Optical measurement in carbon nanotubes formation by pulsed laser ablation

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Abstract

Carbon nanotubes (CNTs) were produced by laser ablation of a graphite composite target in argon and nitrogen ambient gas. To investigate the effect of nitrogen gas on CNTs formation, the plasma plume was examined using optical emission spectroscopy. The vibrational temperature of C₂ molecules was estimated by fitting of a Swan band spectrum. The temperature in N₂ ambient gas is lower than that in Ar ambient gas. In a nitrogen atmosphere, the spectrum intensity of C₂ Swan band was enhanced and CN violet system was also observed. Soot collected in the reaction tube was observed using FE-SEM and TEM. The soot deposited in the nitrogen gas contained more bundled CNTs than those in Ar ambience.

Keywords: Pulsed laser ablation; Carbon nanotubes; Nitrogen; C₂ Swan band

1. Introduction

Since their discovery by Iijima from the soot of an arc process used for making fullerenes [1], carbon nanotubes (CNTs) have been the focus of considerable attention, because of many possible applications in nanostructure [2], super-strong materials [3] and hydrogen storage [4]. Several process methods such as arc discharge, chemical vapor deposition (CVD) and laser ablation have been used to produce CNTs. In particular, pulsed laser ablation (PLA) is well known to produce high yield single wall carbon nanotubes (SWNTs) [5].

In production of SWNTs, a graphite composite target containing Ni and Co as catalyst have been ablated by a pulsed Nd:YAG laser in argon ambient gas. So far, there has been much research on this process. Scott et al. reported the growth mechanism for SWNTs using spectral emission and laser-induced fluorescence measurement of plasma plume from a composite carbon target [6,7,10]. Yudasaka et al. studied Raman spectra of SWNTs grown by laser ablation at different ambient gas pressures [8]. Recently Nishide et al. [9] reported that SWNTs can be produced in nitrogen ambient gas at higher yield than in an argon atmosphere. Moreover, it was found that SWNTs produced in nitrogen gas were thinner than those formed in other gases. However, a detailed growth mechanism for SWNTs under nitrogen ambient gas has not been investigated. In the present work, optical emission spectroscopy was performed on a plasma plume produced by the laser ablation to investigate the effect of nitrogen gas on formation of SWNTs. Collected soot in the reactor was examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results were analyzed and compared with those measured in argon ambient gas.

2. Experiment

Fig. 1 shows an experimental set-up for CNT formation by PLA and an optical measurement of the plasma plume. A graphite composite target rod containing 1 at.% nickel (Ni) and cobalt (Co) was used. The target set in a quartz glass tube (i.d. 36 mm) is ablated by a pulsed Nd:YAG laser. The repetition rate, wavelength and energy of the laser are 10 Hz, 532 nm (second harmonic light), and 240 mJ/pulse, respectively. Laser
fluorescence at the target surface is approximately 2.6 J/cm². The quartz tube is heated to 1273 K by an openable and closable electric furnace and filled with pure argon or nitrogen gas. A water-cooled copper block was set in the quartz tube at the exit of the furnace behind the target to collect CNTs. During ablation, gas pressure is kept at 80 kPa (600 Torr) and the gas flow rate is 100 sccm. The gas flow velocity at a heated zone in the quartz tube is approximately 0.7 cm/s.

Spontaneous emission from the plasma plume near the target surface was collected by a lens and transferred to a spectroscopy (Acton Research Corp., SpectraPro-308i) via an optical fiber. Spectrum images of the spectrometer were observed using an ICCD detector (Princeton Instruments, ITE/CCD-576G). A delayed pulse generator was used to trigger the laser and to gate the ICCD detector. The ICCD was exposed for 100 ns at 100 ns to 20 μs after laser ablation. The plasma plume was observed at 1 mm from the target surface by opening one side of the furnace by 2–3 cm. Using measured spontaneous emission spectra, vibrational temperatures of C₂ molecules were estimated by fitting the Swan band spectrum calculated theoretically. The soot in the reactor tube were observed without purification by FE-SEM and TEM to compare the SWNTs produced in ambient argon gas with those in nitrogen gas.

3. Measurements and discussion

3.1. SEM and TEM images of soot

Fig. 2 shows the images of FE-SEM (a,b,c,d) and FE-TEM (e,f) of the soot deposited at the collector after laser ablation in argon gas (a,b,c) and in nitrogen gas (c,d,f). Since an amount of the amorphous carbon found in Fig. 2c,d is less than that in Fig. 2a,b, the production yield of SWNTs in nitrogen ambient gas seems to be larger than that in argon ambient gas.

From TEM images, the CNT bundles consisted of some SWNTs of approximately 1 nm in diameter. It is difficult to discuss the influence of ambient gas on the CNT diameter using the low-resolution TEM images. Raman spectra measurement may be necessary for further discussion.

3.2. Spontaneous emission from the carbon plume

Figs. 3 and 4 show the spontaneous emission spectrum observed in argon and nitrogen ambient gas at various time delays, respectively. Each spectrum is measured at a delay time of (a) 100 ns, (b) 500 ns, (c) 1 μs, (d) 5 μs, (e) 10 μs, and (f) 20 μs, is obtained by integration of 20 spectra. In Fig. 3, C₂ a Swan band spectrum ($a^3Π_u - d^3Π_g$) consists of various vibrational transitions, 450–470 nm ($Δν = -1$), 480–520 nm ($Δν = 0$) and 520–570 nm ($Δν = 1$), clearly recognized. The intensity decreases rapidly after 1 μs. In Fig. 4 for nitrogen ambient gas, the intensity of the C₂ Swan band spectrum is larger than those in argon gas, and the CN violet system is also observed at approximately 360–390 nm. It indicates that C₂ molecules are excited by nitrogen molecules more effectively than argon gas, and CN molecules are formed by the reaction between the C and N atoms produced by dissociation of the nitrogen molecule.

In Fig. 5 C₂ Swan band spectrum ($Δν = 0$) from the plasma plume in argon ambient gas observed at 100 ns after laser ablation is shown (thick line). In this figure, to estimate the vibrational temperature, C₂ Swan band ($Δν = 0$) spectrum calculated for 6700 K (thin line) is fitted to measured data. Fig. 6 shows the C₂ vibrational temperatures estimated by the method mentioned above as a function of time from laser ablation. Within 1 μs after ablation, estimated C₂ temperatures for both argon and nitrogen ambient gases are over 8000 K, which is higher than the furnace temperature. In argon ambient gas, C₂ temperature increases until 300 ns and then decreases. In nitrogen gas, an initial temperature is higher and decreases faster than that in argon atmosphere. This seems to be explained that C₂ molecules excited by laser loose less energy by collision with nitrogen molecules of lighter mass than argon at early stage. At a later phase C₂ molecules seem to lose much energy due to inelastic collisions with reactive nitrogen gas.

4. Conclusions

Spontaneous emission spectra of the plasma plume are measured by ablating a graphite composite target in...
argon and nitrogen ambient gas. In both gases, C$_2$ Swan band spectra were dominant and the CN violet system was observed in nitrogen atmosphere. It was found nitrogen gas enhanced the C$_2$ emission and decreased vibrational temperature of C$_2$ molecules after ablation. From the results of SEM images of soot, amorphous phase contained in the soot in the nitrogen ambient gas was less than those in argon gas. PLA in nitrogen...
Fig. 3. Spontaneous emission spectra measured at various delay times after laser ablation in argon ambient gas: (a) 100 ns, (b) 500 ns, (c) 1 μs, (d) 5 μs, (e) 10 μs and (f) 1 μs.

Fig. 4. Spontaneous emission spectra measured at various delay times after laser ablation in nitrogen ambient gas: (a) 100 ns, (b) 500 ns, (c) 1 μs, (d) 5 μs, (e) 10 μs and (f) 1 μs.
ambient gas seems to be more effective than in argon gas atmosphere from the viewpoint of suppressing amorphous carbon formation.

Acknowledgments

The authors would like to thank Professor M. Nishida and Mr M. Matsuda of the Department of Material Science for TEM measurement, and Mr K. Sakamoto and Kumamoto Industrial Research Institute for SEM measurements.

References