

Radical density measurements in microwave plasma with carbon-containing gases used for carbon nanotube and nanocrystalline diamond film growth

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Abstract: Optical absorption spectroscopy was applied to measure radical densities in the microwave plasma with carbon-containing gas mixtures used for the growth of carbon nanotube and nanocrystalline diamond films. C₂ (carbon dimer) radical density at the lowest excited state was measured using white-light absorption spectroscopy with Xe lamp emitting a continuous spectrum as a light source. Furthermore, carbon (C) atom density was measured using vacuum ultraviolet absorption spectroscopy with micro-discharge hollow-cathode lamp as a VUV light source. The correlation between the formation of carbon nanostructures and radical densities in the plasma is discussed.

Keywords: carbon, radical density, plasma CVD, absorption spectroscopy

1. Introduction

High-density plasmas such as microwave plasma employing carbon-containing gas mixtures have been used to fabricate carbon allotropes including diamond, nanocrystalline diamond (NCDs), and carbon nanotubes (CNTs). The main reaction mechanisms of deposition using plasmas are determined by the species produced in the plasma. To realize high-performance plasma process, it is important to first elucidate the specific species that contribute to the deposition. Second, on the basis of the knowledge of the species, it is desirable to supply important species in a controlled manner, in combination with monitoring technique. In the present study, optical absorption spectroscopy was applied to measure radical densities in the microwave plasma with carbon-containing gas mixtures. C₂ (carbon dimer) radical density at the lowest excited state was measured using white-light absorption spectroscopy with Xe lamp emitting a continuous spectrum as a light source. Furthermore, carbon (C) atom density was measured using vacuum ultraviolet (VUV) absorption spectroscopy with micro-discharge hollow-cathode lamp as a VUV light source.

2. Experiments

Microwave plasma is one of high-density plasmas and is suitable for decomposing H₂ molecules to generate H atoms effectively. Figure 1 shows a microwave plasma-enhanced chemical vapor deposition (CVD) system, which has been called ASTeX (Applied Science and Technology, Inc.) type. This system has been extensively used for the growth of diamond and NCD films and CNTs. The ASTeX-type reactor consists of a cylindrical stainless steel chamber. The microwave (2.45 GHz) is coupled from the rectangular waveguide into the cavity via an axial antenna. A discharge called a “plasma ball” is generated above the substrate. The plasma ball provides the substrate heating. In this system, the CVD process would be operated at pressures of a few tens of Torr (10³–10⁴ Pa), and the reactor pressure and microwave power cannot be varied completely independently. At too high pressure or low microwave power, plasma cannot be sustained. On the other hand, if the microwave power is too high for a given pressure, the plasma becomes unstable and tends to jump to the quartz (fused silica) window, occasionally resulting in the destruction of the window by the heat.

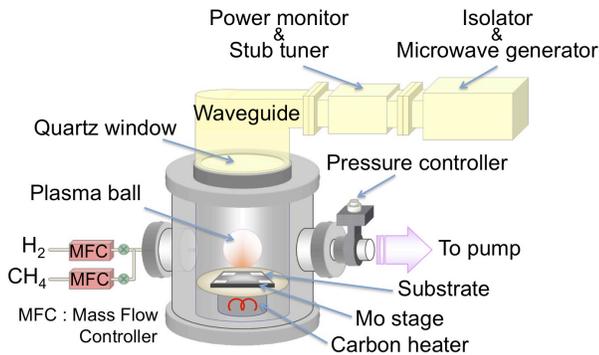


Figure 1. Schematic of microwave plasma-enhanced CVD system used for the growth of diamond, NCD and CNT.

CNT and NDC films were grown using conventional microwave plasma-enhanced CVD with a 2.45 GHz, 1.5 kW microwave generator, as shown in Fig. 1. The reactor consists of a cylindrical stainless steel chamber with an inner diameter of 11 cm, and a Mo substrate stage with a graphite heater that allows for control of the substrate temperature, independent of the microwave input power.

The C_2 radical density in a conventional microwave plasma-enhanced CVD with CH_4/H_2 mixture was measured using white-light absorption spectroscopy. Figure 2 shows an experimental setup used for the C_2 radical density measurement in the microwave plasma. The C_2 radical density at the lowest excited state $a^3\Pi_u$ was measured using absorption spectroscopy. A Xe lamp emitting a continuous spectrum was used as a light source, and transmittance spectra through the plasma were obtained at approximately 516 nm of ($v'=0, v''=0$) bandhead of C_2 Swan ($d^3\Pi_u - a^3\Pi_u$) system. The optical emission intensity of the (0,0) bandhead of the C_2 Swan system was also measured.

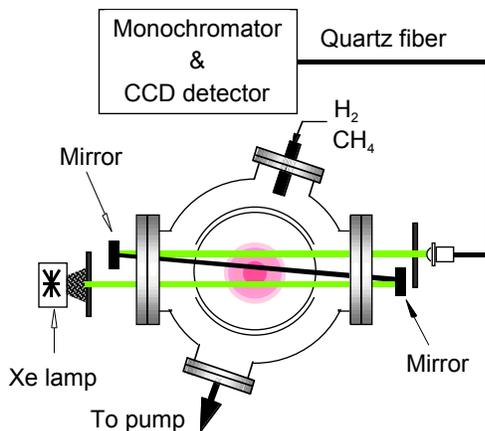


Figure 2. Schematic of experimental setup used for C_2 radical density measurement.

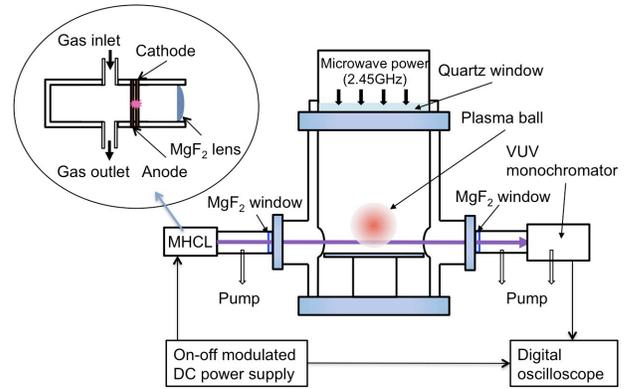


Figure 3. Schematic of experimental setup used for C atom density measurement.

Carbon (C) atoms can be produced in the gas phase by electron-impact dissociation of carbon-containing molecules or radicals and are considered to be extremely reactive in the gas phase, and their sticking probability at the surface is expected to be close to unity. Therefore, C atoms likely play important roles in the mechanism of carbon nanostructure formation. Therefore, measurements of C atoms in the plasma were carried out using the VUVAS technique. The VUVAS system for measuring the absolute densities of C atoms was setup as shown in Fig. 3. In the case of the measurement of absolute C atom density, a high-pressure CO_2 microdischarge hollow-cathode lamp (C-MHCL) was used as a VUV light source for absorption spectroscopy. The transition lines used for C atom density measurements were $2s^22p^2\ ^3P_1 - 2s^22p3s\ ^3P_2^o$ at 165.626 nm, $2s^22p^2\ ^3P_0 - 2s^22p3s\ ^3P_1^o$ at 165.692 nm, $2s^22p^2\ ^3P_2 - 2s^22p3s\ ^3P_2^o$ at 165.700 nm, $2s^22p^2\ ^3P_1 - 2s^22p3s\ ^3P_1^o$ at 165.737 nm, $2s^22p^2\ ^3P_3 - 2s^22p3s\ ^3P_1^o$ at 165.789 nm, and $2s^22p^2\ ^3P_5 - 2s^22p3s\ ^3P_3^o$ at 165.811 nm for the C atom. Since the wavelength resolution of the VUV monochromator was 0.4 nm, the total absorption intensity of six transition lines $2s^22p^2\ ^3P_J - 2s^22p3s\ ^3P_J^o$ ($J=0, 1, 2$) at 165.7 nm was measured for the absolute C atom density. He line at 164.0 nm was used for the evaluation of background absorption.

3. Results and discussion

Figures 4(a)–4(c) show SEM images of carbon-related materials fabricated by microwave plasma-enhanced CVD employing CH_4 and H_2 mixtures at different CH_4 concentrations. As shown in Fig. 4(a),

diamond films were grown typically at the H_2/CH_4 flow rate ratio of 50–100, total pressures of 45–55 Torr, and substrate temperature of approximately 700 °C on a scratched Si substrate. NCD films were grown at the H_2/CH_4 flow rate ratio of 10–30, as shown in Fig. 4(b) [1, 2]. In the case of the synthesis of aligned CNT films, on the other hand, deposition process was carried out at a low H_2/CH_4 flow rate ratio of 1–4 (Fig. 4(c)) [3, 4].

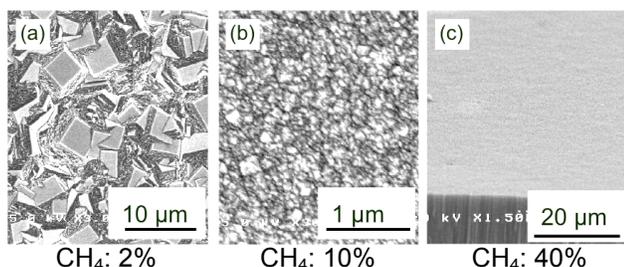


Figure 4. SEM images of carbon-related materials fabricated by microwave plasma-enhanced CVD at different flow rate ratios of H_2/CH_4 , (a) diamond film, (b) NCD film, and (c) aligned CNT film.

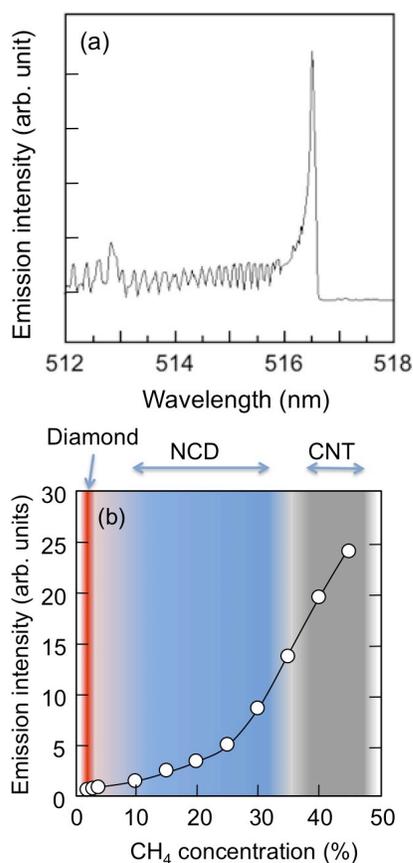


Figure 5. (a) Typical C_2 Swan band emission spectrum and (b) optical emission intensity of (0,0) bandhead of C_2 Swan system as a function of CH_4 concentration at total flow rate of 200 sccm, total pressure of 55 Torr, and microwave power of 800 W.

Figure 5(a) shows typical emission spectrum of the (0,0) vibrational band of the C_2 Swan system obtained at CH_4 concentration of 35% and microwave power of 800 W. Figure 5(b) shows the optical emission intensity of (0,0) bandhead of C_2 Swan system as a function of CH_4 concentration at total flow rate of 200 sccm, total pressure of 55 Torr, and microwave power of 800 W. As the CH_4 concentration increased up to 25%, emission intensity increased gradually. By further increasing the CH_4 concentration above 25%, the emission intensity increased rapidly.

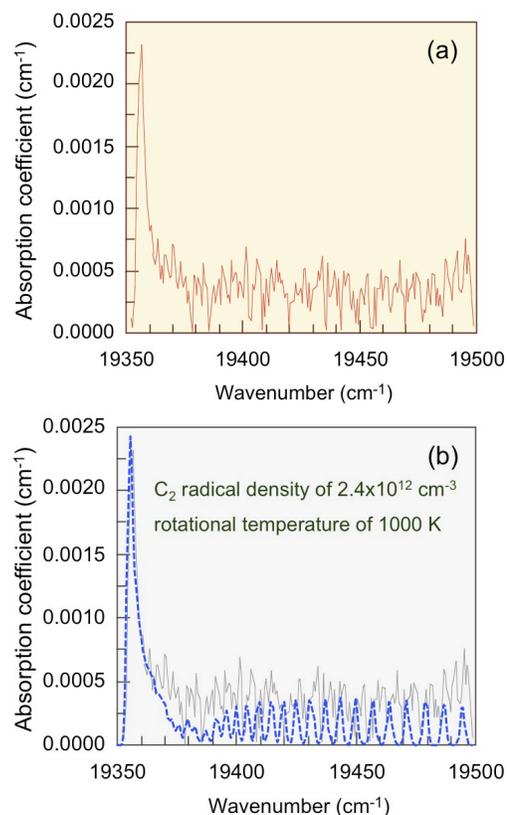


Figure 6. (a) C_2 Swan band absorption spectrum obtained at CH_4 concentration of 35%, total flow rate of 200 sccm, total pressure of 55 Torr, and microwave power of 800 W and (b) calculated absorption spectrum at the C_2 radical density at $v''=0$ level in the $a^3\Pi_u$ state and the rotational temperature to be $2.4 \times 10^{12} cm^{-3}$ and 1,000 K, respectively.

Figure 6(a) shows typical absorption spectrum of the (0,0) vibrational band of the C_2 Swan system obtained at CH_4 concentration of 35% and microwave power of 800 W. The absorption coefficient was obtained by dividing the negative of natural logarithm of the transmittance by an absorption pass length (33 cm), which is approximately equal to a three-fold length of inner

diameter of the cylindrical stainless steel chamber. Due to the overlapping of rotational lines at the bandhead at approximately 516 nm, it is difficult to measure the density for each rotational line. Therefore, the absorption coefficient was calculated as a function of wavenumber by choosing the rotational temperature and C_2 density at the $v''=0$ level in the $a^3\Pi_u$ state appropriately, and the calculated absorption spectrum shown in Fig. 6(b) was compared with the measured absorption spectrum. As a result of fitting the calculated profile to the measured one, the C_2 radical density at $v''=0$ level in the $a^3\Pi_u$ state and the rotational temperature were estimated to be $2.4 \times 10^{12} \text{ cm}^{-3}$ and 1,000 K, respectively, for the absorption spectrum shown in Fig. 6(a).

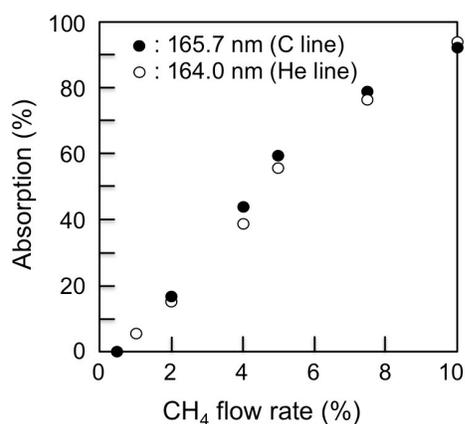


Figure 7. Absorption intensities measured at C and He transition lines as a function of CH_4 flow rate.

Figure 7 shows the absorption intensities measured at 165.7 nm for the C atomic resonance line and 164.0 nm for background absorption as a function of CH_4 flow rate ratio. The absorption intensity at C atomic resonance line increased with the increase of CH_4 flow rate in the microwave CH_4/H_2 plasma. However, the behavior measured at 165.7 nm was almost the same as that measured at 164.0 nm, suggesting that the background absorption by the species produced in plasma was dominant and the determination of C atom density could not be attained in these conditions.

In the case of microwave CH_4/H_2 plasma sustained at relatively high pressures under the typical condition for the growth of aligned CNT and NCD films, C_2 radical density was on the order of 10^{12} cm^{-3} , while the C atom density was below the

detection limit ($\sim 10^{11} \text{ cm}^{-3}$). Moreover, emission from C resonance line at 165.7 nm was hardly observed in the microwave CH_4/H_2 plasma. In this case, a lot of by-product molecules such as acetylene were generated in the plasma and absorbed dominantly the VUV light including C resonance line. This background absorption deteriorated the sensitivity of C atom detection at large flow rate of CH_4 seriously.

It is likely in CH_4 plasmas that C atoms are generated in stepwise processes via CH_3 , CH_2 , and CH. On the other hand, C atoms would be removed due to the reactions with CH_x radicals to produce acetylene and higher-order hydrocarbons. It was reported that acetylene molecules on the order of 10^{13} cm^{-3} were generated in hot filament CVD employing CH_4/H_2 mixture at 20 Torr [5]. Moreover, C atoms can react with acetylene [6].

Therefore, in the case of microwave plasma employing CH_4/H_2 mixture at relatively high pressures, it is considered that the direct effect of C atoms by way of the surface reaction might be negligible for the growth of NCD and CNT films.

References

- [1] M. Hiramatsu M, C.H. Lau, A. Bennett, and J.S. Foord, *Thin Solid Films* **407**, 18 (2002).
- [2] M. Hiramatsu, K. Kato, C.H. Lau, J.S. Foord, and M. Hori, *Diamond Relat. Mater.* **12**, 365 (2003).
- [3] M. Hiramatsu, H. Nagao, M. Taniguchi, H. Amano, Y. Ando, and M. Hori, *Jpn J. Appl. Phys. Exp. Lett.* **44**, L693 (2005).
- [4] M. Hiramatsu, T. Deguchi, H. Nagao, and M. Hori, *Diamond Relat. Mater.* **16**, 1126 (2007).
- [5] J. B. Wills, M. N. R. Ashfold, A. J. Orr-Ewing, Y. A. Mankelevich, and N. V. Suetin, *Diamond Relat. Mater.* **12**, 1346 (2003).
- [6] J. Benedikt, M. Wisse, R. V. Woen, R. Engeln, and M. C. M. van de Sanden, *J. Appl. Phys.* **94**, 6932 (2003).