

Selective growth of single-walled carbon nanotubes by plasma enhanced chemical vapor deposition

プラズマCVDによる単層カーボンナノチューブの選択合成

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Atmospheric pressure radio-frequency discharge (APRFD) has advantage over vacuum-oriented plasma enhanced chemical vapor deposition (PECVD) in terms of single-walled carbon nanotube (SWCNT) growth. Plasma-generated C_2H_2 is the main CNT growth precursor in PECVD. In the cathode sheath of APRFD, approximately 30% of the CH_4 (initial feedstock) was converted into C_2H_6 , C_2H_4 and C_2H_2 . A trace amount of C_2H_2 enabled the synthesis of SWCNTs in the thermal CVD regime. Hydrogen is necessary to grow SWCNTs under non-thermal plasma environment because H_2 suppresses formation of excess amount of C_2H_2 ; however, H_2 does not eliminate amorphous carbon even at H_2/C_2H_2 ratios of 300. Atmospheric-pressure PECVD performed with a $He/CH_4/H_2$ system is equivalent to C_2H_2 -assisted thermal CVD without an etching gas. Depending on pressure, in other words C_2H_2 content, SW and MWCNTs can be selectively synthesized.

1. Introduction

There were no reports on SWCNT synthesis in the PECVD regime by 2003 [1]. Tremendous effort has been made towards the control growth of desired CNTs using unique properties of reactive plasma, enabling SWCNTs under the low-pressure remote plasma CVD system [2]. However, due to limited supply of plasma-generated reactive species, SWCNT growth rate is unexpectedly low and dense SWCNT film is hardly synthesized. Exceptionally, microwave remote plasma CVD successfully grew millimeter-tall SWCNTs [3]. Atmospheric pressure plasma enhanced CVD (AP-PECVD) was originally highlighted because of its simplicity and flexibility over the process parameters. More recently, it is recognized as one of the promising technique to grow vertically aligned SWCNTs [4,5].

In PECVD, conversion of initial feedstock into acetylene (C_2H_2) is the key to determining CNT morphology and to enhance overall growth rate. Main role of H_2 , as supposed to be an etchant, is actually to suppress C_2H_2 formation during plasma-induced decomposition of initial feedstock. Note C_2H_2 -sensitized thermal CVD does not fully reproduce plasma-grown SWCNTs due to the presence of ions [5]. In this paper, we focus on the gas analysis to identify the key species responsible for SWCNT growth in the non-thermal plasma environment. The role of plasma-generated C_2H_2 on CNT growth is highlighted as a major CNT growth precursor and selective growth of SW and MWCNTs are discussed.

2. Experimental

A capacitively coupled RF discharge (13.56 MHz) was generated between two parallel-plate metallic electrodes separated by 5 mm. The RF power was transmitted through the upper electrode (40 mm diameter) equipped with water-cooled sintered metallic mesh plate [6]. The sintered metal plate was manufactured from stainless steel powders with an average grain size of 100 μm .

A catalyst-coated substrate was located on the heated bottom electrode. A detailed catalyst preparation procedure is described in Refs. [4]. Briefly, an aluminum oxide thin film with estimated thickness 20 nm was initially coated on a silicon substrate (15 × 15 mm). The iron catalyst was dip-coated using an iron-acetate-containing ethanol solution. The dip-coated substrate was annealed in air at 400 °C for five minutes. The iron oxide was reduced by atmospheric pressure RF discharge in the He and H_2 mixtures (1500, 10 $cm^3 min^{-1}$). After a five-minute plasma treatment at 500 °C, the substrate temperature was elevated to 700 °C, and the flow rates of He, H_2 and CH_4 were adjusted for CNT growth.

3. Online gas analysis in the plasma sheath

The gas component in the cathode plasma sheath was analyzed qualitatively using a quadrupole mass spectrometer (QMS; Prisma, Pfeiffer Vacuum Technology). A thin metallic capillary tube (outer diameter, 450 μm ; inner diameter, 250 μm) with an outer diameter one-half of the sheath thickness was

inserted into the sheath. The reacting gas was extracted directly for online gas analysis, and fragment peaks from $m/e = 1$ to 100 were recorded. A clear difference is observed between $m/e = 25$ and 30. Except for methane, the main hydrocarbon component is C_2H_6 , although a trace amount of C_2H_2 and C_2H_4 are possible. Other fragment peaks related to higher hydrocarbons, such as propane ($m/e < 44$) and butane ($m/e < 58$), were not detected. For quantitatively gas analysis, the reacting gas was accumulated in a gas bag and then analyzed by gas chromatography (Shimadzu, GC-8A).

Figure 1 shows the CH_4 conversion and selectivity for the C_2 hydrocarbons at different conditions. At 100 kPa, the main product is C_2H_6 that corresponds well with mass spectrometry analysis. In addition, 20% of the C_2H_4 and a trace amount of C_2H_2 were detected and the product selectivity is influenced by H_2 content. C_2H_2 content was approximately 70 ppm with H_2 dilution and 220 ppm without H_2 . C_2H_6 selectivity is remarkably decreased at 20 kPa. C_2H_6 is produced by a three-body recombination of CH_3 ($CH_3 + CH_3 + M = C_2H_6 + M$). The overall reaction rate is pressure dependent, thus C_2H_6 formation is suppressed as the total pressure decreases. Correspondingly, the selectivity for C_2H_4 and C_2H_2 was increased at reduced pressures.

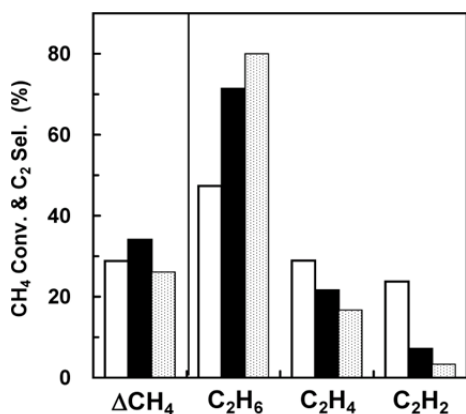


Figure 1 CH_4 conversion and selectivity for the C_2 hydrocarbon. □ 20 kPa, $H_2 = 0$; ■ 100 kPa, $H_2 = 0$; ▨ 100 kPa, $H_2 = 90 \text{ cm}^3 \text{ min}^{-1}$. He/ $CH_4 = 3000/48 \text{ cm}^3 \text{ min}^{-1}$ and 60 W.

3. Pressure-dependent selective growth of CNTs

CNTs produced at different total pressure and fixed input power (60 W) were characterized by micro-Raman spectroscopy equipped with 514 nm excitation laser (Seki Technotron STR750 Laser Raman Spectrometer). Figure 2 shows pressure-dependent change in the peak intensity ratio of G-band to D-band of Raman spectrum (hereafter the G/D ratio). The G/D ratio decreases as total

pressure decreases, implying formation of defective graphite structure is enhanced in the reduced pressure. In other word, G/D ratio deteriorates as C_2H_2 increases. TEM analysis clearly showed that MWCNTs were preferentially synthesized at reduced pressure. In addition to total pressure, the G/D ratio depends greatly on initial amount of catalyst metal [8]. There is an optimum value for the initial amount of catalyst precursor for SWCNT growth.

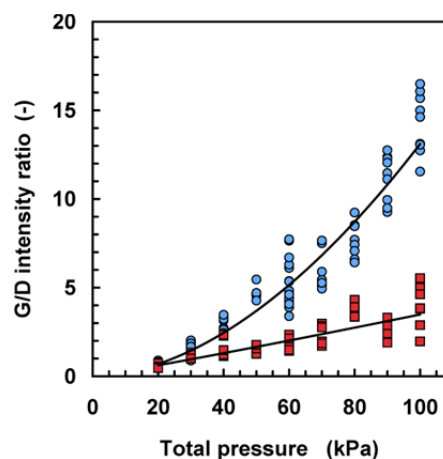


Figure 2 Pressure-dependent change in the G/D ratio of CNTs: He/ CH_4/H_2 , 3000/48/90 $\text{cm}^3 \text{ min}^{-1}$; 60 W; 700°C; 3 min synthesis; Fe catalyst, ● 0.15 and ■ 0.05 wt%

Concluding remarks

Plasma-produced C_2H_2 is the key component to grow CNTs. Atmospheric pressure RF discharge enabled SWCNTs because it suppressed C_2H_2 formation. SWCNTs turned MWCNTs as total pressure decreased where C_2H_2 content increased. Note that ions are unique in plasma process thus C_2H_2 -assisted thermal CVD does not fully reproduce plasma grown CNTs.

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