Application of High Reproducible Intelligent MPCVD System in CNTs Process Control

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ABSTRACT
This study integrates intelligent remote monitoring and control technology into microwave plasma chemical vapor deposition (MPCVD) system with the reflected microwave power as the main feedback signal. An automatic fuzzy control scheme is used to adjust electromagnetic field distribution, plasma density, and reflected microwave power of the MPCVD system. The intelligent control includes establishment of database, fuzzification of principal component, membership function, fuzzy inference rules, and defuzzification. An (X, Y) position of (19.3 cm, 10 cm) for E-H tuner adjustment is found to have the lowest average reflected power. The averaged films thickness is 15.44 µm, the averaged tube diameter is 42 nm, and the \( I_G/I_D \) ratio is 1.12 for as-grown carbon nanotubes (CNTs) film. With the as-obtained CNT films as the field emission, which area is 0.33 cm², the turn-on voltage is 1.3 V/µm and the threshold voltage is 4.7 V/µm.

Keywords: MPCVD system, fuzzy control, CNTs, \( I_G/I_D \) ratio

1. INTRODUCTION
After carbon nanotubes were discovered by Iijima [1]. It becomes one of the most important materials in recent years and there are many fabrication methods for CNTs [2-4]. But there are less information about the relationship between the micro structure of CNTs and its applications. In this study, we use the MPCVD system to grow CNTs and control its micro structure. This MPCVD system utilizes microwave to produce the plasma and deposit the carbon atom on the substrate [5]. The microwave from magnetron travels through the wave-guide to reaction chamber, then it vibrates, after adjusting E-H tuner, back and forth to produce a stationary wave in reaction chamber. The molecules of inserted pumped-in gases, such as methane, hydrogen and nitrogen, are ionized by stationary microwave energy to grow the CNTs. Besides, this energy also transfers the energy of electromagnetic to heat the substrate [6].

The E-H tuner which is controlled by automatic linear cylinder to produce the plasma is the main characteristic of this MPCVD system, and it is combined with the PC-based controller to complete an automatic control system. The PC-based controller with a fuzzy logic function can figure out the corresponding positions of E-H tuner which can grow the CNTs that the micro structure is we want, and the motivation of E-H tuner will drive by linear cylinder to the specific position after controller calculated. Therefore, the MPCVD system combined with the PC-based controller which has the database of the relationship between CNTs structure and E-H tuner position, the system can achieve high reproducible coating equipment by intelligent control system. This system can raise the quality of thin films and also can combine with on line detector such as thickness or micro structure measure to achieve the mass produce in the future. The equipment is shown as fig. 1.

According to Raman spectra detect in the CNTs structure analysis, the G-band represents degree of graphite, the D-band represents the defect of carbon bonding, and \( I_G/I_D \) ratio is an index of randomness [7]. This study showed the ratio of these two peaks are different by change the microwave electromagnetic field and reflective power, therefore it focused on positions control of E-H tuner in MPCVD system because the position of E-H tuner is relate to plasma density, then MPCVD system could produce the CNTs which the structure was we wanted. Both the CNTs process and micro structure analysis are integrated in the intelligent MPCVD system; each position has its corresponding \( I_G/I_D \) ratio which is calculated by the membership function of fuzzy logic to help the processing system achieve a high reproducible performance.

2. EXPERIMENT
In this MPCVD system, the reaction chamber is a vertical quartz tube (diameter is 50 mm, thickness is 205 mm, height is 600 mm), the microwave source from magnetron is a 2.45 GHz with 2 kW power output; it crossed the rectangle wave guide (WR340) into the wave guide chamber. In order to reduce the reflective power after resonated, adjusted the E-H tuner (as fig. 2) to match plasma source is necessary. In the quartz tube (chemical reactant), the electromagnetic energy of microwave excited the gas to ionize and produced plasma to proceed chemical vapor deposition to grow the CNTs thin film. The system is shown in fig. 3. [8]
In terms of experimental parameters, this study divides the E-H tuner in the MPVCD system into the three axes of X, Y and Z. Axis Z represents stationary wave that would appear at the center of the quartz tube when the position of Z-tuner is set at 5 cm (as fig. 4) [9]. As the Z-tuner remains fixed, both axes X and Y need to be changed to facilitate a series of experiments. The study utilizes a reflective power lower than 50% to choose the position, perform the experiment, and analyze the structure of CNTs in different E-H tuner positions. The results are then edited into a database for the fuzzy controller system.

![Fig. 4 Stationary wave at center of quartz tube](#)

The X, Y tuner positions were figured out by triangular membership function of fuzzy rule and the database of relationship between E-H tuner position and micro structure as a fuzzy rule base for inference engine to defuzzification. The specific \(I_D/I_G\) ratio we entered was a fuzzy singleton which calculated by center of area (COA) method that was from database in this study. After position decided, MPCVD system orientated by linear motor which had optical grating feedback, the block diagram as shown in fig. 5. Let the MPCVD system become to a closed loop system and to optimize parameters which are suitable for growth CNTs in MPCVD system.

On the other hand, the fixed parameters of CNTs deposition process were shown as table 1, these were decided from optimize database which were suitable for CNTs growing, so that these were chosen to the fixed parameters at this stage of all intelligent MPCVD control study, the only changed parameter was the position of X and Y tuners.

![Fig. 5 Block diagram of MPCVD system](#)

<table>
<thead>
<tr>
<th>Table 1. Fixed parameters of CNTs growth process</th>
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<tbody>
<tr>
<td><strong>Gas ratio</strong> ([\text{CH}_4]:[\text{H}_2]:[\text{N}_2])</td>
</tr>
<tr>
<td><strong>Power source</strong></td>
</tr>
<tr>
<td><strong>Working distance</strong></td>
</tr>
<tr>
<td><strong>Growth time</strong></td>
</tr>
<tr>
<td><strong>Total pressure</strong></td>
</tr>
<tr>
<td><strong>Substrate</strong></td>
</tr>
<tr>
<td><strong>Preprocess</strong></td>
</tr>
<tr>
<td><strong>Catalyst</strong></td>
</tr>
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### 3. RESULTS and DISCUSSION

The main purpose of this study is to examine with the relationship between E-H tuner and the micro structure of CNTs. There had three parts of results in this study. First is the proof of reproducible performance in MPVCD system that is the relationship between different E-H tuner positions and CNTs structure. Fig. 6 shown the reproducibility of MPVCD system which was by the same E-H tuner position that \((X, Y)\) is \((15.2 \text{ cm}, 12.9 \text{ cm})\) location to grow the CNTs, the average of \(I_D/I_G\) ratio is 1.12, the standard deviation is 0.059, and the plasma geometry is the most uniform shown as Fig. 7, the reflect is also lowest at 7.6%. After compared, it can prove the reproducible of CNTs process by MPVCD system, because the same plasma electromagnetic field and the same parameters.

Fig. 8 shown that changed the positions of E-H tuner could influenced not only plasma density but also reflective power, moreover it could influenced the \(I_D/I_G\) ratio of CNTs, therefore establish database of MPVCD system is an important step for intelligent controller in this study.

![Fig. 6 Raman spectra of the same E-H tuner position](#)

![Fig. 7 The uniform geometry of plasma in MPVCD](#)

![Fig. 8 Raman spectra of different E-H tuner positions](#)
by intensity ratio, this method was took the intensity value of D-band and G-band peaks to calculate the \(\frac{I_D}{I_G}\) ratio.

Because of the microwave source belong to 2.45 GHz frequency, the wavelength about 12.2 cm, it caused there were some positions of E-H tuner couldn’t to achieve the turn on electric field of plasma, fig. 9 and fig. 10 shown the distribution model of two kinds \(\frac{I_D}{I_G}\) ratio methods. After the database established, the results showed that the database could lead out the trend of plasma turn on electric field position and CNTs structures.

\[
y = y_0 + \frac{2 \cdot A}{\pi} \cdot \frac{w}{4(x-x_0)^2 + w^2} 
\]

\(y_0\)= baseline offset  
\(A\)= total area under the curve from the baseline  
\(X_0\)= center of the peak  
\(W\)= full width of the peak at half height

Fig. 9 The relation between \(\frac{I_D}{I_G}\) ratio and E-H tuner positions which calculated by Lorentz

Fig. 10 The relation between \(\frac{I_D}{I_G}\) ratio and E-H tuner positions which calculated by intensity ratio

Fig. 11 Compare with two kinds of \(\frac{I_D}{I_G}\) ratios

The third result compares the characteristics of different aspect ratios. According to SEM morphologies, different E-H tuner positions also affected each aspect ratio. Because of the higher aspect ratio the larger partial electric filed is necessary in field emission technology and the electrons are easier to through into vacuum gap from CNTs [10], so that besides structure ratio, the aspect ratio is also an important index of MPCVD system.

Both reproducible of CNTs structure at the same position and the aspect ratio are needed to prove, so that utilize the E-H tuner position of lowest reflective power (X, Y)is (15.2 cm, 12.9 cm) that to proceed experiment. The average of aspect ratio (thickness/diameter) is 364, the average thickness is 16.42 µm, the average of diameter is 45.32 nm and the field emission shows as fig. 12, the turn on voltage can go down to 1.3 V/µm, the I-V curve as shows in fig. 13. Table 2 shows the length and diameter of CNTs are in the allow range of tolerance, moreover these had well align, therefore this study have high reproducibility.

Table 3 shows that utilize the minimum of \(\frac{I_D}{I_G}\) ratio to correspond the aspect ratio of CNTs. After combined the aspect ratio and \(\frac{I_D}{I_G}\) ratio, the intelligent controller can make the decision and fuzzy logic control for CNTs process. Finally, the MPCVD system can get the CNTs that has optimize structure and well performance.

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Diameter</th>
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<tr>
<td>15.44 µm</td>
<td>45.43 nm</td>
</tr>
<tr>
<td>17.61 µm</td>
<td>46.67 nm</td>
</tr>
<tr>
<td>15.22 µm</td>
<td>48.89 nm</td>
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</tbody>
</table>
Table 3. Utilize the minimum of $I_D/I_G$ ratio to correspond the aspect ratio of CNTs

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Diameter</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.9 $\mu$m</td>
<td>26.52 nm</td>
<td>0.44</td>
</tr>
<tr>
<td>31.48 $\mu$m</td>
<td>20.77 nm</td>
<td>0.39</td>
</tr>
<tr>
<td>30.33 $\mu$m</td>
<td>27.11 nm</td>
<td>0.6</td>
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4. CONCLUSIONS
In this study, we carried out the MPCVD system with intelligent control system which combined with fuzzy logic to grow CNTs. The results showed that this system can achieve a high reproducible ability in CNTs process, such as micro structure and thickness of thin films. Apply the automation electromagnetic regulator (E-H tuner), utilized the reflective power meter and stepping motor encoder to feedback the parameters for controller to automate the system. Input the values of $I_D/I_G$ ratio or aspect ratio into the MPCVD system controller and through the fuzzy logic to regular the electromagnetic and reflective power. Finally, the products of CNTs have a high yield and it can be applied on many kinds of industries, such as field emission display or fuel cell etc.

5. REFERENCES
[8] Shi-Hao Yan, Chii-Ruey Lin, Chun-Hsi Su “Study of Plasma Shape and Working Distance between Substrate and Plasma Core on Synthesizing Diamond Films” National Taipei University of technology Institute of Mechatronic Engineering July, 2004