Factors determining single-walled carbon nanotube growth by PECVD

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Abstract: Atmospheric pressure radio-frequency discharge (APRFD) has great advantage over vacuum-oriented plasma enhanced chemical vapor deposition (PECVD) as well as other types of atmospheric pressure plasma sources in terms of single-walled carbon nanotube (SWCNT) growth. It was found that the plasma-generated C\textsubscript{2}H\textsubscript{2} is the main CNT growth precursor in PECVD. Approximately 30\% of the CH\textsubscript{4} (initial feedstock) was converted into C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{2} at atmospheric pressure and 700 °C. A trace amount of C\textsubscript{2}H\textsubscript{2} enabled the synthesis of SWCNTs in the thermal CVD. Hydrogen is necessary to grow SWCNTs using PECVD because H\textsubscript{2} suppresses formation of excess amount of C\textsubscript{2}H\textsubscript{2}; however, H\textsubscript{2} does not eliminate amorphous carbon even at H\textsubscript{2}/C\textsubscript{2}H\textsubscript{2} ratios of 300. PECVD using a binary mixture of C\textsubscript{2}H\textsubscript{2} and isotope-modified 13CH\textsubscript{4} demonstrated that CH\textsubscript{4} does not contribute to CNT growth in C\textsubscript{2}H\textsubscript{2}-assisted thermal CVD. Atmospheric-pressure PECVD performed with a He/CH\textsubscript{4}/H\textsubscript{2} system is equivalent to C\textsubscript{2}H\textsubscript{2}-assisted thermal CVD without an etching gas. APRFD appears to produce a hidden species, which influences the CNT growth process.

Keywords: Carbon nanotubes, Atmospheric pressure PECVD, Non-equilibrium, C\textsubscript{2}H\textsubscript{2}-assisted chemical vapor deposition.

1. Introduction

Until 2003, there were no reports on SWCNT synthesis in the PECVD regime [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 grow millimeter-tall SWCNT mat [3]. Atmospheric pressure plasma enhanced CVD (AP-PECVD) was originally highlighted because of its simplicity and flexibility over the process parameters. However, SWCNTs have not been synthesized by AP-PECVD except atmospheric pressure radio-frequency discharge (APRFD) [4].

In PECVD, conversion of initial feedstock into acetylene (C\textsubscript{2}H\textsubscript{2}) is the key to determining CNT morphology and to enhance overall growth rate. Main role of H\textsubscript{2}, as supposed to be an etchant, is actually to suppress C\textsubscript{2}H\textsubscript{2} formation during plasma-induced decomposition of initial feedstock. Interestingly, H\textsubscript{2} does not contribute amorphous carbon removal from the catalysts. It must be emphasized that C\textsubscript{2}H\textsubscript{2}-sensitized thermal CVD does not fully reproduce plasma-grown SWCNTs. For further understanding of CNT growth mechanism, we should not exclude plasma-generated "hidden species" and their role on CNT growth process. 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\textsubscript{2}H\textsubscript{2} on CNT growth is highlighted as a major CNT growth precursor. The results are compared with APRFD-grown CNTs using isotope-modified 13C methane for the kinetic analysis. Finally, the role of non-thermal plasma on CNT growth is presented.

2. Experimental

Figure 1 schematically shows the APRFD during CNT synthesis [4]. The 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. The sintered metal plate was manufactured from stainless steel powders with an average grain size of 100 μm. The atmospheric pressure glow discharge has been characterized empirically as a spatially uniform non-thermal plasma by optical emission spectroscopy, high-speed camera imaging and electrical current measurements [5–8]. In addition, gas flow pattern is an essential parameter that influences the gas-phase plasma chemistry and the species transportation between the gap [9]. Previously, a showerhead electrode with 20-pinholes having 1 mm diameter was used; however, this electrode creates a complex flow pattern and does not guarantee uniform CNT growth over the substrate as the total gas flow rate increases. The sintered metal plate is more reliable than the showerhead electrode.

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 an estimated thickness 20 nm was 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 APRFD using He and H2 mixtures (1500, 10 cm3min−1). After a five-minute plasma treatment at 500 °C, the substrate temperature was elevated to 700 °C, and the flow rates of He, H2 and CH4 were adjusted for CNT growth.

3. Online gas monitoring in the sheath

The gas component in the cathodic 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; length, 1000 mm) 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 C2H6, although a trace amount of C2H2 and C2H4 are possible. Other fragment peaks related to higher hydrocarbons, such as propane (m/e < 44) and butane (m/e < 58), were not detected. The detailed gas components are not clear because the mass fragments originating from C2H6, C2H4 and C2H2 overlap. For quantitatively gas analysis, the reacting gas was accumulated in a gas bag and then analyzed by gas chromatography with an FID detector (Shimadzu, GC-8A).

Figure 2 shows the CH4 conversion and selectivity for the C2 hydrocarbons at different conditions. At 100 kPa, the main product is C2H6, according to the QMS online gas analysis. In addition, 20% of the C2H4 and a trace amount of C2H2 were detected and the product selectivity is influenced by H2 content. The C2H2 content was approximately 70 ppm with H2 dilution and 220 ppm without H2. C2H6
selectivity is remarkably decreased at 20 kPa. $\text{C}_2\text{H}_6$ is produced by a three-body recombination of $\text{CH}_3$:  
$$\text{CH}_3 + \text{CH}_3 + \text{M} = \text{C}_2\text{H}_6 + \text{M} \quad \text{R1}$$

The overall reaction rate is pressure dependent, thus $\text{C}_2\text{H}_6$ formation is suppressed as the total pressure decreases. Correspondingly, the selectivity for $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_2$ was increased at reduced pressures. $\text{C}_2\text{H}_2$ is preferentially produced in the low-pressure plasma [3,10].

### 4. $\text{C}_2\text{H}_2$-assisted thermal CVD

Recent advances in CNT growth mechanisms revealed that $\text{C}_2\text{H}_2$ is an important precursor of CNT growth. Maruyama and co-workers performed SWCNT growth in the thermal CVD regime using $\text{C}_2\text{H}_5\text{OH}$ as the carbon source. Addition of a trace amount of $\text{C}_2\text{H}_2$ in the presence of $\text{C}_2\text{H}_5\text{OH}$ accelerates the SWCNT growth rate by 10-fold [11]. In addition to $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_5\text{OH}$ was intrinsic to prolonging the catalyst activity and enhancing the SWCNT growth rate. Zhong et al. performed a similar experiment using $\text{C}_2\text{H}_2$ as the reaction promoter [3]. The chirality distributions of the SWCNTs synthesized by the $\text{C}_2\text{H}_2$-assisted thermal CVD and microwave remote plasma CVD were almost identical: They concluded that the plasma-generated $\text{C}_2\text{H}_2$ is the main CNT growth precursor in PECVD. Unlike the $\text{C}_2\text{H}_2/\text{C}_2\text{H}_5\text{OH}$ system, growth acceleration was not observed in the $\text{C}_2\text{H}_2/\text{CH}_4/\text{H}_2$ system.

We also performed $\text{C}_2\text{H}_2$-assisted thermal CVD because a trace amount of $\text{C}_2\text{H}_2$ was identified by gas analysis. Figure 3 shows a cross-sectional SEM micrograph of the CNT layers (scanning electron microscope; Hitachi, S-800). The first CNT layer was synthesized by APRFD (60 W) for one minute using a He/CH$_4$/H$_2$ = 3000/48/90 cm$^3$/min mixture. The second CNT layer was synthesized in the thermal CVD regime for five minutes by adding 100 ppm C$_2$H$_2$ while the He/CH$_4$/H$_2$ flow rates were kept constant. The cross-section Raman spectrum is shown in Fig. 4 (Seki Technotron, STR750 Laser Raman Spectrometer). It proves that the CNTs were grown in the root growth regime. Although the first and the second CNT layers are clearly distinguished by the SEM micrograph, the CNTs at locations I and II exhibit similar Raman spectra. The CNT growth rate was more than doubled in the second layer. The average growth rate for the first layer was 3.7 $\mu$m/min and 8.3 $\mu$m/min for the second layer. The radial breathing mode (RBM) peaks were no longer observed at location III, implying $\text{C}_2\text{H}_2$ promotes amorphous carbon deposition simultaneously. Note, a similar experiment was performed using $\text{C}_2\text{H}_6$, which is the dominant plasma-generated species (see Figure 2). However, the carbon precipitation was absent.

![Figure 3. Cross-sectional SEM micrograph of CNT layers. The second layer was grown by $\text{C}_2\text{H}_2$-assisted thermal CVD.](image)

![Figure 4. Cross-sectional Raman spectra of the CNTs shown in Figure 3.](image)

### 5. $^{13}\text{CH}_4$ isotopic labeling study

A trace amount of $\text{C}_2\text{H}_2$ enables the synthesis of SWCNTs in the thermal CVD regime with Fe/Al$_2$O$_x$ catalysts at 700 °C. However, SWCNT growth is eventually terminated because $\text{C}_2\text{H}_2$ excessively precipitates a carbon species on the catalysts. Although the $\text{C}_2\text{H}_2$ concentration was adjusted so that APRFD-generated $\text{C}_2\text{H}_2$ is re-produced, the CNT growth rate was accelerated more than two-fold when the $\text{C}_2\text{H}_2$ was 100 ppm and $\text{C}_2\text{H}_2$-assisted
thermal CVD does not fully reproduce AP-PECVD. To investigate the individual contribution of CH$_4$ and C$_2$H$_2$ on CNT growth, CNTs were synthesized using isotope-modified CH$_4$, hereafter designated as $^{13}$CH$_4$. Figure 5 shows the Raman spectra of CNTs synthesized under three different conditions (see Table 1). All of the Raman peaks shift towards lower wavenumbers when the CNTs consist of $^{13}$C isotopes [12] (Figure 5(I)). SWCNTs consisting of $^{12}$C were grown by C$_2$H$_2$ without H$_2$ and CH$_4$ (III). By comparing conditions II and III, the G- and D-band peaks do not shift to lower wavenumbers, indicating that $^{13}$CH$_4$ does not contribute to CNT growth during C$_2$H$_2$-assisted thermal CVD. In PECVD, H$_2$ is considered to be an effective etching gas and is frequently used for CNT growth. However, H$_2$ does not seem to contribute to amorphous carbon elimination. The selectivity for C$_2$H$_2$ increases at reduced pressures, which is an essential mechanism for the transformation of SWCNTs into DW- and MWCNTs as the pressure decreases [9]. AP-PECVD in a He/CH$_4$/H$_2$ system is equivalent to C$_2$H$_2$-assisted thermal CVD in the absence of an effective etching gas. The addition of an appropriate amount of an oxygen-containing species as an etchant could be effective to enhance the catalyst activity and to prolong their lifetime in AP-PECVD [13].

![Figure 5. Raman spectra of CNTs synthesized by different gas mixtures.](image)

Table 1. Initial gas components (units: cm$^3$/min$^{-1}$), 700 °C and 100 kPa.

<table>
<thead>
<tr>
<th>Method</th>
<th>CH$_4$</th>
<th>H$_2$</th>
<th>C$_2$H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I AP-PECVD (60 W)</td>
<td>40</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>II Thermal CVD</td>
<td>40</td>
<td>90</td>
<td>0.3</td>
</tr>
<tr>
<td>III Thermal CVD</td>
<td>0</td>
<td>0</td>
<td>0.3</td>
</tr>
</tbody>
</table>

**Concluding remarks**

The results presented here are similar to Zhong et al. in terms of the initial feedstock and the type of catalyst [3]. Nevertheless, we were unable to fully reproduce APRFD-grown CNTs by C$_2$H$_2$-assisted thermal CVD. In the microwave remote plasma CVD, the point electrode becomes the cathode that attracts the majority of the plasma-generated positive ions. Eventually a neutral species such as C$_2$H$_2$ should contribute to SWCNT growth. In contrast, APRFD is characterized as capacitively coupled RF discharge. Ionic species, such as CH$_4^+$ and H$_2^+$, are populated in the bulk plasma as a result of the RF operation. Subsequently, a sufficient amount of ions can be transported to the substrate because the electron-ion recombination is likely absent due to the low electron density in the sheath [8]. Indeed, the CNT growth rate was notably decelerated in the mesh-inserted AP-PECVD, which minimizes the ion flux to the substrate [14]. For deeper understanding of CNT growth mechanisms, we should not exclude the plasma-generated hidden species and their role in CNT growth processes.

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**References**