbon vapour might be oxidised and emitted as carbon dioxide gas.[9].

2.1.2 Synthesis of MWNT

Both the electrodes are graphite, the main product will be MWNTs. But next to MWNTs a lot of side products are formed such as amorphous carbon, and some graphite sheets. Purifying the MWNTs means loss of structure and disorders the walls.

2.1.2.1 Synthesis in Liquid Nitrogen

A first, possibly economical route to highly crystalline MWNTs is the arc-discharge method in liquid nitrogen[2], with this route mass production is also possible.

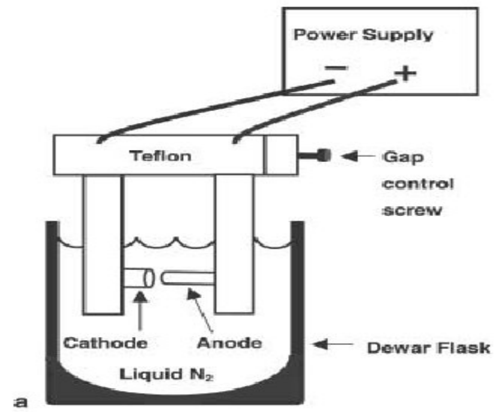

Fig. 3: Schematic drawings of the arc discharge apparatus in liquid nitrogen.

The content of the MWNTs can be as high as 70 % of the reaction product. Analysis with Auger-spectroscopy revealed that no nitrogen was incorporated in the MWNTs.

2.1.2.2 Magnetic Field Synthesis

Synthesis of MWNTs in a magnetic field[10] gives defect-free and high purity MWNTs that can be applied as Nano sized electric wires for device fabrication. In this case, the arc discharge synthesis was controlled by a magnetic field around the arc plasma.

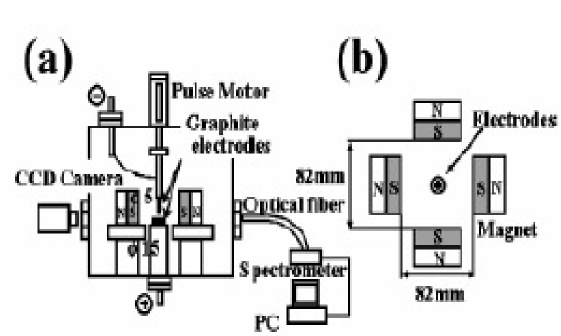

Fig. 4: Schematic diagram of the synthesis system for MWNTs in a magnetic field.

Pure graphite rods were used as electrodes. Highly pure MWNTs were obtained without further purification.

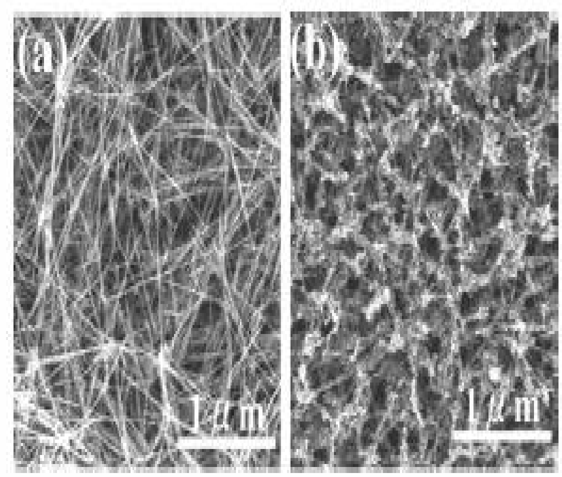

Fig. 5: SEM images of MWNTs synthesised (a) with and (b) without the magnetic field.

2.1.2.3 Plasma Rotating Arc Discharge

A second probably economical route to mass production of MWNTs is synthesis by plasma rotating arc discharge technique[11]. The centrifugal force caused by the rotation generates turbulence and accelerates the carbon vapour perpendicular to the anode. In addition, the rotation distributes the micro discharges uniformly and generates stable plasma..

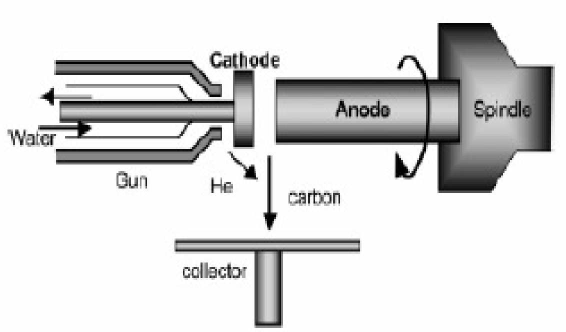

Fig. 6: Schematic diagram of plasma rotating electrode system.

2.2 Arc Discharge

Smalley's group[12] at Rice University reported the synthesis of carbon nanotubes by laser vaporisation. A pulsed [13-14] or continuous[15-16] laser is used to vaporise a graphite target in an oven at 1200 °C. The particles become that much coated with a carbon layer that they cannot absorb more and the nanotube stops growing. The SWNTs formed in this case are bundled together by van der Waals forces [18].

Subsequent laser pulses excite fullerenes to emit C_2 that adsorbs on catalyst particles and feeds SWNT growth. However, there is insufficient evidence to conclude this with certainty[18].

2.2.1 SWNT versus MWNT

The condensates obtained by laser ablation are contaminated with carbon nanotubes and carbon nanoparticles. In the case of pure graphite electrodes, MWNTs would be synthesized, but uniform SWNTs could be synthesized if a mixture of graphite with Co, Ni, Fe or Y was used instead of pure graphite. [15][18].

2.2.2 Ultra Fast Pulses from a Free Electron Laser (FEL) Method

Usually the pulses in an Nd:YAG system have width of approximately 10 ns, in this FEL system the pulse width is ~ 400 fs. The repetition rate of the pulse is enormously increased from 10 Hz to 75 MHz. The intensity of the laser bundle behind the lens reaches ~5 x 10^{11} W/cm^2, which is about 1000 times greater than in Nd:YAG systems[14].

2.2.3 Continuous Wave Laser-Powder Method

This method is a novel incessant, very productive laser-powder method of SWNT synthesis based on the laser ablation of uniform graphite and metallic catalyst. The introduction of micron-size particle powders, thermal conductivity losses are significantly decreased compared with laser heating of the bulk solid targets in known laser techniques. As a result, more effective utilization of the absorbed laser power for material evaporation was achieved [16].

2.3 Chemical Vapour Deposition

Chemical vapour deposition (CVD) synthesis is achieved by putting a carbon source in the gas phase and using an energy source such as a plasma to transfer energy to a gaseous carbon molecule. Carbon nanotubes will be formed if the proper parameters are maintained. Excellent alignment [19], as well as positional control on nanometer scale[20], can be achieved by using CVD. Control over the diameter, as well as the growth rate of the nanotubes can also be maintained. The appropriate metal catalyst can preferentially grow single rather than multi-walled nanotubes[1].

The catalyst is normally arranged by sputtering a transition metal onto a substrate and then using either chemical etching or thermal annealing to induce catalyst particle nucleation. Thermal annealing results in cluster formation on the substrate, from which the nanotubes will grow. Ammonia may be used as the etchant[19-22].

2.3.1 Plasma Enhanced Chemical Vapour Deposition

The plasma enhanced CVD method generates a glow discharge in a chamber or a reaction furnace by a high frequency voltage applied to both electrodes. Figure 14 shows a schematic diagram of a typical plasma CVD apparatus with a parallel plate electrode structure.

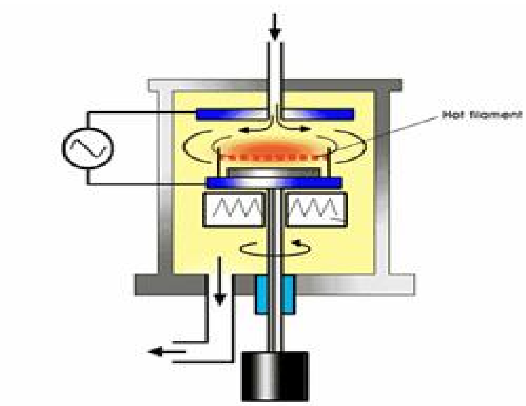

Fig.7: Schematic diagram of plasma CVD apparatus.

A substrate is placed on the grounded electrode. A carbon containing reaction gas, such as C_2H_2, CH_4, C_2H_4, C_2H_6, CO is supplied to the chamber during the discharge [23].

The catalyst has a strong effect on the nanotube diameter, growth rate, wall thickness, morphology and microstructure. Ni seems to be the most suitable pure-metal catalyst for the growth of aligned multi-walled carbon nanotubes (MWNTs)[24].

2.3.2 Thermal Chemical Vapour Deposition

Figure 15 shows a schematic diagram of thermal CVD apparatus in the synthesis of carbon nanotubes.

When growing carbon nanotubes on a Fe catalytic film by thermal CVD, the diameter range of the carbon nanotubes depends on the thickness of the catalytic film.The carbon nanotubes formed are multiwalled[25].

2.3.3 Alcohol Catalytic Chemical Vapour Deposition

Alcohol catalytic CVD (ACCVD) is a technique that is being intensively developed for the possibility of large-scale production of high quality single wall nanotubes SWNTs at low cost. In this technique, evaporated alcohols, methanol and ethanol, are being utilised over iron and cobalt catalytic metal particles supported with zeolite. The diameter of the SWNTs is about 1 nm. Figure 16 shows the ACCVD experimental apparatus.

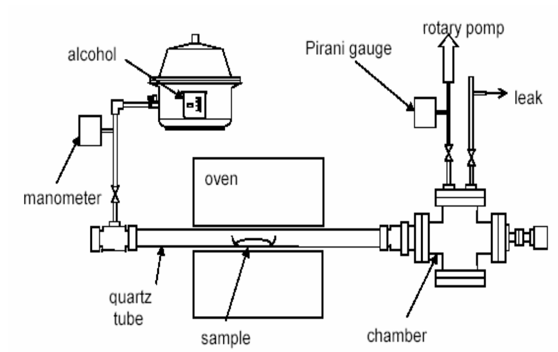

Fig. 8: ACCVD experimental apparatus.

The lower reaction temperature and the high-purity features of this ACCVD technique guarantee an easy possibility to scale production up at low cost. [26].

2.3.4 Vapour Phase Growth

Vapour phase growth is a synthesis method of carbon nanotubes, directly supplying reaction gas and catalytic metal in the chamber without a substrate[27].

Two furnaces are placed in the reaction chamber. Here, they are synthesised as carbon nanotubes.

The diameter of the carbon nanotubes by using vapour phase growth are in the range of 2-4 nm for SWNTs[28] and between 70 and 100 nm for MWNTs[27].

2.3.5 Aero Gel-Supported Chemical Vapour Deposition

In this method SWNTs are synthesised by disintegration of carbon monoxide on an aero gel-supported Fe/Mo catalyst. Because of the high surface area, the porosity and ultra-light density of the aero gels, the productivity of the catalyst is much higher than in other methods[29].. The optimal reaction temperature is approximately 860 ^{o}C[30].

2.3.6 Laser-Assisted Thermal Chemical Vapour Deposition

Laser-assisted thermal CVD (LCVD) a medium power, continuous wave CO_2 laser, which was perpendicularly directed onto a substrate, pyrolysis sensitised mixtures of $Fe(CO)_5$ vapour and acetylene in a flow reactor. The carbon nanotubes are formed by the catalysing action of the very small iron particles. Figure 9 shows the experimental set-up for laser-assisted CVD[31].

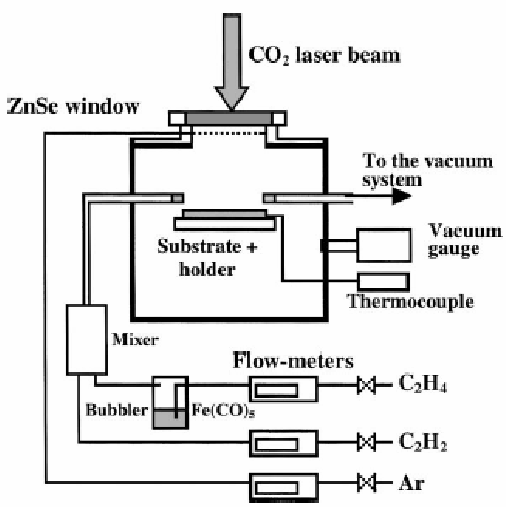

Fig.9: Experimental set-up for laser-assisted CVD.

By using a reactant gas mixture of iron penta-carbonyl vapour, ethylene and acetylene both single and multi-walled carbon nanotubes are produced. [31].

2.4 Flame Synthesis

This method is based on the synthesis of SWNTs in a controlled flame environment that produces the temperature, forms the carbon atoms from the inexpensive hydrocarbon fuels and forms small aerosol metal catalyst islands[35-37]. On these metal islands the SWNTs are grown in the same manner as in laser ablation and arc discharge.

These metal catalyst islands can be made in three ways. The metal catalyst (cobalt) can either be coated on a mesh[35], on which metal islands resembling droplets were formed by physical vapour deposition. These small islands become aerosol after being exposed to a flame. The second way[37] is to create aerosol small metal particles by burning a filter paper that is rinsed with a metal-ion (e.g. iron nitrate) solution. The third way is the thermal evaporating technique in which metal powder (e.g. Fe or Ni) is inserted in a trough and heated[36].

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[III] CONCLUSION

Lack of commercially feasible synthesis and purification methods is the main reason that Carbon Nanotubes are still not widely used nowadays. At the moment, nanotubes are too expensive and cannot be produced selectively. Some of the already known and upcoming techniques look promising for economically feasible production of purified Carbon Nanotubes.

At this moment, Laser Ablation produces the cleanest material, but the costs are still rather high. Arc Discharge can produce grams of low purity Nanotubes. The Chemical Vapour Deposition technique is still under development but preliminary results look promising, as do prospects of large scale Chemical Vapour Deposition.

REFERENCES

[1] Sinnot, S. B., Andrews, R., Qian, D., Rao, A. M., Mao, Z., Dickey, E. C., and Derbyshire, Chem.Phys.Lett., 315, (25-30), 1999

[2] Jung, S. H., Kim, M. R., Jeong, S. H., Kim, S.U., Lee, O. J., Lee, K. H., Suh, J. H., and Park, C. K., Applied Physics A-Materials Science & Processing, 76, (2), 285-286, 2003

[3] Ebbesen, T. W. and Ajayan, P. M., Nature, 358, (220-222), 1992

[4] Journet, C. and Bernier, P., Applied Physics A-Materials Science & Processing, 67, (1), 1-9, 1998

[5] Farhat, S., Hinkov, I., Chapelle, D. I., Fan, S. S., Li, G. H., and Scott, C. D., NASA Conference Publication, 2001

[6] Costa, Pedro, Xu, Cigang, Coleman, Karl, Sloan, Jeremy, and Green, Malcolm L H, 2002

[7] Huang, H. J., Marie, J., Kajiura, H., and Ata, M., Nano Letters, 2, (10), 1117-1119, 2002

[8] Takikawa, Hirofumi, Tao, Yoshitaka, Hibi, Yoshihiko, Miyano, Ryuichi, Sakakibara, Tateki, Ando, Yoshinori, Ito, Shigeo, Hirahara, Kaori, and Iijima, Sumio, AIP Conference Proceedings, 590, (Nanonetwork Materials), 2001

[9] Takikawa, H., Ikeda, M., Hirahara, K., Hibi, Y., Tao, Y., Ruiz, P. A., Sakakibara, T., Itoh, S., and Iijima, S., Physica B: Condensed Matter (Amsterdam, Netherlands), 323, (1-4), 2002

[10] Anazawa, Kazunori, Shimotani, Kei, Manabe, Chikara, Watanabe, Hiroyuki, and Shimizu, Masaaki, Applied Physics Letters, 81, (4), 2002

[11] Lee, Seung Jong, Baik, Hong Koo, Yoo, Jae eun, and Han, Jong hoon, Diamond and Related Materials, 11, (3-6), 2002

[12] Guo, T., Nikolaev, P., Thess, A., Colbert, D. T., and Smalley, R. E., Chemical Physics Letters, 243, (1,2), 1995

[13] Yudasaka, M., Yamada, R., Sensui, N., Wilkins, T., Ichihashi, T., and Iijima, S., Journal of Physical Chemistry B, 103, (30), 1999

[14] Eklund, P. C., Pradhan, B. K., Kim, U. J., Xiong, Q., Fischer, J. E., Friedman, A. D., Holloway, B. C., Jordan, K., and Smith, M. W., Nano Letters, 2, (6), 2002

[15] Maser, W. K., Munoz, E., Benito, A. M., Martinez, M. T., de la Fuente, G. F., Maniette, Y., Anglaret, E., and Sauvajol, J. L., Chemical Physics Letters, 292, (4,5,6), 1998

[16] Bolshakov, A. P., Uglov, S. A., Saveliev, A. V., Konov, V. I., Gorbunov, A. A., Pompe, W., and Graff, A., Diamond and Related Materials, 11, (3-6), 2002

[17] Dr. Ir. J.C. Reijenga, The Wondrous World of Carbon Nanotubes (a review), 8-23, 2003

[18] Scott, C. D., Arepalli, S., Nikolaev, P., and Smalley, R. E., Applied Physics A: Materials Science & Processing, 72, (5), 2001

[19] Ren, Z. F., Huang, Z. P., Xu, J. W., Wang, J. H., Bush, P., Siegel, M. P., and Provencio, P. N., Science (Washington, D.C.), 282, (5391), 1998

[20] Ren, Z. F., Huang, Z. P., Wang, D. Z., Wen, J. G., Xu, J. W., Wang, J. H., Calvet, L. E., Chen, J., Klemic, J. F., and Reed, M. A., Applied Physics Letters, 75, (8), 1999

[21] Yudasaka, Masako, Kikuchi, Rie, Matsui, Takeo, Ohki, Yoshimasa, Yoshimura, Susumu, and Ota, Etsuro, Applied Physics Letters, 67, (17), 1995

[22] Yudasaka, Masako, Kikuchi, Rie, Ohki, Yoshimasa, Ota, Etsuro, and Yoshimura, Susumu, Applied Physics Letters, 70, (14), 1997

[23] Chen, M., Chen, C. M., and Chen, C. F., Journal of Materials Science, 37, (17), 3561-3567, 2002

[24] Huang, Z. P., Wang, D. Z., Wen, J. G., Sennett, M., Gibson, H., and Ren, Z. F., Applied Physics AMaterials Science & Processing, 74, (3), 387-391, 2002

[25] Park, J. B., Choi, G. S., Cho, Y. S., Hong, S. Y., Kim, D., Choi, S. Y., Lee, J. H., and Cho, K. I., Journal of Crystal Growth, 244, (2), 211-217, 2002

[26] Maruyama, S., Chiashi, S., and Miyauch, Y., Thermal Engineering Joint Conference, 6, (2003)

[27] Lee, Cheol Jin, Lyu, Seung Chul, Kim, Hyoun Woo, Park, Chong Yun, and Yang, Cheol Woong, Chemical Physics Letters, 359, (1,2), 2002

[28] Ge, M. and Sattler, K., Applied Physics Letters, 64, (6), 710-711, 1994

[29] Su, M., Zheng, B., and Liu, J., Chemical Physics Letters, 322, (5), 2000

[30] Zheng, B., Li, Y., and Liu, J., Applied Physics A: Materials Science & Processing, 74, (3), 2002

[31] Alexandrescu, R., Crunteanu, A., Morjan, R. E., Morjan, I., Rohmund, F., Falk, L. K. L., Ledoux, G., and Huisken, F., Infrared Physics & Technology, 44, (1), 2003

[32] Nikolaev, Pavel, Bronikowski, Michael J., Bradley, R. Kelley, Rohmund, Frank, Colbert, Daniel T., Smith, K. A., and Smalley, Richard E., Chemical Physics Letters, 313, (1,2), 1999

[33] Smalley, Richard E. and Yakobson, Boris I., Solid State Communications, 107, (11), 1998

[34] Bronikowski, Michael J., Willis, Peter A., Colbert, Daniel T., Smith, K. A., and Smalley, Richard E., Journal of Vacuum Science & Technology, A: Vacuum, Surfaces, and Films, 19, (4, Pt. 2), 2001

[35] Vander Wal, Randall L., Hall, Lee J., and Berger, Gordon M., Journal of Physical Chemistry B, 106, (51), 2002

[36] Vander Wal, Randall L. and Ticich, Thomas M., Journal of Physical Chemistry B, 105, (42), 2001

[37] Wal, R. L. V., Berger, G. M., and Hall, L. J., Journal of Physical Chemistry B, 106, (14), 3564-3567, 2002

[38] Endo, Morinobu, Takeuchi, Kenji, Igarashi, Susumu, Kobori, Kiyoharu, Shiraishi, Minoru, and Kroto, Harold W., Journal of Physics and Chemistry of Solids, 54, (12), 1993