Journal of Experimental Nanoscience
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t716100757

Defect reduction of multi-walled carbon nanotubes by rapid vacuum arc annealing

Jeff T. H. Tsai[a]; Anders A. Tseng[a]
[a] Graduate Institute of Electro-Optical Engineering, Tatung University, Taipei, Taiwan

To cite this Article Tsai, Jeff T. H. and Tseng, Anders A.(2009) 'Defect reduction of multi-walled carbon nanotubes by rapid vacuum arc annealing', Journal of Experimental Nanoscience, 4: 1, 87 — 93
To link to this Article: DOI: 10.1080/17458080802512502
URL: http://dx.doi.org/10.1080/17458080802512502

Journal of Experimental Nanoscience
Vol. 4, No. 1, March 2009, 87–93

Taylor & Francis
Taylor & Francis Group

Defect reduction of multi-walled carbon nanotubes by rapid vacuum arc annealing

Jeff T.H. Tsai* and Anders A. Tseng

Graduate Institute of Electro-Optical Engineering, Tatung University, Taipei, Taiwan

(*Received 13 August 2008; final version received 29 September 2008*)

A rapid thermal annealing process using a DC vacuum arc discharge system was shown to reduce defects in carbon nanotubes (CNTs). Multi-walled CNTs (MWCNTs) exhibit high-density structural imperfections when deposited via chemical vapour deposition at relatively low temperatures (~650°C). These defects can be thermally annealed to reconstruct the graphitic structure. A vacuum arc discharge system was used to anneal the MWCNTs through several cycles at high temperatures (~1800°C) followed by rapid cooling. The annealed MWCNTs were characterised by Raman spectroscopy and transmission electron microscopy. Rapid heating rearranged the imperfect graphitic structure and removed the weakly bonded defects. After eliminating a defect segment, the graphene shell was reconstructed during the cooling process to produce multi-shell perfection. This method effectively reduced MWCNT defects.

Keywords: carbon nanotubes; rapid thermal annealing; defects

1. Introduction

High-temperature thermal growth of carbon nanostructures such as nanocones [1], bundles of double-walled carbon nanotubes (DWCNT) [2], and single-walled carbon nanotubes (SWCNTs) [3] has been demonstrated via pulsed laser vapourisation and electric arc discharge processes. Recently, many groups have striven to develop novel fabrication methods to produce high-quality products and control the growth of specific types of nanotubes. High temperature (1600–2000°C) treatment has been shown to morphologically transform bundled SWCNTs into multi-walled carbon nanotubes (MWCNTs) [4]. In this temperature regime, tubes undergo massive bond rearrangement, transforming into different carbon nanostructures such as graphitic nanoribbons [5]. It has also been reported that MWCNTs can be purified by thermally annealing the defect-containing nanotubes at graphitisation temperatures [6].

In general, carbon nanotubes (CNTs) fabricated at high temperatures (~2800°C) via methods that utilise the vapour–solid (VS) growth mechanism (e.g., laser vaporisation) present highly ordered structures and show little formation of amorphous carbon on the

*Corresponding author. Email: thtsai@ttu.edu.tw

ISSN 1745–8080 print/ISSN 1745–8099 online

DOI: 10.1080/17458080802512502
http://www.informaworld.com

outer shell surface. Raman spectra reveal this structure by exhibiting much larger G band intensity ($I_G \sim 1600\,cm^{-1}$) than D band intensity ($I_D \sim 1350\,cm^{-1}$). Although these fabrication methods create good quality CNTs, the product is usually mixed with large amounts of graphite clusters or graphite powders. Additional purification processes are required to remove these external impurities. On the contrary, when CNTs are grown by the plasma enhanced chemical vapour deposition (PECVD) at relatively low temperatures (below 850°C) via a vapour–liquid–solid (VLS) process, the nanostructure exhibits less order in the graphitic layer structure. Many defects are also observed inside the hollow tube and the thick amorphous carbon film coating on the other shell. This process creates CNTs that display Raman spectra with low I_G/I_D ratios (usually approaching 1 or less) that indicate long-range C–C bonds, dangling carbon bonds and impurities. No large graphite clusters or powders are generated using PECVD to produce CNTs. Hence, the purification process only entails catalytic metal removal and nanotube structure refinement.

Single-walled carbon nanotubes have been proposed for use in many advanced electronic applications such as low-dimensional transistors [7] and high-density logic circuits [8]. MWCNTs have also been successfully incorporated as interconnections and nano-conductors [9,10]. Dai et al. [11] using a nano-probe to measure individual MWCNTs, found that the most structurally perfect nanotubes have resistivities an order of magnitude lower than nanotubes with high defect densities. Therefore, it is important to perfectly reconstruct the nanotubes' graphitic layer structures to improve conductivity.

Several post-treatment methods have been proposed to purify CNTs and remove defects. CNT structural rearrangement has been demonstrated through high temperature annealing. For example, Wang and co-workers used high temperatures (2000°C) to anneal MWCNTs before acid treatment (140°C), thereby producing well-separated nanotubes with high aspect ratios and 99.9% purity. These highly dispersed CNTs contained few impurities and minimal defects in their tube bodies [12]. Metallic catalyst removal has been achieved via a two-step process. Chen and co-workers used acidic treatment in a microwave digestion system to dissolve metal catalysts. The acid-treated CNTs absorbed the energy and the metal dissolved completely without damaging the nanotubes. The two-step microwave-assisted and acid-treatment process led to high levels (95%) of MWCNT purification [13].

Here, we report defect reduction in MWCNTs by a rapid thermal annealing (RTA) process. Tubes were originally prepared with a microwave-assisted PECVD (MW-PECVD) with Sm–Co catalyst at low process temperatures (~650°C) [14]. It was observed that these MWCNTs contained significant amounts of amorphous carbon, defects, and growth catalyst. Most of the defect structures contained nitrogen, significantly changing the nanotube morphology and leading to compartmentalised bamboo nanotubes [15].

2. Experimental

A vacuum arc system was modified to create a RTA processor to remove defects in MWCNTs. Figure 1 shows the schematic of the vacuum arc rapid thermal annealing system (VARTA). The process chamber was made with a graphite rod drill containing a 2 mm central hole that was filled with CNT samples. MWCNTs, prepared via our standard fabrication process, which is described in [14], were corrected and mixed with

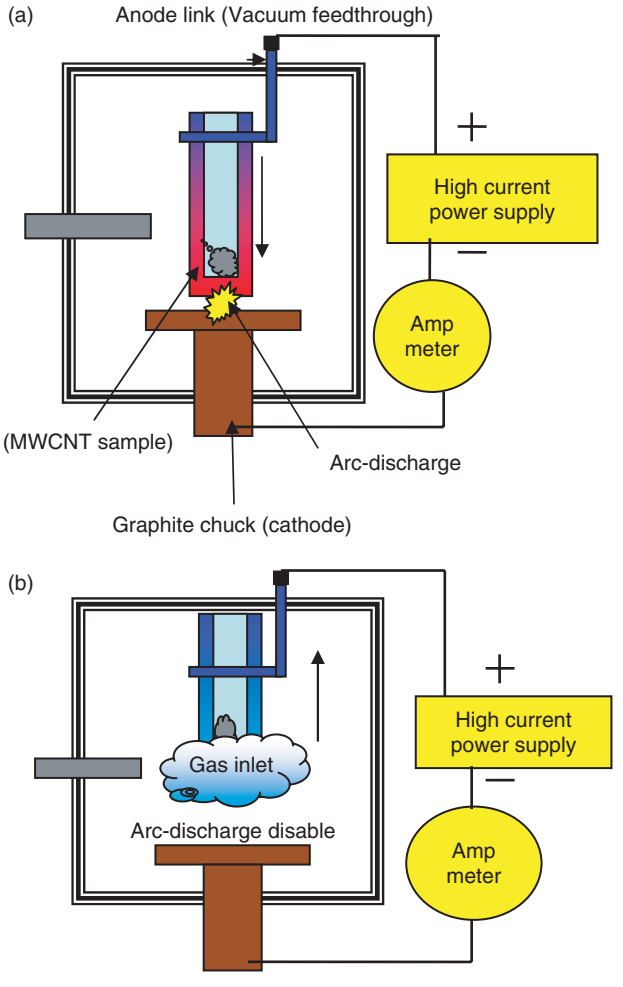

Figure 1. Schematic representation of the VARTA system. (a) Heating cycle happen when the anode move toward the cathode and strike the arc. (b) Cooling cycle occurs when the anode is away from the cathode which ceases the arc and inlets large amount of gas to cool down the process chamber.

deionised (DI) water in an ultrasonic bath for 2 h. After filtering out large particles, three groups of CNTs were prepared for VARTA experiments: Group A as a sticky paste of mixed CNTs and DI water, Group B as a mixture of CNTs and liquid isopropyl alcohol (IPA) and Group C as unmodified control samples of as-grown CNTs.

The process chamber was attached to the graphite anode of the arc system with another segment of the graphite tube. The rapid annealing process was controlled by the arc current and the purging gas flow. In the heating cycle, the heating rate was $300^{\circ}C\,s^{-1}$ with a vacuum arc current of 60 Å. The chamber was maintained at a pressure of 4.3×10^{-2} Torr. The temperature was measured by an infrared thermometer, and the maximum temperature reached 1800°C at 6 s after the arc was struck. Figure 2 shows the saturation temperature *versus* the arc current. A cooling rate of $\sim 70^{\circ}C\,s^{-1}$ was achieved

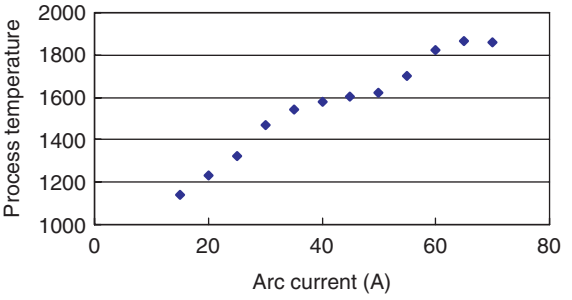

Figure 2. Arc current *vs*. process chamber temperature, the temperatures were measured 2 s after the vacuum arc ignited.

with 10 slm high-flow Ar injected directly into the process chamber. Unlike conventional lamp-heated RTA equipment, the high heating rate of the VARTA produced spike-annealing while under vacuum during the heating cycle.

3. Results and discussion

To evaluate the effects of temperature on defect removal, Group A was annealed rapidly for 20 cycles in 30 min and the saturation temperature was varied from 1000 to 1800°C. After this process, the CNTs were mixed with IPA solution and dispersed onto a silicon wafer for Raman spectroscopy analysis under ambient conditions. A Renishaw inVia micro Raman spectrometer with a microscope and low noise CCD detector was used to collect spectra. Excitation was provided by a 325 nm laser at 20 mW incident power. Transmission electron microscopy samples were prepared by dispersing the CNTs in DI water and dropping the solution onto lacey carbon grids. High-resolution transmission electron microscope (HRTEM) images were obtained with a Hitachi H-7100 transmission electron microscope.

As shown in Figure 3, Raman spectra of processed CNTs indicated that the saturation temperature affected the CNT structure modification. Less efficient reconstruction was achieved with annealing temperatures in the range of 1000–1400°C. The samples annealed in the lower temperature range exhibited I_G/I_D ratios of ~1, similar to unmodified CNTs. At low temperatures, the energy was not sufficient to cause C–C bond rearrangement for reconstruction of the graphene layer. When the annealing temperature was increased to 1600°C or higher, the I_G/I_D ratio increased rapidly. Under optimum conditions, the I_G/I_D ratio approached 10. Structure refinement was clear from the defect distributions obtained from TEM images. At 1800°C, rapid graphitisation created perfect MWCNTs. Figure 4 shows the high defect density found in the as-grown CNTs (Figure 4(a)) and the low defect density present in the rapidly annealed CNTs (Figure 4(b)).

Group C (control sample) was used to verify the effects of the rapid annealing process on the defect reduction efficiency. Samples were annealed at 1800°C for 30 min with varying numbers of thermal cycles (1, 5, or 20). One cycle annealing produced Raman measurements with the lowest I_G/I_D value (1.1). Increasing the thermal cycles increased the I_G/I_D ratios to 1.4 and 2.3 for 5 and 20 thermal cycles, respectively. This result indicated that each rapid annealing cycle produced thermal stresses that helped gradually refine the CNT structure.

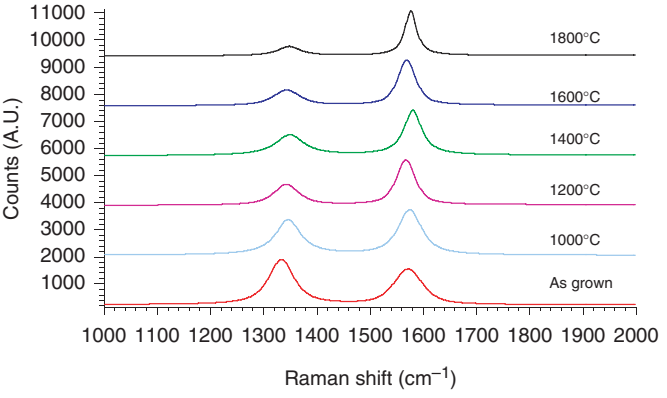

Figure 3. Raman spectra of rapid annealed MWCNTs in different temperature; higher process temperature gives higher I_G/I_D ratio which indicates that the nanotube has better graphitic structure and fewer defects.

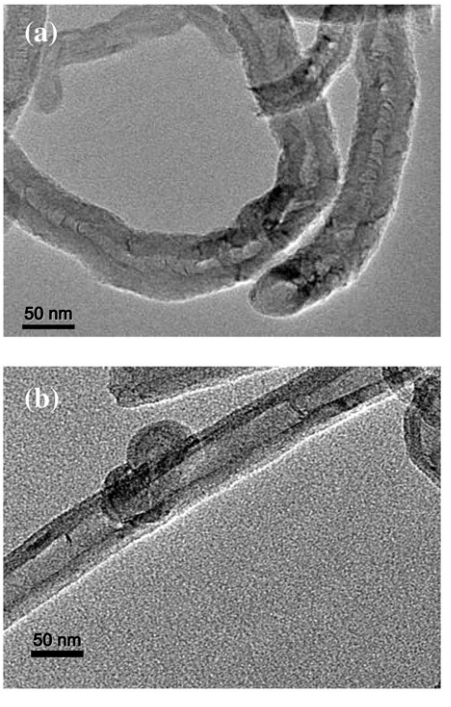

Figure 4. (a) The TEM micrograph of the as-grown MWCNTs from MWCVD reactor. (b) After optimum rapid annealing process, the defects have been reduced.

Water vapour was also found to play an important role during the VARTA process. Samples of Groups A, B, and C were compared using the same annealing conditions (1800°C, 20 thermal cycles in 30 min). The samples containing DI water (Group A) had the highest I_G/I_D values (10.3). This result supported that of Li et al. [16] who reported that

oxygen attacks carbon bonds to break up the atomic structure of graphite. In a perfect CNT, the carbon atoms in the outer shell are bonded to each other in a honeycomb shape to form a graphene layer that seals the tubule structure. These C–C bonds are chemically inert unless there are flaws in the lattice. A defect, containing several weak bonds, is an imperfection in the graphitic structure. When the annealing environment contains water, the dissociated oxygen from water vapour can easily attack the weak bonds and free the carbons during the heating cycle. During the cooling cycle, the mobile carbon atoms are quenched into a graphitic structure, thereby removing the defect. We found that Group B exhibited I_G/I_D ratios of 2.4 in comparison to the value of 10.3 for Group A. Although Group B contained solvent, most of it was pumped out before the annealing process because of the rapid evaporation of IPA. Therefore, addition of IPA in process chamber did not enhance defect reduction.

4. Conclusion

Defect removal in MWCNTs was achieved by the VARTA process. From the rapid spiking thermal stresses at high temperature, the carbon atoms rearranged and annealed out structure defects. The cooling cycle quenched the carbons into a perfect layered graphitic structure. When water was present in the annealing chamber, defect reduction was enhanced due to high concentration of oxygen attacking weakly bonded carbon imperfections and combusted amorphous carbon layers. These results indicate that VARTA is a reliable process for reducing defects and improving material qualities of the MWCNTs.

Acknowledgements

The authors gratefully acknowledge the National Science Council Taiwan under the grants 95-2112-M-036-001-MY2.

References

[1] M. Munoz-Navia, J. Dorantes-Davila, M. Terrones, T. Hayashi, Y.A. Kim, M. Endo, M.S. Dresselhaus, and H. Terrones, *Synthesis and electronic properties of coalesced graphitic nanocones*, Chem. Phys. Lett. 407 (2005), pp. 327–332.

[2] Y.A. Kim, H. Muramatsu, T. Hayashi, M. Endo, M. Terrones, and M.S. Dresselhaus, *Thermal stability and structural changes of double-walled carbon nanotubes by heat treatment*, Chem. Phys. Lett. 398 (2004), pp. 87–92.

[3] M. Yudasaka, T. Ichihashi, D. Kasuya, H. Kataura, and S. Iijima, *Structure changes of single-wall carbon nanotubes and single-wall carbon nanohorns caused by heat treatment*, Carbon 41 (2003), pp. 1273–1280.

[4] R. Zhong, H.T. Cong, and C. Liu, *Fabrication of single-walled carbon nanotubes from multi-walled carbon nanotubes and carbon fibers*, Carbon 40 (2002), pp. 2970–2973.

[5] H.R. Gutierrez, U.J. Kim, J.P. Kim, and P.C. Eklund, *Thermal conversion of bundled carbon nanotubes into graphitic ribbons*, Nano. Lett. 5 (2005), pp. 2195–2201.

[6] R. Andrews, D. Jacques, D. Qian, and E.C. Dickey, *Purification and structural annealing of multiwalled carbon nanotubes at graphitization temperatures*, Carbon 39 (2001), pp. 1681–1687.

[7] S.J. Tans, A.R.M. Verschueren, and C. Dekker, *Room-temperature transistor based on a single carbon nanotube*, Nature 393 (1998), pp. 49–52.
[8] A. Bachtold, P. Hadley, T. Nakanishi, and C. Dekker, *Logic circuits with carbon nanotube transistors*, Science 294 (2001), pp. 1317–1320.
[9] A. Naeemi, R. Sarvari, and J.D. Meindl, *Performance comparison between carbon nanotube and copper interconnects for gigascale integration*, IEEE Elect. Dev. Lett. 26 (2005), pp. 84–86.
[10] K. Ahmad, W. Pan, and S.L. Shi, *Electrical conductivity and dielectric properties of multiwalled carbon nanotube and alumina composites*, Appl. Phys. Lett. 89 (2006), 133122.
[11] H.J. Dai, E.W. Wong, and C.M. Lieber, *Probing electrical transport in nanomaterials: Conductivity of individual carbon nanotubes*, Science 272 (1996), pp. 523–526.
[12] Y. Wang, J. Wu, and F. Wei, *A treatment method to give separated multi-walled carbon nanotubes with high purity, high crystallization and a large aspect ratio*, Carbon 41 (2003), pp. 2939–2948.
[13] C.C. Chen, C.F. Chen, C.M. Chen, and F.T. Chuang, *Modification of multi-walled carbon nanotubes by microwave digestion method as electrocatalyst supports for direct methanol fuel cell applications, Electrochem*, Comm. 9 (2007), pp. 159–163.
[14] J.T.H. Tsai and K.H. Chen, *Enhanced growth of carbon nanotubes on selected area using an aqueous catalyst*, Int. J. Nanosci. 4 (2005), pp. 431–436.
[15] C.P. Ewels and M. Glerup, *Nitrogen doping in carbon nanotubes*, J. Nanosci. Nanotechnol. 5 (2005), pp. 1345–1363.
[16] J.L. Li, K.N. Kudin, M.J. McAllister, R.K. Prud'homme, I.A. Aksay, and R. Car, *Oxygen-driven unzipping of graphitic materials*, Phys. Rev. Lett. 96 (2006), 176101.