Comparison of source gases and catalyst metals for growth of carbon nanotube

Tae Young Lee, Jae-Hee Han, Sun Hong Choi, Ji-Beom Yoo, Chong-Yun Park, Taewon Jung, SeGi Yu, Junghie Lee, Whikun Yi, Jong Min Kim

Abstract

Effects of different carbon source gases and catalyst metals on the growth characteristics and emission properties of carbon nanotubes (CNTs) were investigated. As the flow rate ratio of NH$_3$/C$_2$H$_4$ increased, the growth rate of CNTs was enhanced and the average diameter of CNTs became smaller. Ni was more efficient for the field emission of CNTs than any other catalyst metals when using the C$_2$H$_4$ gas, and in case of C$_2$H$_4$ as the carbon source, Co played an important role as a catalyst. When using the CO gas, Fe was the most activated catalyst for the CNTs growth under the flow rate ratio of CO/NH$_3$ of 18. CNTs grown using different catalyst metals had their corresponding catalyst particles at the top of the tips.

Keywords: Carbon nanotube; Source gas; Catalyst metal; Field emission

1. Introduction

Among various synthesis methods for the carbon nanotube (CNT) growth, chemical vapor deposition (CVD) method has been used for the growth of CNTs [1–3]. Especially, plasma enhanced chemical vapor deposition (PECVD) method has been reported as a promising candidate for the synthesis of CNTs [4–6]. In PECVD method for the CNTs growth, many gaseous precursors such as CH$_4$, C$_2$H$_2$, C$_6$H$_6$ and CO have been employed. These precursors play important roles in the growth characteristics and properties of CNTs because of their own binding energy, type, and role of reactive species under plasma, and thermodynamic properties. However, there have been few reports on the effect these precursors on the growth characteristics and properties of CNTs.

In this study, we used C$_2$H$_2$, CO and C$_2$H$_4$ for the growth of CNTs as a carbon source and investigate effects of different precursors on the growth characteristics and emission properties of CNTs. The effect of the catalyst such as Ni, Co, and Fe on the growth characteristics of CNTs with different precursors was also studied and compared.

2. Experiments

In this work, the growth of vertically aligned CNTs was carried out using various source gases with NH$_3$ as a catalytic gas on different catalyst metals (Ni, Co and Fe) coated glass substrate with Cr buffer layers. The Cr buffer layer of 1700 Å and the catalyst layer of 300 Å were deposited on the glass substrate by electron beam evaporation. The CNT growth was performed at the temperature at approximately 550 °C by the PECVD method. A C$_2$H$_6$, C$_2$H$_4$ and CO gas was used as the carbon source and the NH$_3$ gas was used as the catalyst and a dilution gas, respectively. The experimental details are listed in Table 1. A d.c. plasma was used to grow vertically aligned CNTs. Detailed processes for the growth of CNTs were described in our previous reports [7–9]. Field-emission scanning electron microscopy and high-resolution transmission electron microscopy were used for the analysis of the surface morphology, cross section and the microstructure of CNT films. The emis-

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Table 1
The experimental conditions used in this study for the growth of CNTs

<table>
<thead>
<tr>
<th>Source gas (catalyst metal)</th>
<th>Flow rate (sccm)</th>
<th>Plasma intensity (V/A)</th>
<th>Pressure (Torr)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH₃</td>
<td>NH₃</td>
<td>NH₃</td>
<td>NH₃</td>
</tr>
<tr>
<td></td>
<td>Pre-etching</td>
<td>+ Source gas</td>
<td>Pre-etching</td>
<td>+ Source gas</td>
</tr>
<tr>
<td>C₂H₂ (Ni) or C₂H₄ (Co)</td>
<td>240</td>
<td>60</td>
<td>540/0.04</td>
<td>620/0.12</td>
</tr>
<tr>
<td>CO (Fe)</td>
<td>10</td>
<td>180</td>
<td>540/0.04</td>
<td>620/0.12</td>
</tr>
</tbody>
</table>

Catalyst metals shown are the most effective ones for the growth of CNTs when using the corresponding source gases.

3. Results and discussion

Fig. 1 shows morphologies of CNTs grown on the glass substrate with various catalyst metals (Ni, Co and Fe) and precursors. When C₂H₂ gas was used as the carbon source, vertically aligned CNTs were grown on Ni (denoted by C₂H₂–Ni, in this paper) and Co catalysts (denoted by C₂H₄–Co, in this paper) under the condition that the flow rate of a NH₃ and the C₂H₂ gas was 240 and 60 sccm, respectively. The average diameters of CNTs with C₂H₂–Ni and C₂H₂–Co were 100 and 120 nm, respectively (Fig. 1a and b). However, CNTs were rarely grown on Fe catalyst under this condition and only the initial stage of growth morphology was observed (not shown here). Fig. 1c shows CNTs with the average diameter of CNTs of 140 nm grown using C₂H₄ gas, which indicates that the CNTs growth in C₂H₄ is activated especially with Co catalyst (denoted

![SEM micrographs showing the morphology of CNTs using various source gases and catalyst metals](image)
by C\textsubscript{3}H\textsubscript{4}–Co, in this paper) when the flow rates of the NH\textsubscript{3} and the C\textsubscript{3}H\textsubscript{4} gas were 240 and 60 sccm, respectively.

Using CO gas, CNTs with the average diameter of CNTs 40 nm were well grown on Fe catalyst (denoted by CO–Fe, in this paper) when the flow rates of NH\textsubscript{3} and CO were 10 and 180 sccm, respectively (Fig. 1d). Under such flow rates as mentioned above, CNTs were also well grown on Invar catalysts (consisting of Fe 52%, Ni 42% and Co 6%, respectively) too. To further study growth characteristics of CNTs using the C\textsubscript{3}H\textsubscript{4} gas, the flow rate of the NH\textsubscript{3} gas was only varied to 300 sccm at the constant flow rate of the C\textsubscript{3}H\textsubscript{4} gas of 60 sccm (Fig. 1e and f). As shown in Fig. 1e, CNTs with Ni catalyst (denoted by C\textsubscript{3}H\textsubscript{4}–Ni, in this paper) were grown with the relatively large diameter (∼240 nm). The average diameter of CNTs with C\textsubscript{3}H\textsubscript{4}–Co was reduced to 70 nm (Fig. 1f) compared to those shown in Fig. 1c.

Fig. 2 shows the emission current plots as a function of applied voltage (I–V) of CNTs grown with different catalysts. The turn-on electric field, \(E_{\text{to}}\), was defined as the electric field at 1 \(\mu\text{A/cm}^2\) of the current density. \(E_{\text{to}}\) of CNTs with C\textsubscript{2}H\textsubscript{2}–Ni, C\textsubscript{2}H\textsubscript{2}–Co, C\textsubscript{3}H\textsubscript{4}–Co, and CO–Fe (corresponding to Fig. 1a–d, respectively) were 4.5, 7.7, 10.3 and 6.4 V/\(\mu\text{m}\), respectively. It is noted that the current saturation (indicated by arrows) from CNTs with CO–Fe appeared at the relatively low current density of 0.01 \(\mu\text{A/cm}^2\) at the electric field of 2.8 V/\(\mu\text{m}\) and the rate of increase in the emission current rapidly decreased. However, in the samples using the C\textsubscript{3}H\textsubscript{4} gas (marked by \(\circ\) and \(\triangle\)), the current saturation occurred at higher current density (≈40–50 \(\mu\text{A/cm}^2\)). Thus, \(E_{\text{to}}\) of CNTs with CO–Fe was higher than that of CNTs with C\textsubscript{2}H\textsubscript{2}–Ni although the increment in the emission from CNTs with CO–Fe in the low field region (<2.8 V/\(\mu\text{m}\)) was the promptest among the other CNTs.

From the Fowler–Nordheim (F–N) model, the field enhancement factor \(\beta\) can be calculated from the slope of the F–N plot [\(\ln(I/V^2)\) vs. 1/V] [10]. As shown in the inset of Fig. 2, F–N plots for CNTs using different the carbon source gas and the catalyst metal showed distinct features in the slope of the plot. The field enhancement factors, \(\beta\), of samples with C\textsubscript{2}H\textsubscript{2}–Ni, C\textsubscript{2}H\textsubscript{2}–Co and C\textsubscript{3}H\textsubscript{4}–Co, are determined to 820, 460, and 380/cm, respectively.

Based on results following, two points should be noticed. First, the growth rate of CNTs was much higher and the average diameter became smaller as the flow rate ratio of NH\textsubscript{3}/C\textsubscript{3}H\textsubscript{4} increased. Second, Ni was more efficient for field emission of CNTs as the catalyst metal when using the C\textsubscript{2}H\textsubscript{2} gas; on the other hand, in case of C\textsubscript{3}H\textsubscript{4} as the carbon source, Co played an effective role as the catalyst.
Fig. 3. (a) TEM images of CNT grown with C$_2$H$_2$–Ni. The upper-left image shows Ni cap at the CNT tip and the upper-right image shows the Ni (420) facet of Ni particle. The lower image shows the interior and the wall structures of CNTs. (b) TEM images of CNT grown with CO–Fe. The left image shows the interior and wall structures of the CNTs and the right image indicate an Fe cap at the end of the CNT.

Fig. 3a is the TEM (300 kV, H-9000NA) cross-sectional views showing the Ni tip and wall structures of CNTs with C$_2$H$_2$–Ni. It shows a multiwalled structure with the inner and outer diameter of the tube is approximately 7.5 and 70 nm, respectively. The graphitic walls of the CNT looks like having some cut-off defects, which may be due to the low temperature growth. A Ni cap of 17 nm was observed at the end of each CNTs as shown in the upper-left image of Fig. 3a. The upper-right image of Fig. 3a shows the forefront facet of Ni particle was identified as Ni (4 2 0), and the ring fringes may stem from disordered {0 0 2} planes, which
indicates spacing of 0.34 nm between graphite planes. Microstructure of CNT with CO–Fe was also examined by TEM as shown in Fig. 3b. The interior and wall structures of the CNT were shown in the left image of Fig. 3b. It was shown that the inner and outer diameter of CNT is approximately 6 and 50 nm, respectively. An Fe cap with the diameter of approximately 30 nm was observed at the end of some of CNTs as shown in the right image of Fig. 3b.

4. Conclusion

As the flow rate ratio of NH$_3$/C$_3$H$_4$ increased, the growth rate of CNTs was enhanced and the average diameter became smaller. Ni was more efficient for the field emission of CNTs than any other catalyst metal when using the C$_3$H$_4$ gas, and in case of C$_3$H$_4$ as the carbon source, Co played an important role as the catalyst. When using the CO gas, Fe was the most activated catalyst for the CNTs growth under the flow rate ratio of CO/NH$_3$ of 18. CNTs grown using different catalyst metals had their corresponding catalyst particles at the tips.

Acknowledgments

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References