Plasma mechanism of synthesis and tailoring properties of carbon nanostructures

M. Keidar[1], O. Volotskova[1], A. Shashurin[1] and A.M. Waas[2]

1. Mechanical and Aerospace Engineering, George Washington University, Washington DC 20052, email: keidar@gwu.edu

2. Aerospace Engineering, University of Michigan, Ann Arbor MI 48109

Abstract

The primary focus of this paper is to summarize recent experimental and theoretical advances in understanding of carbon nanostructures synthesis mechanism in arcs, and to describe methods of controlling arc plasma parameters with an ultimate view to tailor properties for design of smart nanocomposites. Fundamental issues related to synthesis of SWNTs, which is relationship between plasma parameters and SWNT characteristics are considered. It is shown that characteristics of synthesized SWNTs can be altered by varying plasma parameters and by adding electrical and magnetic fields. In particular, it is demonstrated that magnetic field has a profound effect on the diameter, chirality and length of a SWNT synthesized in the arc plasma. In addition, synthesis of a few-layer graphene in a magnetic field presence is discovered.

I. Introduction

Carbon nanostructures such as carbon nanotubes and graphene are continuing enjoying much attraction due to their unique properties and great potential in various applications. Since the beginning of 1990s[1], interest in carbon nanotubes has been stimulated by their unique mechanical, thermal and electrical properties and various potential applications that exploit these properties. The most advanced applications of single and multi-wall carbon nanotubes include nanoelectronics[2], field-emitters[3], hydrogen storage[4], biological and chemical gas sensors[5], nanomaterials[6], medicine[7] etc.

Several advanced techniques were developed for CNT synthesis such as arc discharge, laser ablation and chemical vapor deposition (CVD).[8,9,10] Among plasma-based techniques for carbon nanostructures synthesis an arc discharge is probably the most practical from the both scientific and technological standpoints[11,12]. In fact, arc discharge technique has number of advantages in comparison with other techniques[13] such as fewer defects and a high flexibility[14] of carbon nanostructures produced. Arc-grown nanotubes demonstrate the lowest emission capability degradation than those produced by other techniques[15].

Typically anodic arc is employed for synthesis of the carbon nanostructures. Anodic arc is characterized by primary anode ablation during the arc process in contrast to cathodic arc in which cathode ablation prevails[16]. When anodic arc is implemented for carbon nanotube synthesis it is supported by ablation of the anode material and substantial part of the ablated material (about 70%) is deposited on the cathode. Two different textures and morphologies can be observed in the cathode deposit; the grey outer shell and dark-soft inner core deposit. Post-arc examination reveals that the multi-wall carbon nanotubes (MWNT) as well as graphitic particles are found typically in the inner core[17]. On the other hand single wall carbon nanotubes (SWNTs) produced by the anodic arc discharge are found in a “collaret” around the cathode deposit, clothlike soot suspended in the chamber walls and the weblike structure suspended between cathode and walls[17].

Ability to control and tailor the synthesis process is one of the pressing issues. In this respect, the lack of control of the SWNT growth in arc that is due to limited understanding of the arc physics and SWNT synthesis mechanism is the major disadvantage of this technique[18]. It is well-known that the arc plasma parameters can be controlled by a magnetic field[19] and fact allows controlling the nanostructes production. Indeed it was shown that the high-purity MWNTs can be grown in the magnetically-enhanced arc discharge[20] and that the magnetically–enhanced arc leads to production of the long single-wall nanotubes[21,22].

Although the mechanism of the formation and growth of SWNTs in an arc discharge was studied for a decade, location of the region in arc discharge in which SWNT synthesis occurs and the temperature range favorable for SWNT growth remained unclear. Our recent experiments revealed that the nanotube formation occurs on the periphery of an arc column at a moderate temperature range of 1200-1400 K[23].

In this paper we summarize recent effort aiming to describe the entire phenomena associated with carbon nanotube synthesis including arc plasma, electrode erosion, carbon nanostructures synthesis, modeling and post-processing characterization of carbon nanotubes. Our recent experimental results led to better understanding the anode erosion mechanism[24], current-voltage characteristics of the arc[25] and cathode deposit mechanism[26]. Global model[27] developed by coupling anode erosion and interelectrode plasma phenomena is described. This model assists in understanding the arc plasma parameters associated with carbon nanotube synthesis and the controllability as well as the efficiency of arc synthesis of the SWNTs.

II. Arc discharge apparatus to synthesis

Arc discharge synthesis is typically conducted in a cylindrical vacuum chamber (270 mm length and 145 mm diameter) filled with helium under pressure of about 500 Torr. The anode was attached to a linear drive system allowed to keep predetermined desired arc voltage. Arc was ignited by mechanical touching of arc electrodes (using anode feeding system) following by their immediate separation and was supported by welder power supply (Miller Goldstar 500ss). Arc electrodes were produced from the carbon, with the anode being hollow tube and the cathode being solid. The cathode had a length and diameter of about 40 mm and 12.5 mm respectively. The anode had a length of 75 mm before arcing (outer and inner diameters of the anode were 5 mm and 3.2 mm respectively). The anode was packed with metal catalysts - Ni and Y in proportion Ni:Y= 4:1 at.%. Nearly axial magnetic field in the interelectrode gap was produced by permanent magnet located near the arc electrodes (up to 1.5 kG). During the arc the plasma has a sharp boundary that is determined by plasma-helium gas interface interactions. It is the region in which, according to our recent experiments, the nanotube formation occurs[23].

III. Synthesis of carbon nanostructures

Arc plasma can be used as a platform for synthesis various carbon nanostructures including MWNT, SWNT and graphene. Below the synthesis of SWNT and recently discovered graphene structures is mainly considered. In particular we will emphasize the robustness of the arc discharge in ability to tailor some properties of the nanostructures including length, diameter and chirality.

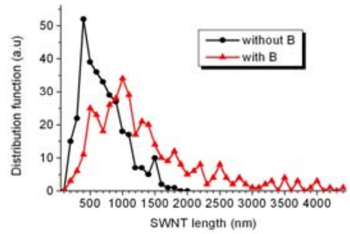

Fig. 1. Length distribution of SWNT with and without magnetic field.

SWNTs are considered the main product of arc discharge synthesis due to their superior properties in comparison with SWNTs grown by other techniques. Based on the observation of the arc during the synthesis as well as on the studies of the thermal stability of the SWNT, it is apparent that the primary synthesis region is the plasma boundary i.e. arc plasma-helium interface. This result led to several approaches for control of the SWNT synthesis including the application of an electric field and a magnetic field[18,21].

Recall that previous models suggested several scenarios for SWNT growth termination in arc discharge (Ref. 18). These scenarios are related to the mechanism of carbon species precipitation. However, in addition, it was shown that SWNT synthesis is coupled with SWNT dynamics and formation time. The SWNT gains a kinetic energy due to momentum transfer from plasma and leave the plasma region having conditions which are optimal for synthesis. Based on this premise, increasing the SWNT residence time in the region of synthesis can be suggested as a possible way for SWNT synthesis control. One possibility to increase SWNT residence time is the electrostatic trapping taking into account that SWNTs are charged. Simulations predicted that very large ratios of the SWNT length to radius (aspect ratio) are possible by application of the electric field of about few V/m in the region of synthesis[18]. On the other hand it was experimentally demonstrated that magnetic field leads to significant increase in the average SWNT length with maximum length increase by a factor of 5 and average length increase by a factor of 2 in comparison with synthesis without magnetic field[21] as shown in Fig.1. This effect was explained by increase of the plasma density (due to plasma focusing) and related to that increase in the SWNT growth rate.

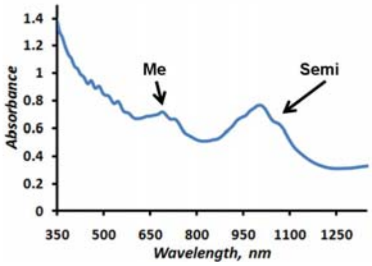

Fig. 2. UV-viz-NIR absorbance spectra.

It is accepted that SWNTs are created by rolling up a hexagonal lattice of carbon. Rolling the lattice at different angles creates a visible twist or spiral in the SWNT's molecular structure, though the overall shape remains cylindrical. This twist is called chirality. SWNTs are characterized by chirality in addition to their diameter and length. The SWNT's chirality, along with its diameter, determines its electrical properties. The armchair structure has metallic characteristics. Both zigzag and chiral structures produce band gaps, making these nanotubes semiconductors. Thus, dependent on chirality SWNT can have metallic or semiconductor conductivity. Ultraviolet visible and near-infrared (UV-viz-NIR) absorbance spectra are standard way to characterize SWNT chirality structure[28]. Typical spectra of SWNT as-grown sample in arc discharge without magnetic field are shown in Fig.2. Intensity of the peak is proportional to SWNT electronic structure. One can see that most arc produced SWNTs have semiconductor conductivity (about 70%) while about 30% nanotubes are metallic.

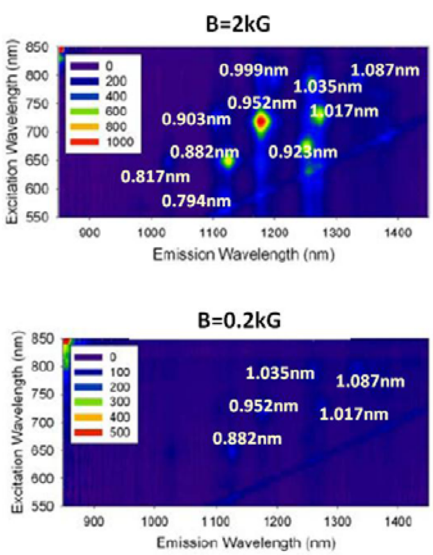

Fig.3. Photoluminescence (PL) characterization of the SWNT sample with magnetic field as a parameter.

Magnetic field leads to significant changes. The PL spectra of samples as function of exciting wavelength are shown in Fig. 3 for different magnetic fields. It is seen that increase of magnetic field leads to increasing number of peaks emitted by the sample which indicates increase variety of produced nanotube chiralities and, in particular, decrease of SWNT diameter. PL spectroscopy indicates that application of a magnetic field leads to decrease in the SWNT diameter and chirality.

Recently it was found that few-layer graphene particles can be growth in an arc plasma controlled by a magnetic field[29,30]. Variety of diagnostics including SEM, TEM, Raman and atomic force microscopy (AFM) was used to identify the single or few-layer graphene particles. Estimated size of sheets is in the order of 0.1-1 μm. Based on these results it can be concluded that arc plasma allow to synthesis of a few-layer graphene particles. These results are very promising opening new robust way for synthesis of this novel and distinct material.

IV. Producing Nanocomposites

Layer by layer (LBL) manufacturing is a nanoscale control technique for producing highly ordered nanocomposites[31]. While clay particles in polymers have produced extremely desirable stiffness and strengths of nanocomposites[32], other attractive features such as thermal and electrical conductivity can be improved by using SWNT as the reinforcing agent. There has been limited success in using SWNT with polymers because the SWNT are not ordered. By suitably combining a magnetic or electric field during LBL manufacturing it may be possible to align the nanotubes within the layers, although such success is yet to be demonstrated. The effect of a magnetic field on SWNT production has been discussed by the authors[21]. Using MWNT, recent work[33] has produced aligned MWNT sheets, but the weak van der Waals bonding between the nanotube layers may be a stiffness and strength limiting drawback of MWNT reinforcement. Thus, much remains to be done with SWNT reinforced nanotubes to realize the full potential of tailored nanocomposites.

V. Conclusions

This paper outlined basic issues related to synthesis of carbon nanostructures in arc discharge. Given that among plasma-based techniques arc discharge stands out as very advantageous in several ways (fewer defects, high flexibility, longer lifetime) this techniques warrants attention from the plasma physics standpoint. It was demonstrated in experiment and theoretically that controlling plasma parameters can affect nanostuctures synthesis altering SWNT properties (length, diamter and chirality) and leading to synthesis of new structures such as a few-layer graphene. Among clearly identified parameters affecting synthesis are magnetic and electric fields. Knowledge of the plasma parameters and discharge characteristics is crucial for ability to control synthesis process by virtue of both magnetic and electric fields.

Acknowledgement

This work was supported in part by NSF/DOE Partnership in Plasma Science and Technology (NSF grant CBET-0853777, DOE grant DE-SC0001169). We would like to acknowledge PPPL Offsite Research Program supported by Office of Fusion Energy Sciences for supporting arc experiments.

References

[1] S. Iijima, *Nature,* **354** 56 (1991).
[2] W.H. Chiang and R.M. Sankaran, Nat. Materials, 20 Sept. (2009).
[3] A. Buldum, J.P. Lu, *Phys. Rev. Lett*., **91** 236801 (2003).
[4] H. Gao, X.B. Wu, Ji. T. Li, G.T. Wu, J. Y. Lin, K. Wu, D.S. Xu, *Appl. Phys. Lett*, **83** 3389 (2003).
[5] J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, H. Dai, *Science,* **287** 622 (2000).
[6] T. Tersoff, *Phys. Rev. B.*, **46** 15546 (1992).
[7] J.Gao and B.Xu, Nano Today, **4**, 37 (2009).
[8] Z. Huang, J. Xu, Z. Ren, J. Wang, M. Siegal, and P. Provencio, Appl. Phys. Lett. **73,** 3845 (1998).
[9] U. Cvelbar, B. Markoli, I. Poberaj, A. Zalar, L. Kosec, S. Spaić, Appl. Surf. Sci. **253**, 1861 (2006).
[10] F.J. Gordillo-Vazquez, V.J. Herrero, I. Tanarro, Chem. Vapor Depos. **13**, 267 (2007).
[11] C. Journet, W.K. Maser, P. Bernier, A. Loiseau, M.L. de la Chapelle, S. Lefrant, P. Deniard, R. Lee, J.E. Fischer, *Nature*, **388** 756 (1997).
[12] K. Ostrikov, Rev. Mod. Phys., **77** 489 (2005).
[13] M. Meyyappan, Ed., Carbon nanotubes: Science and applications, (CRC Press, Boca Raton, 2004).
[14] I. Stepanek, G. Maurin, P. Bernier, J. Gavillet, A. Loiseau, R. Edwards and O. Jaschinski, *Chem. Phys. Lett.*, **331** 125 (2000).
[15] Y. Okawa, S. Kitamura, Y.Iseki, *Proc. 9th Spacecraft charging technology conference*, Japan, April 2005 (unpublished).
[16] I.I. Beilis, IEEE Transaction. on Components and Packaging Technologies, **23** 334 (2000).
[17] A.P. Moravsky, E.M. Wexler, R.O. Loufty in book *Carbon nanotubes: Science and applications*, Ed. M. Meyyappan, (CRC Press, Boca Raton, 2004).
[18] M. Keidar, *J. Phys. D*., **40** 2388 (2007).
[19] M. Keidar I.I. Beilis, R.L. Boxman and Goldsmith, *J. Phys. D: Appl. Phys*., **29** 1973 (1996).
[20] K Anazawa, K. Shimotani, C. Manabe, H. Watanabe, M. Shimizu, *Appl. Phys. Lett.*, **81** 739 (2002).
[21] M. Keidar, I. Levchenko, T. Arbel, M. Alexander, A.M. Waas, K. Ostrikov, *Appl. Phys. Lett.*, **92** 043129 (2008).
[22] M. Keidar, I. Levchenko, T. Arbel, M. Alexander, A.M. Waas, K. Ostrikov, *J. Appl. Phys.* **103** 094318 (2008).
[23] O. Volotskova, A. Shashuring, M. Keidar, Y. Raitses, V. Demidov and S. Adams, Nanotechnology 21 (2010) 095705.
[24] A. Fetterman, Y. Raitses and M. Keidar, *Carbon*, **46** 1322 (2008).
[25] A. Shashurin, M. Keidar, and I.I. Beilis, *J. Appl. Phys*. **104** 063311 (2008).
[26] A. Shashurin and M. Keidar, *Carbon*, **46 (13)** 1826 (2008).
[27] M. Keidar and I.I. Beilis, J. Appl. Phys., **106** 103304 (2009).
[28] J. A. Fagan, B. J. Landi, I. Mandelbaum, J. R. Simpson, V. Bajpai, B. J. Bauer, K. Migler, A. R. Hight Walker, R. Raffaelle, and E. K. Hobbie, J. Phys. Chem. **B 110** 23801 (2006).
[29] O. Volotskova, I. Levchenko, A. Shashurin, Y. Raitses, K. Ostrikov, and M. Keidar, *Nano Lett*., 2010, will be submitted.
[30] M. Keidar, A. Shashurin, O. Volotskova, Y. Raitses and I.I. Beilis, Phys. Plasmas, 2010 in press.
[31] Bong Sup Shim, Zhiyong Tang, Matthew P. Morabito, Nicholas A. Kotov, *Chemistry of Materials*, 2007, 19(23), 5467-5474.
[32] Podsiadlo P., Kaushik A. K., Arruda E. M., Waas A. M., Shim B. S., Xu J., Nandivada H., Pumplin B. G., Lahann J**.,** Ramamoorthy **A.,** Kotov N. A., *Science, 2007,*318, 80-83
[33] Zhang M, Fang SL, Zakhidov AA, et al., SCIENCE Volume: 309 Issue: 5738 Pages: 1215-1219 Published: AUG 19 2005