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journal or publication title	JOURNAL OF APPLIED PHYSICS
volume	90
number	3
page range	1529-1533
year	2001-08-01
URL	<a href="http://id.nii.ac.jp/1476/00004980/">http://id.nii.ac.jp/1476/00004980/</a>

doi: 10.1063/1.1382848(<http://dx.doi.org/10.1063/1.1382848>)

# Growth of aligned carbon nanotubes by plasma-enhanced chemical vapor deposition: Optimization of growth parameters

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(Received 16 April 2001; accepted for publication 7 May 2001)

Direct-current plasma-enhanced chemical vapor deposition (CVD) with mixtures of acetylene and ammonia was optimized to synthesize aligned carbon nanotubes (CNTs) on Co- or Ni-covered W wires with regard to wire temperature, wire diameter, gas pressure, and sample bias. A phase diagram of CNT growth was established experimentally in this optimization process. It was revealed by transmission electron microscopy that Co-catalyzed CNTs encapsulated a Co carbide nanoparticle at their tip, disagreeing with a previous report that Co particles were located at the base of CNTs CVD grown on Co-covered Si substrates [C. Bower *et al.*, *Appl. Phys. Lett.* **77**, 2767 (2000)]. This leads to the conclusion that the formation mechanism of aligned CNTs depends significantly on the catalyst support material as well as the catalyst material itself. Since the sample bias strongly affected the morphology of CNTs, the selective supply of positive ions to CNT tips was possibly responsible for the alignment of growing CNTs. © 2001 American Institute of Physics. [DOI: 10.1063/1.1382848]

## I. INTRODUCTION

Since their discovery by Iijima,<sup>1</sup> carbon nanotubes (CNTs) have attracted great attention in materials science and technology. Due to their high aspect ratios, small tip radii of curvature, and high chemical stability, CNTs are expected to be very promising as field electron sources, e.g., for flat panel displays.<sup>2,3</sup> In the practical application of CNTs as field electron sources, aligned CNTs should be grown directly onto the desired locations of a large substrate.

Li *et al.*<sup>4</sup> first demonstrated that aligned CNTs can be grown directly on Fe nanoparticles embedded in mesoporous silica by chemical vapor deposition (CVD). Efforts have since been made to synthesize aligned CNTs on various substrates using CVD-based techniques.<sup>5–11</sup> Recently, several groups applied these techniques to the selective and direct growth of aligned CNTs on patterned substrates.<sup>12–14</sup> Thus, CVD-based methods might be promising as techniques to align CNTs for their field emission applications. Very recently, we synthesized aligned CNTs on W wires covered with Co or Ni films using direct-current (dc) plasma-enhanced CVD (PECVD), and were able to optimize the growth conditions of aligned CNTs. In this optimization process, we noticed that positive ions in plasma played a key role in controlling the growth morphology of CNTs, and that CNTs grew on Co-covered W wires via so-called tip growth mode.<sup>15–17</sup> In what follows, we report these recent findings,

including a phase diagram of CNT growth experimentally determined for a  $C_2H_2-NH_3/W$ -wire system.

## II. EXPERIMENTAL DETAILS

Figure 1 schematically shows a dc PECVD system used for growing CNT. A W wire spot-welded to two stainless steel rods is set at a distance of  $\sim 10$  mm from a disc electrode of Co or Ni (wire diameters employed were 10–100  $\mu m$ ). After evacuating the CVD chamber to  $1 \times 10^{-5}$  Torr or lower, a thin film of Co or Ni ( $\sim 80$  nm thick) catalyzing the CNT growth was deposited onto the W wire by  $Ar^+$ -sputtering the disk electrode at 0.1 Torr. Mixtures of  $C_2H_2$  and  $NH_3$  (0.012–2.4 Torr) were then introduced to the reevacuated chamber. The partial pressure ratio of  $C_2H_2$  and  $NH_3$  was always kept at 1:2. Application of a negative dc potential ( $-500$  V) to the resistively heated W wire induced a glow discharge, growing CNTs on the W wire. The CNT growth behavior was investigated at wire temperatures (growth temperatures) from 300 K to 1200 K. The growth duration was 20 min. The morphology and structure of samples thus prepared were determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. For TEM, CNT-covered W wires were directly mounted on a sample holder.

## III. RESULTS AND DISCUSSION

### A. Optimization of growth temperature

Figure 2 shows typical SEM images of Co-coated W wires after PECVD at different growth temperatures. CNTs

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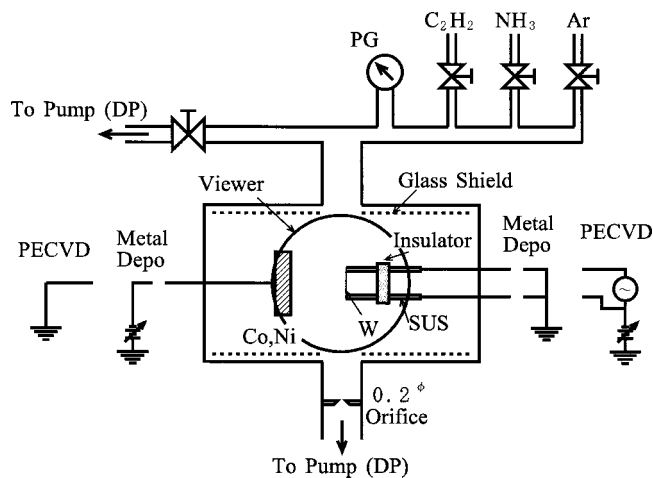


FIG. 1. Schematic diagram of the experimental setup for PECVD. During metal deposition, the disk electrode was kept at  $-4$  kV.

aligned themselves perpendicular to the wire surface at a narrow temperature range of  $750$ – $800$  K [Fig. 2(b)]. No CNT formed on wire surfaces at the temperatures outside this range [Figs. 2(a) and 2(c)]. The diameter, averaged length, and site density of the CNTs in Fig. 2(b) were  $20$ – $130$  nm,  $\sim 5$   $\mu\text{m}$ , and  $\sim 6 \times 10^7$   $\text{mm}^{-2}$ , respectively. The optimum temperature for aligning CNTs was independent of the catalyst material, CVD pressure, and wire diameter. CNT growth was limited to the catalyst-covered area on the wire surfaces (Fig. 3), suggesting that the growth area of CNTs is easily controllable by the selective deposition of catalyst film.

Figure 4 shows the TEM image of a typical CNT grown on a Co-covered surface, proving that the CNT actually possesses a tubular structure. The tip of the CNT is closed and encapsulates a nanoparticle (arrowhead). The electron-diffraction pattern (EDP) of the tip area (inset in Fig. 4) is composed of regularly arranged spots, ensuring the monocrystallinity of the nanoparticle. By careful analysis, the spot arrangement was confirmed to match the  $(2\bar{1}0)$  reciprocal lattice net of  $\text{Co}_3\text{C}$  (tri-cobalt carbide), allowing us to conclude that the CNTs grown with Co catalyst encapsulated a cobalt carbide nanoparticle at their tip.

No structural difference was recognized between Co- and Ni-catalyzed CNTs. For the Ni-catalyzed CNTs, however, the nanoparticles occupying the CNT tips were pure Ni, as determined by EDP, i.e., the carbide formation did not take place for Ni-catalyzed CNTs. This result may reflect the fact that there exists no stable carbide in the Ni–C phase diagram.<sup>18</sup>

The encapsulation of a nanoparticle at CNT tips suggests that CNTs grew via the so-called tip growth mechanism.<sup>15–17</sup> In this mechanism, carbon species produced by the adsorption and decomposition of  $\text{C}_2\text{H}_2$  on the “front-exposed” surface of catalyst nanoparticles diffuse around the nanoparticle surface and/or through the nanoparticle, and ultimately precipitate at the “rear” of the nanoparticle to form a CNT (Fig. 5). Thus, the catalytic nanoparticle is raised from the substrate surface. Such an encapsulation of nanoparticles at CNT tips has been reported for CNTs CVD grown with Ni

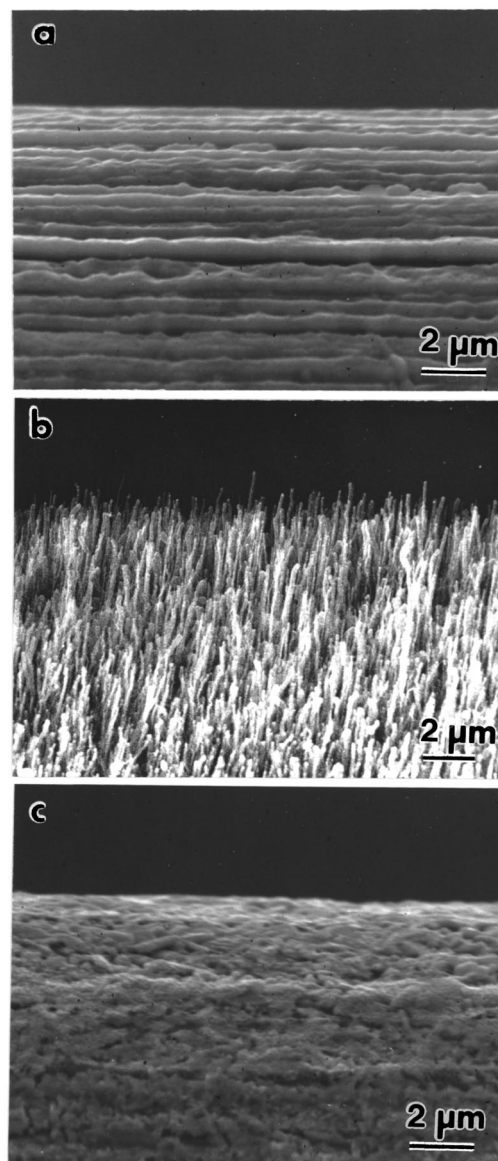


FIG. 2. SEM images of Co-coated  $30$   $\mu\text{m}$  wire surface after PECVD at  $\text{C}_2\text{H}_2/\text{NH}_3=0.2/0.4$  Torr. Growth temperature: (a) room temperature, (b)  $750$  K, and (c)  $1200$  K.

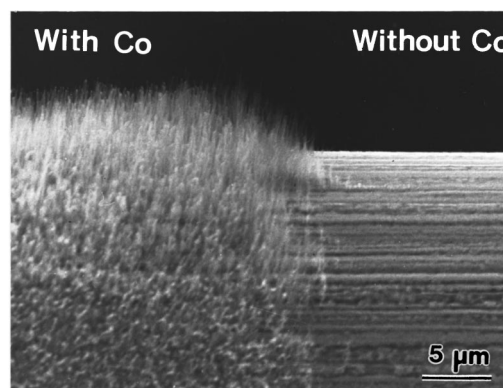


FIG. 3. SEM image of CNTs grown on a Co-patterned  $30$   $\mu\text{m}$  wire surface after PECVD at  $\text{C}_2\text{H}_2/\text{NH}_3=0.2/0.4$  Torr. Growth temperature:  $750$  K.



FIG. 4. TEM image of a Co-catalyzed CNT grown on a 30  $\mu\text{m}$  wire by PECVD at 750 K;  $\text{C}_2\text{H}_2/\text{NH}_3=0.2/0.4$  Torr. Inset: EDP from the CNT top region.

and Pd catalysts.<sup>6,7,12</sup> Bower *et al.*, however, synthesized CNTs on Co-covered Si using microwave PECVD of a mixture of  $\text{C}_2\text{H}_2$  and  $\text{NH}_3$ , and found no particle at the CNT tips.<sup>10,13</sup> They detected by TEM Co particles, not cobalt carbide particles, at the base of CNTs, and concluded that CNTs grew on Co-covered Si via the so-called base growth mechanism.<sup>15,19</sup> We suppose that the formation mechanism of CNTs strongly depends on the catalyst support material as well as on the catalyst itself.

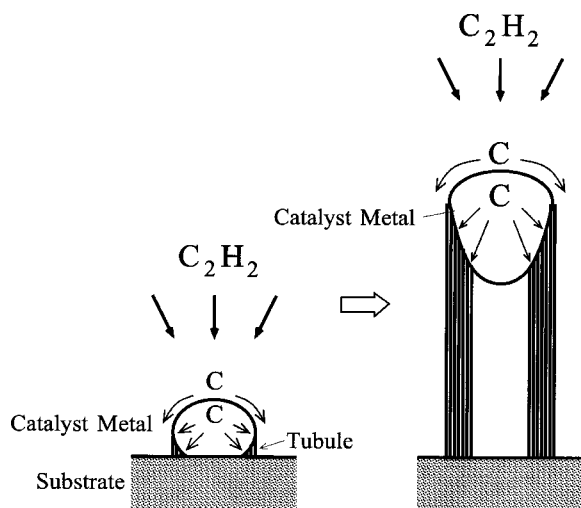


FIG. 5. Schematic representation of the tip-growth mechanism of CNTs.

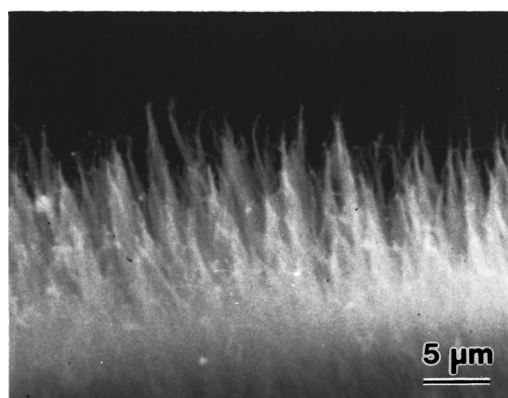


FIG. 6. SEM image of 10  $\mu\text{m}$  wire surface after PECVD at 750 K;  $\text{C}_2\text{H}_2/\text{NH}_3=0.4/0.8$  Torr. Catalyst: Ni.

### B. Effect of CVD gas pressure and wire diameter

The effect of CVD gas pressure up to 2.4 Torr ( $\text{C}_2\text{H}_2 \leq 0.8$  Torr,  $\text{NH}_3 \leq 1.6$  Torr) on the growth behavior of CNTs was examined at the optimum temperature previously described. Since the partial pressure ratio of  $\text{C}_2\text{H}_2$  and  $\text{NH}_3$  was always kept at 1:2, we hereafter represent the PECVD pressure with  $\text{C}_2\text{H}_2$  pressure ( $P_{\text{ace}}$ ).

With Ni catalyst, densely distributed aligned CNTs could be grown on 10  $\mu\text{m}$  wires at  $P_{\text{ace}}=0.1-0.3$  Torr, but no CNT at  $P_{\text{ace}}<0.1$ . The CNTs increased their length as  $P_{\text{ace}}$  increased. The average length of CNTs grown at  $P_{\text{ace}}=0.3$  Torr was up to 6  $\mu\text{m}$ . Lengthened CNTs aggregated into conical shaped bundles on a 10  $\mu\text{m}$  wire at  $P_{\text{ace}}=0.4$  Torr (Fig. 6). On a 30  $\mu\text{m}$  wire, by contrast, CNTs even aligned at  $P_{\text{ace}}$  as high as 0.8 Torr. Thus, the optimum pressure range for aligned CNT growth crucially depended on the wire diameter.

Compared with Ni catalyst, Co catalyst shifted the optimum pressure zone to a lower side. On 10  $\mu\text{m}$  wires, CNTs aligned at  $P_{\text{ace}}<0.2$  Torr, while conical shaped bundles and stalactitelike structures (arrowheads in Fig. 7) formed at  $P_{\text{ace}}=0.2$  and 0.8 Torr, respectively. By contrast, aligned CNTs grew at  $P_{\text{ace}}\leq 0.2$  Torr (see Fig. 2) on 30  $\mu\text{m}$  wires and even at  $P_{\text{ace}}=0.8$  Torr on thicker wires.

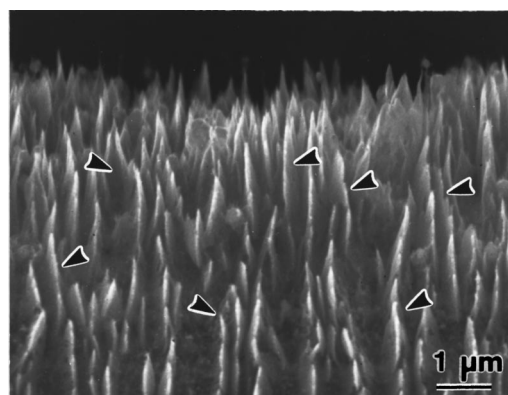


FIG. 7. SEM image of 10  $\mu\text{m}$  wire surface after PECVD at 750 K;  $\text{C}_2\text{H}_2/\text{NH}_3=0.8/1.6$  Torr. Catalyst: Co. Arrowheads indicate typical stalactitelike structure.

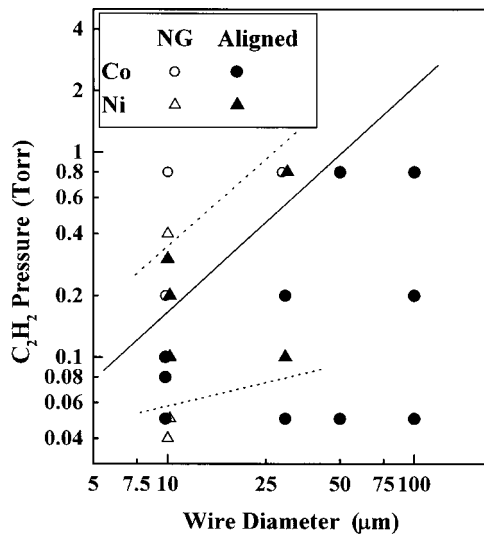


FIG. 8. Phase diagram of the  $C_2H_2-NH_3/W$ -wire system for CNT growth. Solid and dashed lines indicate empirical demarcation lines of pressure of aligned CNT growth for Co ( $\circ$ ,  $\bullet$ ) and Ni ( $\triangle$ ,  $\blacktriangle$ ) catalysts, respectively. NG indicates nongrowth or nonaligned.

A phase diagram of the  $C_2H_2-NH_3/W$ -wire system for CNT growth determined with the aid of SEM is presented in Fig. 8. In the figure, experimentally determined upper and lower limits of pressure for the CNT alignment are also depicted as a function of the wire diameter. For both catalysts, with an increase in the wire diameter, the upper limit for aligned CNT rises, resulting in a wider optimum pressure regime. The synthesis of aligned CNTs on wide-area substrates will therefore readily be achieved in our PECVD system.

### C. Effect of sample bias

To elucidate the role of plasma in the PECVD process, CVD with and without plasma at  $P_{ace} = 0.2$  Torr were carried out for Co-coated  $30 \mu m$  wires. This combination of the pressure and wire diameter is one of the optimum growth conditions of aligned CNTs (see Fig. 8). As previously demonstrated, CNTs grown by CVD with plasma, or PECVD, were well aligned and densely distributed [see Fig. 2(b)]. By contrast, CNTs due to CVD without plasma, namely, pyrolysis of hydrocarbon gas, were sparsely distributed and exhibited a complicated growth mode [Fig. 9(a)]. Some of them were characterized by helical or looped structures. A higher CVD pressure merely led to an increase in the site density of lengthened CNTs of random figure [Fig. 9(b)]. Such a random configuration has been reported for CNTs grown by the pyrolytic decomposition of hydrocarbon gases at elevated temperatures.<sup>20–23</sup> Since pyrolysis methods generally require higher temperatures (900–1300 K) for CNT growth,<sup>4,5,11,14,20–23</sup> CVD at temperatures up to 1200 K was also examined. Well-aligned CNTs were, however, never formed by pyrolysis in our experimental system. Thus, we may conclude that plasma-composing positive ions, rather than radicals or excited molecules, play a decisive role in the alignment of growing CNTs. To confirm this conclusion, a positive potential (500 V) was applied to a  $30 \mu m$  wire

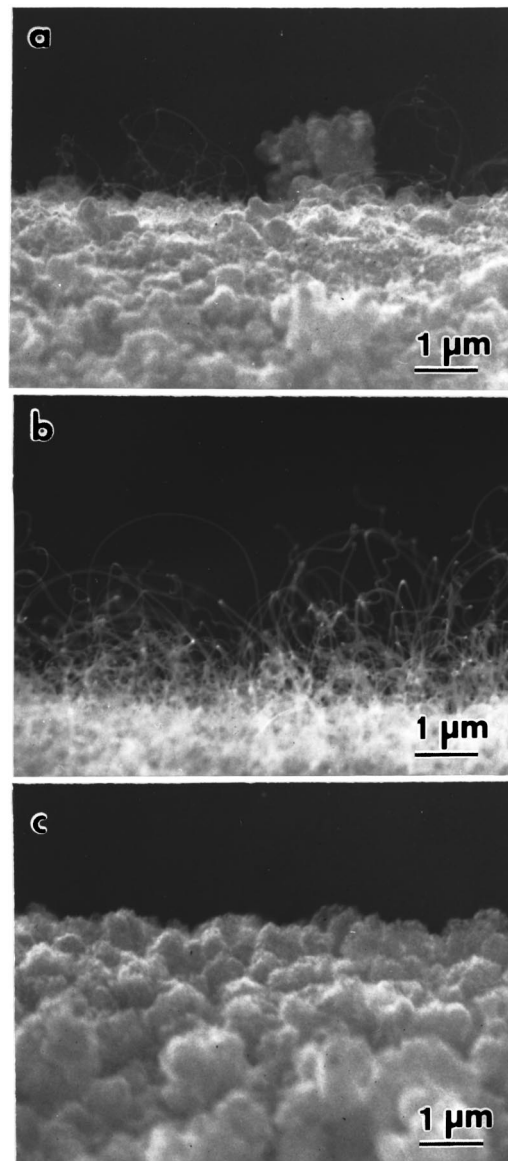


FIG. 9. SEM images of Co-coated  $30 \mu m$  wire surface after (a), (b) CVD without plasma, and (c) inverse mode PECVD.  $C_2H_2/NH_3$  pressure: (a), (c) 0.2/0.4 Torr, and (b) 0.8/1.6 Torr. Growth temperature: 750 K.

sample to induce plasma during CVD at  $P_{ace} = 0.2$  Torr. As expected, no CNT was grown by this inverse mode of PECVD [Fig. 9(c)].

As is well known, an electric field is locally enhanced around protrusions present on an electrostatically biased surface. This suggests that the electrostatic field at the tips of CNTs would be strong enough to attract positively charged ions to their tips. In fact, for a fiber 40 nm in diameter protruding from a biased ( $-500$  V) substrate surface, for example, the field strength ( $F$ ) at the tip is estimated to reach  $5 \times 10^7$  V/cm from a calculation widely used for CNT field emitter tips.<sup>24,25</sup>

$$F = V / (\alpha r_0),$$

where  $V$ ,  $\alpha$ , and  $r_0$  are the bias potential, the geometrical factor (usually  $\alpha = 5$  for CNTs), and the tip radius, respectively. Positive ions in CVD plasma would therefore be fed

selectively to tips rather than to tube bodies. This selective supply of positive ions might reduce the lateral mechanical stress exerted on the tube, and hence align CNTs along the field lines.

#### IV. CONCLUDING REMARKS

DC PECVD with  $C_2H_2$  and  $NH_3$  gas mixtures was optimized to synthesize aligned CNTs on Co- or Ni-covered W wires with regard to wire temperature, gas pressure, wire diameter, and sample bias. Each aligned CNT tip was capped with a Co carbide or Ni nanoparticle, suggesting that the tip-growth mode dominated in the Co and Ni/W wire system. The optimum PECVD temperature (750–800 K) was independent of catalyst material, PECVD pressure, and wire diameter. The optimum pressure region for aligned CNT growth became wider with an increase in wire diameter, implying that the fabrication of aligned CNTs on large-area substrates would readily be achievable in our PECVD system. Excess PECVD pressures led to the aggregation of lengthened CNTs into conical and stalactitelike structures. Since the sample bias significantly affected the morphology of CNTs, our final conclusion is that the selective feeding of positive ions to CNT tips is responsible for the alignment of growing CNTs.

#### ACKNOWLEDGMENT

This work was partially supported by the Ministry of Education, Science, Sports and Culture of Japan, through the Grant-in-Aid for Scientific Research B, No. 12450038.

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