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# Aligned conical carbon nanotubes

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Aligned conical carbon nanotubes (CCNTs) have been synthesized on catalyst-coated Si (100) substrates by a D.C. plasma-assisted hot filament chemical vapor deposition process. The same technique under slightly different deposition conditions has been used to grow aligned conventional carbon nanotubes. The conical shape is due to secondary graphitic growth on the main nanotube. This growth results in the formation of a series of inverted lampshade-type structures stacked over each other, which gives the CNT the appearance of a cone. The CCNT structures are typically 2 $\mu$m at the base with an inner diameter of 100 nm and 2000 nm long. Patterned growth, e.g., arrays of 6 $\mu$m $\times$ 6 $\mu$m square, has been achieved. Field emission from CCNTs for use in flat panel displays is also reported. 

## 1. Introduction

Hot filament chemical vapor deposition (HFCVD) is a conventional method for synthesizing diamond films from a mixture of hydrogen and hydrocarbons [1, 2]. Recently, crystalline carbon nitride films [3] and aligned carbon nanotubes (CNTs) [4] have been produced by adding a D.C. discharge plasma to this method. This D.C. plasma-assisted HFCVD method has been used effectively to control the diameter, length, and orientation with respect to substrate surface of the CNT [5]. The low growth temperature of 350°C–400°C makes the method suitable for integration into other semiconductor processing techniques [6]. The paper reports on variations in the growth conditions that lead to the formation of a conical structure on the CNT (CCNT). The proposed growth mechanism of the CCNT is based on transmission electron microscopy (TEM) observations. The field emission property is also reported.

## 2. Experimental

Si (100) substrates, 10 $\times$ 5 $\times$ 0.5 mm in size, were used for the growth of CCNTs. They were cleaned in HF acid before depositing the catalyst films. 50–200 nm thick catalyst films (a composite of Ni, Fe, and Co) were first deposited on the substrate surface by a pulsed laser (ArF laser, 193 nm, 5 Hz and 200 mJ/pulse). A mixture of Fe and Co (1 : 1) was used as the laser target. Pure Ni target was used for the patterned growth of CCNTs. The deposition chamber was pumped to less than $1 \times 10^{-4}$ Torr, and then back-filled with hydrogen to a pressure of $5 \times 10^{-2}$ Torr. The substrate temperature was 300 K during the deposition. The catalyst-coated substrate was then transferred to the D.C. plasma-assisted HFCVD system where the aligned CNTs were grown. The same system was previously used to synthesize aligned CNTs [4, 5]. In this system, a Ta mesh is placed above the hot filament and acts as the anode. A D.C. discharge plasma is generated between the anode and the substrate holder. The diameters of the CNTs were controlled by varying the catalyst film thickness, plasma intensity, and substrate temperatures. In contrast to the previous works [4, 5], the catalyst coated Si(100) substrate was pre-treated in the HFCVD system feed by hydrogen at 40 Torr for 10 minutes. Filament and substrate temperatures were 2000°C and 800°C, respectively. The filament and gas are then turned off and the chamber pumped to below $1 \times 10^{-3}$ Torr. A mix of nitrogen (99.999% purity) and acetylene (99.9% purity) with a $C_2H_2$ concentration of 3 vol% was then introduced into the chamber. During the growth process, the pressure was 20 Torr, the filament temperature was 2200°C, and the D.C. plasma intensity was 15 mA/cm$^2$ (450 bias voltage). The growth lasted for 20 min. The films obtained were characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM, Hitachi-4000), and TEM (JEOL JEM-2010).

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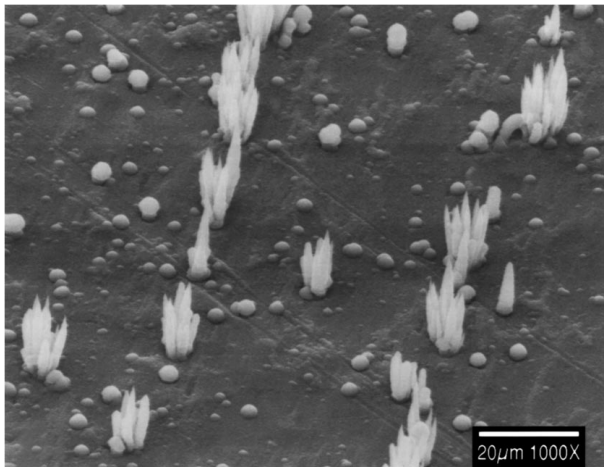
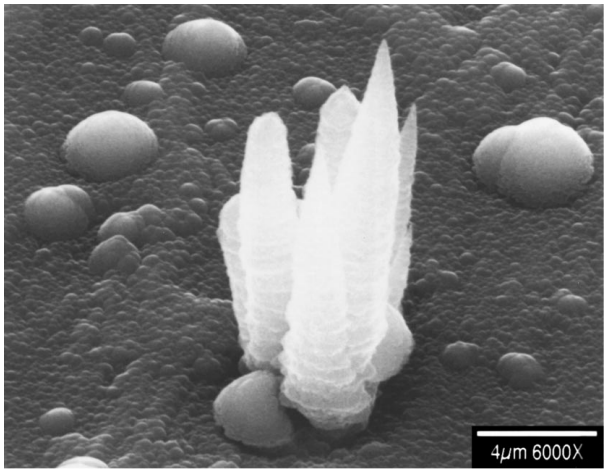
## 3. Results and discussions

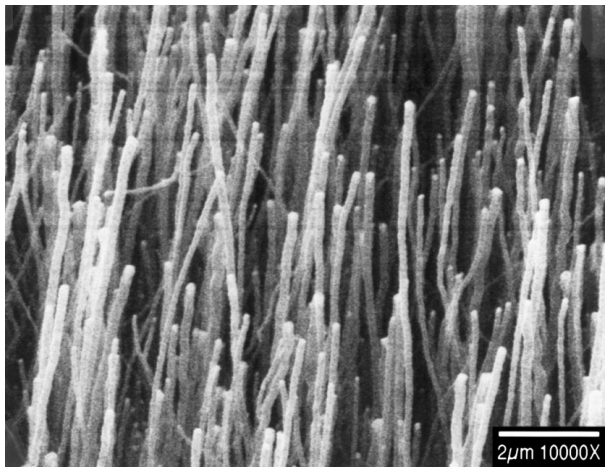
Fig. 1A shows a SEM picture of several clusters of CCNTs growing normal to the substrate. The density of the CCNT is $10^3$–$10^4$/cm$^2$. This density can be controlled by the concentration of the Ni catalyst particles generated by a strong D.C. plasma prior to the growth of the CCNT. The size of the catalyst particles can be




(A)

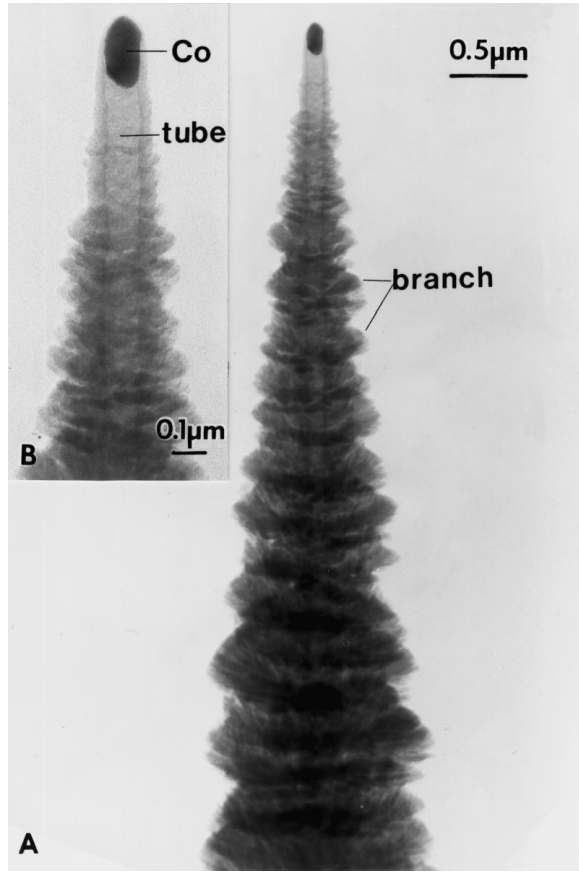



(B)




(C)

*Figure 1* SEM pictures of the conical carbon nanotubes synthesized by D.C. plasma-assisted HFCVD. (A) A low magnification image showing several clusters; (B) a closer view of a CCNT cluster; and (C) the normally aligned CNT synthesized when no hydrogen annealing was used, and the filament temperature was 2000°C.



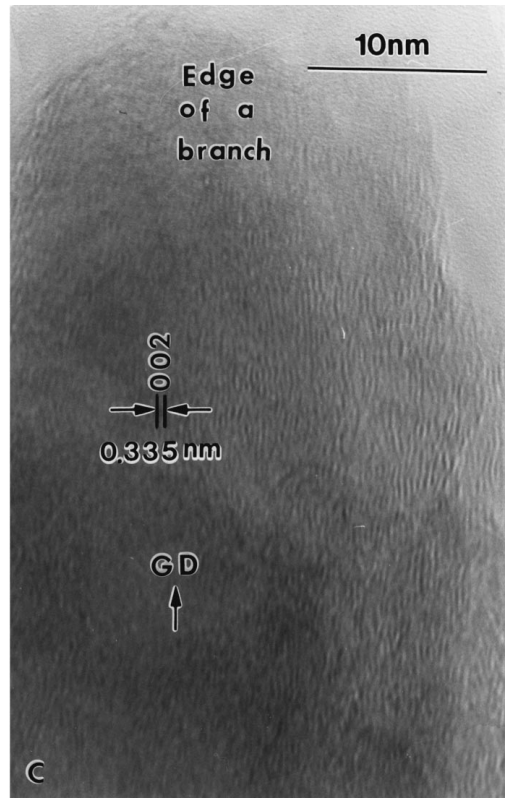




*Figure 2* (A) A low magnification TEM image of a CCNT showing numerous graphite branches are grown around the main tube; (B) a closer view of the tip where the hollow tube and catalyst particle decorating the tip are clear; and (C) a high-resolution TEM image of the end of the branch tip. It is formed by aligned (002) graphite planes. The growth direction of the branch is parallel to the (002) graphite planes.

controlled by varying the thickness of the Ni film, the substrate temperature, and the plasma conditions [5]. Fig. 1B is a magnified SEM picture of a CCNT cluster. The diameter at the base of the cone is 2 $\mu$m, which decreases at about a rate of 100 nm/$\mu$m along the length of the CCNT. The average length of the CCNT is about 8 $\mu$m for a 20 minute deposition. XPS analysis indicates that the film is almost wholly carbon—89 at% C, 3 at% Fe and Co, 3 at% O and 5 at% N. A small fraction of O and N would come from the adsorption of atmosphere after the deposition. For comparison, the normally generated high-density CNTs are show in Fig. 1C. For the CNT growth, the substrate was not pre-annealed in a hydrogen environment, and the growth was performed at a relatively lower filament temperature (2000°C).

The CCNTs were transferred onto an amorphous carbon coated copper grid and observed by TEM. Fig. 2A shows a low magnification image of a CCNT. Numerous branch-like material grows outwards from the main nanotube to form a conical-shaped morphology. A hollow tube with an inner diameter of 100 nm is clearly visible. A cylinder-shaped catalyst particle decorates the tip. A high resolution image of the material at the tip of a branch is shown in Fig. 2C. Analysis indicates these are well-aligned (002) graphite planes.

The growth process of this material has been elucidated from TEM observations of the CCNTs at various stages of the growth process. The results (Fig. 3) indicate that graphitic branches originate from nucleation sites on the outer wall of the nanotube. These nucleation sitese are either defects in the outer layers of the nanotube such as open ends of the graphitic layer [5], especially in the area with the graphite interconnected layer areas [Fig. 3B], or sites generated by the highly activated hydrocarbons resulting from the higher filament temperature. These branches initially grow perpendicular to the nanotube, but then bend slightly inwards in the direction of the nanotube. These branches nucleate and grow simultaneously as the main nanotube grows. Consequently, the base branches form first and are longer compared to the upper branches, giving the entire structure a conical shape. This kind of growth style is different from the conventional growth of CNTs [7–9] and from fiber thickening processes [10], which keep the same morphology during the growth process. It should be mentioned that a relatively low density of the active catalytic particles for the growth of CCNTs is needed. During the growth process, the low density allows sufficient space for the active hydrocarbons to reach all parts of the growing tube, allowing for the simultaneous growth of branches and the nanotube. Thus, CCNT growth requires relatively low-density catalyst particles (usually less than $10^7/cm^2$) and a high filament temperature (more than 2000°C). From Figs 1A and 2A, it can be observed that there is symmetrical growth around the tube at any given elevation. This indicates that some of these branches grow around the center tube to form complete graphite disks or rings. Such structured materials were not observed when conventional thermal decomposition methods were used [9–11].

The reason for the aligned growth of CCNTs is the same as that described in Ref. [5] for the growth of aligned CNTs. In the presence of the D.C. plasma, the charged catalytic particles at the tip of the nanotubes

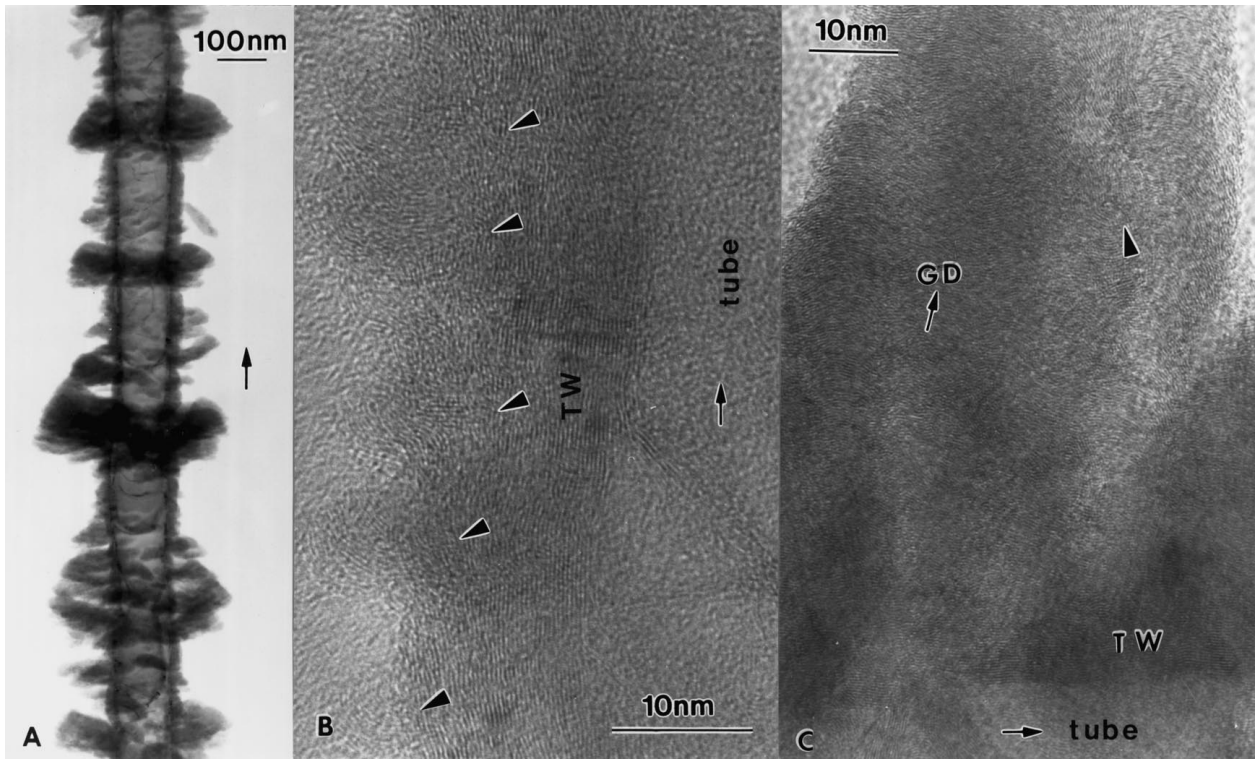
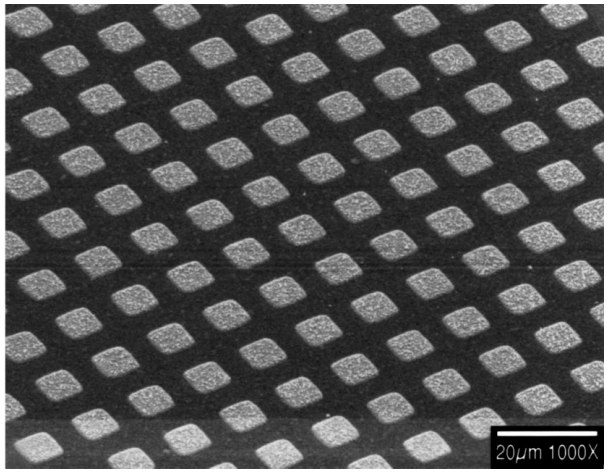
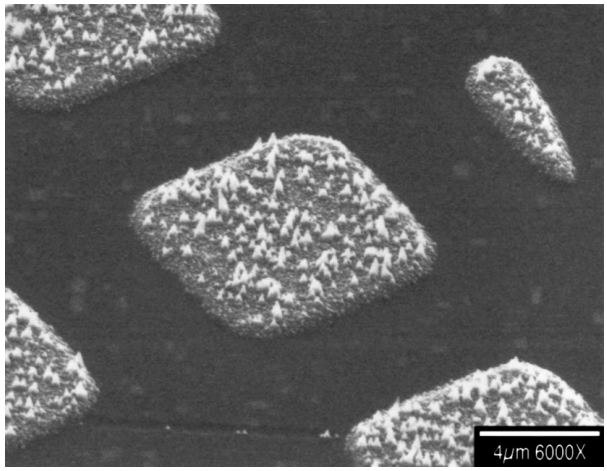



*Figure 3* (A) A low magnification TEM image of a CCNT after 5 min. growth. Branches with different lengths have formed; (B) A high-resolution TEM image of the onset of initial nucleation of branches on the outer wall. The graphite planes are curved and randomly oriented. The nucleation sites are marked by "**?**"; (C) An image of a relatively longer branch. The growth direction at this stage is not the same as that of (002) plane. The following growth tends to the aligned growth of branches [Fig. 2C]. "GD" and "TW" in the figures represent the growth direction of the branch, and the tube wall, respectively.




(A)




(B)

*Figure 4* SEM pictures of the patterned growth. (A) A low magnification SEM picture of the patterned arrays of squares ($6 \times 6$ $\mu$m) has been obtained; (B) A magnified picture of one square. Pyramidal nanotubes are seen clearly.

are pulled in the direction of the electric field, in this case normal to the substrate. This directs the growth of the nanotube in that direction. From Fig. 2, it is obvious that the graphite branches are also aligned, at almost the same angle to the central tube (∼70–80°). This indicates that the electrical field also affects the growth of these branches, but without any catalytic particle decoration.

Fig. 4 shows the patterned growth of CCNTs. Copper mesh (2000#) was used to mask the Si(100) substrate before the deposition of catalyst films to form a pattern of catalyst film. It was removed before the growth of CNTs. The pyramidal nanotubes were only grown on the catalytic film surface. Ni was used as the catalyst, and a gas mixture of $N_2$ and $CH_4$ ($CH_4$ concentration was 3 vol%) was used at this time. The deposition time is 30 min. The growth rate is lower than for Fig. 1, but it is easier to control the length. The ability to control the growth of CCNTs in such manner is important when integrating CCNTs with other microelectronic processing techniques. CCNT patterns of different sizes and shapes can be obtained using standard lithographic techniques. The size and density of this material are controllable through the control of catalyst film thickness, annealing, and growth processes.

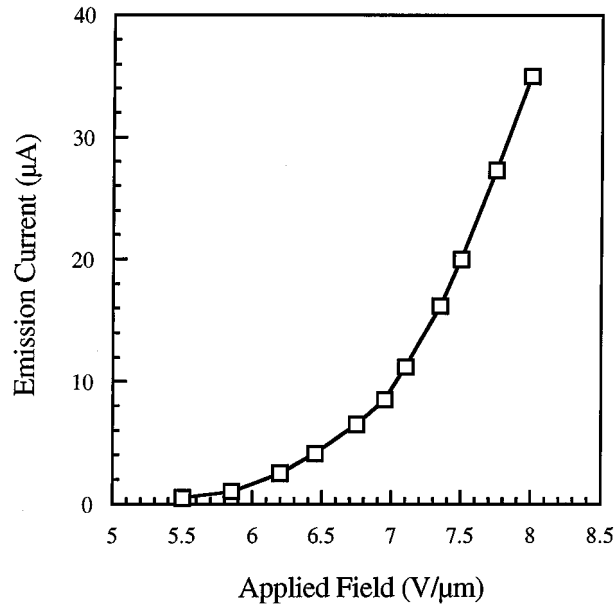



*Figure 5* $I \sim V$ curve measured.

The CCNT structure is expected to be highly active because of the large number of graphite branches and may be a good candidate for hydrogen storage. The CCNTs are possibly more suitable as tips for AFM and STM than conventional CNTs because of their increased rigidity due to their shapes. CCNTs also have excellent field emission properties. The field emission was measured in the system described in Ref. [4]. The vacuum during the measurement was $1 \times 10^{-5}$ Torr. The distance between the anode and the sample was 80 $\mu$m. The area with only one CCNT cluster (4 nanotubes) was selected for the measurement. The measurement was performed under room temperature. An emission current of 1 $\mu$A was obtained at an electrical field of 5 V/$\mu$m, and a 30 $\mu$A current was obtained at 8 V/$\mu$m. Fig. 5 shows the $I \sim V$ curve measured. Comapared with the previous measured results from high density ($10^9$–$10^{10}$/cm$^2$) aligned CNTs [4], the emission ability from the single CCNT is higher than that of a single CNT.

## 4. Conclusion

In conclusion, aligned concial carbon nanotubes have been obtained, as well as their patterned growth. Their growth mechanism is proposed by the observations of TEM. Their field emission data indicate that they are good emission source. Their unique morphology indicate that they would have many applications.

## Acknowledgements

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## References

1. S. MATASUMOTO, Y. SATO, M. TSUTSUMI and N. SETAKA, *J. Mater. Sci.* **17** (1982) 3106.
2. J. C. AUGUS and C. C. HAYMAN, *Science* **241** (1988) 887.
3. Y. CHEN, L. P. GUO and E. G. WANG, *J. Phys., Condens Matt.* **8** (1996) L685; *Philo. Mag. Lett.* **75** (1997) 155.

4. Y. CHEN *et al.*, *Chem. Phys. Lett.* **278** (1997) 178; *Appl. Phys. Lett.* **73** (1998) 2119.
5. Y. CHEN, S. PATEL, Y. YE, D. T. SHAW and L. P. GUO, unpublished.
6. Y. CHEN, L. P. GUO, J. J. JOHNSON and R. H. PRINCE, *J. Crystal Growth* **193** (1998) 342.
7. R. T. BAKER, *Carbon* **27** (1989) 315.
8. M. ENDO *et al.*, *Carbon* **33** (1993) 873.
9. W. Z. LI *et al.*, *Science* **274** (1996) 1701.
10. G. G. TIBBETTS, *J. Crystal Growth* **73** (1985) 431.
11. W. A. DE HEER, A. CHATELAIN and D. UGRADE, *Science* **270** (1995) 179.
12. Q. H. WANG *et al.*, *Appl. Phys. Lett.* **70** (1997) 3308.
13. P. G. COLLINS and A. Z. ZETTL, *ibid.* **69** (1996) 1069.

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