Effects of buffer layer materials and process conditions on growth mechanisms of forming networks of SWNTs by microwave plasma chemical vapor deposition

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Abstract

This study investigates the growth mechanism of IC compatible processes and to the feasibility of synthesizing networks of single-walled carbon nanotubes (SWNTs) at lower temperatures (\( \sim 610^\circ\)C) on Si wafer using microwave plasma chemical vapor deposition (MPCVD) with \( \text{CH}_4 \) and \( \text{H}_2 \) as source gases. The effects of the buffer layer materials (\( \text{ZnS-SiO}_2 \), \( \text{Al}_2\text{O}_3 \), \( \text{AlON} \), and \( \text{AlN} \)) and process conditions on growth of carbon nanostructures with Co as catalyst were also examined, where the buffer layers and Co catalyst were deposited in sequence by physical vapor deposition (PVD), followed by H-plasma pretreatment before deposition of carbon nanostructures. Additionally, the morphologies and bonding structures of carbon nanostructures were characterized by field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), and Raman Spectroscopy. Analytical results demonstrate that networks of SWNTs are more favorable to be synthesized by selecting proper buffer layer material (e.g., \( \text{AlON} \)), and under higher temperatures, thinner catalyst thickness (e.g., 5 nm) and lower \( \text{CH}_4 /\text{H}_2 \) ratio (e.g., 5/100 sccm/sccm). The networks of SWNTs can be fabricated at temperatures as low as \( \sim 610^\circ \)C by manipulating these parameters. In conclusion, the growth mechanism determines the conditions for the formation of nano-sized extrusions on catalyst particles surface.

Keywords: Buffer layer; Networks; Single-walled carbon nanotubes (SWNTs); Microwave plasma chemical vapor deposition (MPCVD)

1. Introduction

CNTs have recently been were considered as a promising candidate material for application as field emitters, nano-electronic devices (e.g., single electron transistor) [1–3], et al., owning to their unique physical and chemical properties, such as, ultrahigh aspect ratio, ultrahigh mechanical strength, tunable electrical and thermal conductivities [4–6]. For such applications, the deposition temperature must be lowered, particularly for compatibility with IC processes and structural manipulation (e.g., networks of CNTs). Therefore, to fabricating SWNTs with desired morphology at low temperatures attracts significant interest among academic researchers and technology users. For SWNTs synthesis, Arcos et al. [7] presented a thermal CVD process to produce Fe-assisted CNTs by using 20 nm thickness of \( \text{Al}_2\text{O}_3 \) as the buffer layer, and concluded that buffer layer applications can enhance the yield of CNTs production with detectable amount of SWNTs formation. However, their deposition temperatures are as high as 840 \( ^\circ \)C, and the possible growth mechanisms have not been discussed. Concerning the architecture of SWNTs, a networks morphology is proposed as the optimal structure for the application of nanotube sensors and nanotube-based computers. However, only networks of multi-walled carbon nanotubes (MWNTs) have been grown successfully until now, and their synthesizing temperature is as high as 900 \( ^\circ \)C [8].

To investigate the growth mechanisms of networks of SWNTs on Si wafer at low synthesizing temperatures, the carbon nanostructures were synthesized using an MPCVD system under various buffer layer materials, catalyst thicknesses, substrate temperatures and \( \text{H}_2 /\text{CH}_4 \) ratios to examine possible growth mechanisms.

2. Experimental

This study used four buffer layer materials (\( \text{ZnS-SiO}_2 \), \( \text{Al}_2\text{O}_3 \), \( \text{AlON} \), \( \text{AlN} \)). First, the \( \text{ZnS-SiO}_2 \) buffer layer was
Table 1 Specimen designations and their process conditions of the nanostructures on Si wafer with various buffer layer materials

<table>
<thead>
<tr>
<th>Specimen designation</th>
<th>Buffer layer material and thickness (nm)</th>
<th>Co catalyst layer thickness (nm)</th>
<th>Nanostructure morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>ZnS–SiO₂ (10)</td>
<td>5</td>
<td>None</td>
</tr>
<tr>
<td>A2</td>
<td>Al₂O₃ (10)</td>
<td>5</td>
<td>MWNTs and SWNTs</td>
</tr>
<tr>
<td>A3</td>
<td>Al₂O₃ (10)</td>
<td>5</td>
<td>None</td>
</tr>
<tr>
<td>A4</td>
<td>AlN (10)</td>
<td>5</td>
<td>None</td>
</tr>
<tr>
<td>A5</td>
<td>AlON (10)</td>
<td>5</td>
<td>MWNTs and SWNTs</td>
</tr>
<tr>
<td>A6</td>
<td>AlN (10)</td>
<td>10</td>
<td>None</td>
</tr>
<tr>
<td>A7</td>
<td>AlN (15)</td>
<td>10</td>
<td>MWNTs</td>
</tr>
</tbody>
</table>

ª Other deposition conditions of carbon nanostructures: pressure ~32 Torr; microwave power, 400 W; deposition temperature, 10 min and H₂ flow rate, 100 sccm.

Table 2 Specimen designations and their process conditions of the nanostructures on silicon wafer with AlON (10 nm) as buffer layer

<table>
<thead>
<tr>
<th>Specimen designation</th>
<th>Co catalyst thickness (nm)</th>
<th>CH₄/H₂ ratio (sccm/sccm)</th>
<th>Substrate temperature (°C)</th>
<th>Pressure (Torr)</th>
<th>Nanostructure morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>5</td>
<td>5/50</td>
<td>610</td>
<td>16</td>
<td>Trace MWNTs</td>
</tr>
<tr>
<td>B2</td>
<td>5</td>
<td>5/50</td>
<td>580</td>
<td>8</td>
<td>None</td>
</tr>
<tr>
<td>B3</td>
<td>5</td>
<td>5/100</td>
<td>610</td>
<td>16</td>
<td>MWNTs and SWNTs</td>
</tr>
<tr>
<td>B4</td>
<td>10</td>
<td>5/50</td>
<td>640</td>
<td>32</td>
<td>Trace MWNTs and SWNTs</td>
</tr>
<tr>
<td>B5</td>
<td>10</td>
<td>5/50</td>
<td>610</td>
<td>16</td>
<td>Trace MWNTs and SWNTs</td>
</tr>
<tr>
<td>B6</td>
<td>10</td>
<td>5/50</td>
<td>580</td>
<td>8</td>
<td>Trace MWNTs and SWNTs</td>
</tr>
<tr>
<td>B7</td>
<td>10</td>
<td>5/100</td>
<td>610</td>
<td>16</td>
<td>MWNTs and SWNTs</td>
</tr>
</tbody>
</table>

ª H-plasma pretreatment conditions: pressure ~30 Torr; microwave power, 400 W; deposition time, 10 min and H₂ flow rate, 100 sccm.

3. Results and discussion

Fig. 1(a) to (e) illustrate the FESEM morphologies of the nanostructures of Specimens A1 to A5, respectively, under the same process conditions but different buffer layer materials. The wafers in Fig. 1(a), 1(b) and 1(d) for Specimens A1, A2 and A4 with no buffer application, ZnS–SiO₂ and AlN as buffer layer materials, respectively, have not CNTs. By contrast, the networks of small sized CNTs can be found in Fig. 1(c) and 1(e) for Specimens A3 and A5 with Al₂O₃ and AlON as buffer layers, respectively, where the networks are linked between the neighboring catalyst nanoparticles. This finding indicates that the process is highly promising for 3D circuit manufacture.

To study the nanostructures of the CNTs in Fig. 1(c) and 1(e), the typical HRTEM image of CNTs for Specimens A3 and A5 is shown in Fig. 2, comprising MWNTs (~10 nm in diameter) and SWNTs (~1 nm in diameter). Restated, Al₂O₃ and AlON materials can be the buffer layer candidate materials to encourage the formation of SWNT networks by MPCVD. Notably, the deposition temperature in these cases is around 640 °C, which is much less than that found in the previous works [7–11].

To clarify combination effects of thickness of buffer and catalyst layers on nanostructures growth for ZnS–SiO₂ and AlN materials, the analytical results show that no CNTs can be identified by raising the thickness of the buffer, catalyst or both layers; except for the AlN buffer layer, MWNTs can be synthesized by raising the thickness of both the buffer and catalyst layers (Specimen A7). This conclusion is conformed to Raman spectroscopy to identify the types of CNTs, as discussed in next paragraph. In conclusion, AlN is not a good candidate buffer layer material for promoting SWNTs synthesis.

The effects of CH₄/H₂ ratio, catalyst thickness and process temperature on FESEM morphologies of the deposited nanostructures were then examined on the same AlON buffer material with 10 nm thickness. According to Fig. 1(e), the obvious CNT networks can be found between the Co catalyst particles under 640 °C substrate temperature. However, under the same catalyst thickness of 5 nm, and when the substrate temperature was reduced from 640 to 610...
or 580 °C (Specimens A5, B1 and B2) changing the system pressure, no detectable CNTs networks were found for temperatures below 610 °C. By contrast, at the same 610 °C substrate temperature, CNTs networks appeared again when the CH$_4$/H$_2$ ratio was reduced from 5/50 to 5/100 sccm/sccm (Specimen B3). In summary, the preferred conditions to form CNT networks between the Co catalyst nanoparticles are high substrate temperatures and low CH$_4$/H$_2$ ratios.

To examine how catalyst thickness affects the deposited nanostructures, the same experimental conditions in the above paragraph were performed again, except that the catalyst thickness was increased from 5 to 10 nm (Specimens B4 to B7). Experimental results indicate that a substrate temperature of 640 °C is insufficiently high to form networks of CNTs under a high CH$_4$/H$_2$ ratio. By contrast, CNT networks can be formed for substrate temperatures as low as 610 °C under a lower CH$_4$/H$_2$ ratio (Specimen B7). These findings suggest that the most favorable conditions for synthesizing networks of CNTs are a low CH$_4$/H ratio, high substrate temperature and low catalyst thickness. Conversely, the findings agree with our previous results that the CH$_4$/H ratio is the most important process parameter for varying the deposited structures among diamond film, diamond-like carbon, Si–C–N microcrystals, Si–C–N nanotubes and CNTs [12,13].
3.2. Raman spectra of the nanostructures

To explore the types of CNTs or nanostructures, Fig. 3 shows the Raman spectra of the nanostructures with no buffer layer and with four different buffer layer materials (Specimens A1 to A5). The Raman spectra for Specimens A1, A2 and A4 contained no obvious G-band and D-band peaks with no buffer layers, ZnS–SiO₂ and AlN buffer layer materials. Conversely, a strong peak of radial breath mode (RBM) and a high $I_G/I_D$ ratio were obtained for Specimens A3 and A5 with Al₂O₃ and AlON as buffer layers, respectively, showing the existence of highly graphitized MWNTs and SWNTs. This finding is based on the proposition that the peak intensity of RBM is linked to the quantity of SWNTs in the nanostructures [14]. Moreover, the RBM peak is stronger in nanostructures with a buffer layer of AlON than those with Al₂O₃, indicating that AlON promotes SWNT formation more effectively than Al₂O₃. This finding agrees with that of FESEM examination.

Under the same 10 nm thickness AlON buffer material and the same 5 nm catalyst thickness, the Raman spectra of the nanostructures are shown in Fig. 4 under various substrate temperatures and CH₄/H₂ ratios (Specimens B1 to B3), showing that no significant Raman peaks can be identified by reducing the substrate temperatures from 640 to 610 or 580 °C (Specimens A5, B1 and B2). By contrast, a strong RBM peak and high $I_G/I_D$ ratio can be observed by reducing the CH₄/H₂ ratio from 5/50 to 5/100 sccm/sccm under the same 610 °C substrate temperature (Specimens B3). In other words, a high substrate temperature and a low CH₄/H₂ ratio are the two favorable conditions for forming SWNTs.

Fig. 5 shows the Raman spectra of deposited nanostructures under the same experimental conditions as above, except that the catalyst thickness was increased from 5 nm to 10 nm (Specimens B4 to B7). The results imply that a substrate temperature of 640 °C is not high enough to form SWNTs. The results also indicate that a CH₄/H₂ ratio of 5/100 sccm/sccm is sufficiently low to form SWNTs with strong RBM peaks and high $I_G/I_D$ ratio even at 610 °C (Specimens B7). In summary, the favorable conditions for forming SWNTs are a high substrate temperature, low CH₄/H₂ ratio and low catalyst thickness.

Tables 1 and 2 also summarize the relationships between morphologies of the nanostructures and processing conditions. In terms of buffer layer material, these findings suggest that the better materials to increase formation of SWNTs are AlON followed by Al₂O₃, both of which are Al-based materials. The other two materials (AIN, ZnS–SiO₂) are poor in these applications, although AIN can be employed to promote formation of MWNTs, but not SWNTs.
3.3. Growth mechanism of CNTs networks

Significantly, CNTs networks closely resemble root-growth CNTs from a catalyst particle, which is much larger than the tubes in size [15]. Fig. 6, with a magnified inset, shows the HRTEM image of the typical CNTs under AlON buffer layer and substrate temperature of \( \approx 640 \) °C (Specimen A5). The inset demonstrates that nanotubes grow from the small extrusion of a large catalyst. This finding is similar to the proposed mechanisms of the catalyst-split and root-growth models [15,16], where the split catalysts are frequently found at the locations of changing the growth direction. The favored conditions for forming SWNTs are small split catalysts and low growth rates. A high substrate temperature can increase the mobility for splitting and a low CH\(_4\)/H\(_2\) ratio generally results in a low growth rate due to a small carbon concentration. Furthermore, a thin catalyst thickness produces small nanoparticles following H-plasma pretreatment. Concerning the buffer layer material, which may cause the catalysts to deposit to form more nano-extrusions, may favor to form SWNTs from these extrusions. Therefore, the most favorable buffer layer material is AlON, because of its strong tendency to become nano-sized pores on the surface. Further study on this subject is necessary.

4. Conclusions

The growth mechanism and the favorable conditions for fabricating the networks of SWNTs on Si wafers were successfully identified in a MPCVD system with CH\(_4\) and H\(_2\) as source gases. The lowest temperature in the present conditions to form SWNTs is \( \approx 610 \) °C. Experimental results demonstrate that the materials which most effectively promote SWNTs formation are AlON followed by Al\(_2\)O\(_3\). Our results further demonstrate that AlN buffer material is good only for MWNT fabrication, while ZnS–SiO\(_2\) is not a candidate buffer material for CNTs growth. Moreover, the results also indicate that the favorable conditions for synthesizing SWNTs networks are a high substrate temperature, low CH\(_4\)/H\(_2\) ratio and thin catalyst thickness with AlON as the buffer material. In summary, the favorable conditions for forming networks of SWNTs are the conditions for forcing catalyst surfaces to form nano-sized extrusions.

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References