Creation of Novel Structured Nanocarbons Based on Plasma Technology*

Rikizo HATAKEYAMA, Takamichi HIRATA, Wataru OOHARA,
Toshiaki KATO and Takeshi IZUMIDA

Department of Electronic Engineering, Tohoku University Aoba 6-6-05, Aramaki, Aobaku, Sendai 980-8579, Japan

(Received October 29, 2004, Accepted February 12, 2005)

Original approaches using plasma processing technology have been performed in order to develop fullerene- and nanotube-based materials with new functions, where various kinds of plasma sources are devised: pair-ion plasma, alkali-fullerene plasma, and radio-frequency reactive plasma. As a result of the process control of these plasmas we have succeeded in creating novel structured nano carbons such as fullerene dimers, alkali-metal encapsulated fullerenes, individually-aligned pristine single-walled carbon nanotubes, and alkali-metal and/or fullerene encapsulated single-walled carbon nanotubes.

1. Introduction

Fullerenes¹⁾ and carbon nanotubes²⁾ as a new form of carbon allotropes have been actively investigated for a past decade, and the understanding of their physics and chemistry has rapidly progressed, enlarging their applications.

Among various kinds of nanocarbons, the fullerene C_{60} is characterized by a soccer-ball like structure composed of 60 carbon atoms. Since a mass production of the fullerene family was established by a resistance heating method³⁾, fullerene properties have been investigated in various fields not only physics and chemistry but also electronic-device engineering and medicine. Furthermore, since the discovery of single-walled carbon nanotubes (SWNTs) in 1993⁴⁾, they have attracted intense attention in a variety of application fields because of their prominent electric and mechanical properties. However, SWNT thick bundles inherently conglomerated by van der Waals attraction have confined their potential application due to the difficulty of manipulation of the individual nanotube.

On the basis of these historical background, we have pursued an interdisciplinary research covering plasma science, cluster science, and nano science & technology for the purpose of creating new functional fullerene- and nanotube-based materials.

2. Fullerene-Dimer Formation by Pair-Ion Plasma

A pair-ion plasma with ion species of fullerene C_{60} is generated under a background uniform magnetic field (0.3 T)⁵⁾. The commercially available purified (>99.5%) fullerene is introduced in a hollow electron beam with energy E_e , and positive ions C_{60}^+ are generated by impact ionization. Electrons with low energy attach to neutral fullerene molecule, and negative ions C_{60}^- are generated. Separation between electrons and the ions can be performed by a magnetic filtering effect. Thus the pair fullerene-ion plasma without electrons is successfully generated (Fig. 1(a)). A grounded substrate is exposed to the pair-ion plasma for 60 minutes, where deposited films are formed. The film components are analyzed by a LD-TOF mass spectrometer (Fig. 1(b)). It is found that

Fig. 1 (a) Experimental setup for pair-ion plasma. (b) LD-TOF mass spectrum of deposited film on substrate.

the dimer C_{120} ($C_{60} + C_{60}$) is contained at the ratio of $C_{120}/C_{60} = 0.016$. The dimerization takes place in the energy range between $E_e = 80$ and 120 eV. This method of the dimerization in the pair-ion plasma is quite different from current ones accompanied with stepwise procedures in solid- or solution-phase reactions using catalysts or nonallotropic fullerene derivatives.

3. High-Yield Production of Novel Alkali-Endohedral Fullerenes by Alkali-Fullerene Plasma

Endohedral metallofullerenes, which encapsulate metal atoms in empty fullerenes, have fascinating potential in various fields for their chemical stability and unique properties. Alkali-endohedral fullerenes ($A@C_{60}$: Li, Li_2 , Na, K, Cs) are produced on circular concentric segmented substrates using alkali-fullerene plasmas consisting of positive alkali-metal ions, negative C_{60} ions, and residual electrons (Fig. 2(a))^{7,8)}. The substrates are independently biased and kinetic energy of the ions rushing into the substrate ($e\Delta\phi_{ap} = e(\phi_s - \phi_{ap})$) can be controlled, where ϕ_s and ϕ_{ap} denote the plasma and substrate potentials, respectively. Production ratios of $A@C_{60}/C_{60}$

* 平成16年10月29日 第45回真空に関する連合講演会で発表

Fig. 2 (a) Experimental setup for alkali-fullerene plasma. (b) Production ratios of alkali-endohedral fullerenes depending on substrate bias.

depending on $\Delta\phi_{ap}$ are shown in **Fig. 2(b)**. The maximum production ratio increases in inverse proportion to the diameter of the alkali-metal ions. This originates from the size relation between the diameters of the ions and the C_{60} six-membered ring. Furthermore it is found that $A@C_{60}$ is abundantly produced in an edge region of the plasma.

4. Individually Well-Aligned SWNT Formation by Controlled Reactive Plasma

Growing individually well-aligned SWNTs becomes an ultimate goal in the carbon nanotube (CNT) synthesis. Plasma-enhanced chemical vapor deposition (PECVD) method has a variety of advantages in the CNT synthesis stage such as freestanding CNT growth, low temperature synthesis, and so on. Since grown state control of SWNTs has not been achieved because of damageable ion impact, the process time of PECVD is precisely adjusted here. An radio-frequency (13.56 MHz) magnetron-type plasma source under a mixture gas phase of methane and hydrogen is used for the SWNT synthesis on a heated substrate with zeolite as a catalyst materials⁹⁾. **Figure 3** shows a typical SEM image of produced materials on the substrate after short process time (30 sec) of PECVD, where the inset is TEM image. The filament shape materials are identified to be standing on the zeolite surface, which are clearly found to be individual SWNTs. High electric field in the sheath in front of the substrate contributes to the individually well-

Fig. 3 Typical SEM image of vertically-aligned SWNTs. Inset describes TEM image of freestanding individual SWNT, which is directly produced on TEM grid.

Fig. 4 Typical TEM images of SWNTs irradiated by (a) C_{60}^- and (b) Cs^+ in $Cs-C_{60}$ plasma.

aligned SWNT formation. Furthermore, the substrate temperature is lowered below 550°C . Therefore the controlled PECVD method carries a considerable advantage in the freestanding SWNT growth. The freestanding individual SWNTs will be applied to wide-range nano electric devices such as field emitter, gas storage, DNA sensor, and so on.

5. Control of Doping into SWNT by Different-Polarity Ion Plasma

The inner hollow region of CNTs affords a one-dimensional confined space with a uniqueness and importance in not only novel physical and chemical features but also various potential applications. From the standpoint of nano-technological applications, the encapsulated CNTs are very attractive materials, where various foreign atoms, molecules, and their derivatives are doped into the hollow region. The encapsulated SWNTs are produced on a biased substrate with pristine SWNTs using the $Cs^+-C_{60}^-$ plasma. When the substrate potential is changed positively or negatively, SWNTs on the substrate are irradiated by C_{60}^- and Cs^+ , respectively, same as mentioned in Sec. 3. **Figures 4(a)** and **(b)** display typical TEM images of SWNTs irradiated by C_{60}^- and Cs^+ ,

respectively. SWNT is completely filled by closed-packed C_{60} molecules in (a) and this is called a peapod¹¹⁾. Cs atoms can be observed as an aggregate like a spiral chain in (b). Moreover, the existence of Cs atoms in SWNTs have also been evidenced by using Z-contrast observation and energy dispersive X-ray spectrometry analysis¹²⁾. It is worth emphasizing that our results open a new possibility for novel structured material synthesis using plasma technology.

Acknowledgments

The authors would like to thank Dr. K. Tohji, G.-H. Jeong, and K. Motomiya for their collaboration. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

References

- 1) H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley: *Nature*, **318** (1985) 162.
- 2) S. Iijima: *Nature*, **354** (1991) 56.
- 3) W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman: *Nature*, **347** (1990) 354.
- 4) S. Iijima and T. Ichihashi: *Nature*, **363** (1993) 503.
- 5) W. Oohara and R. Hatakeyama: *Phys. Rev. Lett.*, **91** (2003) 205005.
- 6) W. Oohara and R. Hatakeyama: *Thin Solid Films*, **435** (2003) 280.
- 7) T. Hirata, R. Hatakeyama, T. Mieno and N. Sato: *J. Vac. Sci. Technol. A*, **14** (1996) 615.
- 8) T. Hirata, Y. Sugimoto, R. Hatakeyama and N. Sato: *Proc. XXV International Conf. on Phenomena in Ionized Gases*, **3** (2001) 83.
- 9) T. Kato, G.-H. Jeong, T. Hirata, R. Hatakeyama, K. Tohji and K. Motomiya: *Chem. Phys. Lett.*, **381** (2003) 422.
- 10) T. Kato, G.-H. Jeong, T. Hirata, R. Hatakeyama and K. Tohji: *Jpn. J. Appl. Phys.*, **43** (2004) L1278.
- 11) G.-H. Jeong, R. Hatakeyama, T. Hirata, K. Tohji, K. Motomiya and N. Sato: *Appl. Phys. Lett.*, **79** (2001) 4213.
- 12) G.-H. Jeong, A. A. Farajian, R. Hatakeyama, T. Hirata, T. Yaguchi, K. Tohji, H. Mizuseki and Y. Kawazoe: *Phys. Rev. B*, **68** (2003) 075410.