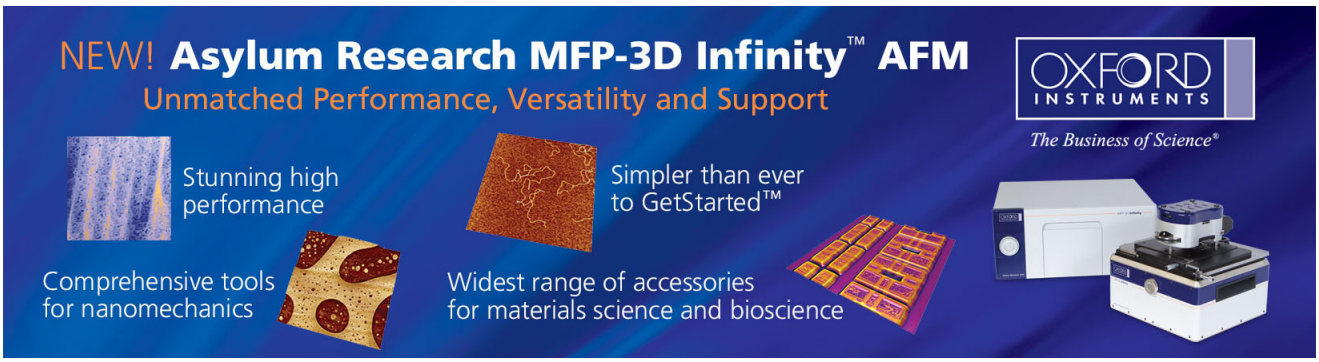
AIP Applied Physics Letters

Bias effect on the growth of carbon nanotips using microwave plasma chemical vapor deposition

C. L. Tsai, C. F. Chen, and L. K. Wu

Citation: Applied Physics Letters **81**, 721 (2002); doi: 10.1063/1.1494839
View online: http://dx.doi.org/10.1063/1.1494839
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/81/4?ver=pdfcov
Published by the AIP Publishing



Bias effect on the growth of carbon nanotips using microwave plasma chemical vapor deposition

C. L. Tsai,[a] C. F. Chen, and L. K. Wu
Department of Materials Science and Engineering, National Chiao Tung University, 1001 Ta Hsueh Road, Hsinchu 30050, Taiwan, Republic of China

(Received 15 March 2002; accepted for publication 24 May 2002)

Carbon nanotips with a high-aspect ratio were directly grown on Pt films. Carbon nanotips grew up to 5.4 μm length and 64 nm diameter under a -120 V bias. Compared to the hollow structure of carbon nanotubes, transmission electron microscopy images indicate its solid body, which is made of graphite. Carbon nanotips possess good field emission characteristics, that is, a turn-on field of 1.5 V/μm and 761 μA/cm^2 under 2.2 V/μm. The Pt films provide a good conduction path for electron transport from the cathode to the emission site and do not act as catalysts. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1494839]

A good candidate for use in field emission must have a high-aspect-ratio structure, a low work function, and chemical stability. Carbon nanotubes, since their first discovery in 1991,[1] have been considered for many different applications. Their small dimension, strength, and the remarkable physical properties of these materials make them the most promising emitters for field emission devices. Due to the size effect and structural diversity of nanomaterials, the physical properties strongly depend on their atomic-size structure, size, and chemistry.[2] Applications of nanomaterials in nanotechnology are focused on four fields: material preparation, property characterization, device fabrication, and system integration.

In this study, new carbon nanomaterials are developed in field emission. Well-aligned carbon nanotips were grown on the platinum (Pt) films in the chemical vapor deposition system. Basically, carbon nanotubes were synthesized with metal catalysts such as Fe, Co, Ni, and others.[3–5] These metal catalysts play a key role in the deposition. However, a Pt film which is highly chemically inert provides only a good conduction path for electron transport from the cathode to the emission sites instead of catalysts. Therefore, the intrinsic properties of carbon nanotips are different from carbon nanotubes.

Five nanometer Ti (the improvement of adhesion between Si and Pt) and 20 nm Pt films were pre-coated sequentially on Si by using electron beam evaporation. The reactive gas mixture was CH_4/H_2 with a flow rate of 10/10 sccm. The applied microwave power and the pressure during the growth of carbon nanotips were 400 W and 15 Torr, respectively. An optical pyrometer was used to monitor the substrate temperature, that was maintained at about 700 °C. The growth time was 45 min, but nanotips grown on Si under a -120 V bias only lasted for 30 min.

It is considered that the carbon active species in the plasma are accelerated to the substrate by the negative bias to form sp^2 and noncrystalline clusters in the nucleation period. Some clusters are then transformed into sp^3 clusters through the collision of carbon species in the growth period. Meanwhile, the accelerated active hydrogen radicals will remove the other sp^2 clusters with lower active energy. In this situation, the competition between etching and deposition is repeated. Nevertheless, biasing the samples can cause their rate of deposition to exceed the rate of etching. Many reports have presented the method to enhance the nucleation density of diamond by applying negative bias.[6–8] This study focuses mainly on determining the optimum negative bias to synthesize the carbon nanotips. Figures 1 and 2 present the scanning electron microscope (SEM) pictures of carbon nanotips grown under various biases and substrates. The photograph on the right of each figure is the enlarged image. Figure 1(a) displays that only a low density of tiny nanotips can be grown under -80 V. This also implies that samples grown under a bias less negative than -80 V cause little carbon materials to be deposited on the Pt films. Increasing the bias to -120 V, it generates the high-density carbon nanotips. Figure 2(a) shows these well-aligned carbon nanotips grown upward to 5.4 μm length and 64 nm diameter under -120 V. Sharper nanotips have a higher-aspect ratio, indicating good

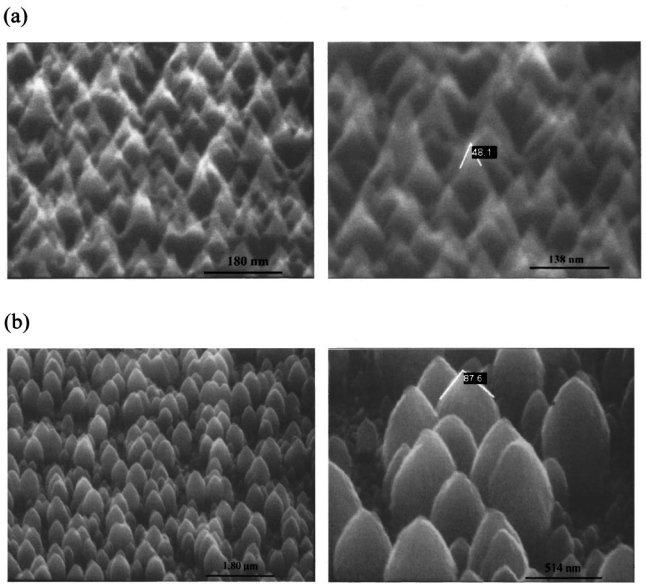


FIG. 1. SEM photographs of carbon nanotips grown on Pt under (a) -80 V and (b) -150 V.

[a]Electronic mail: lun@ms15.url.com.tw

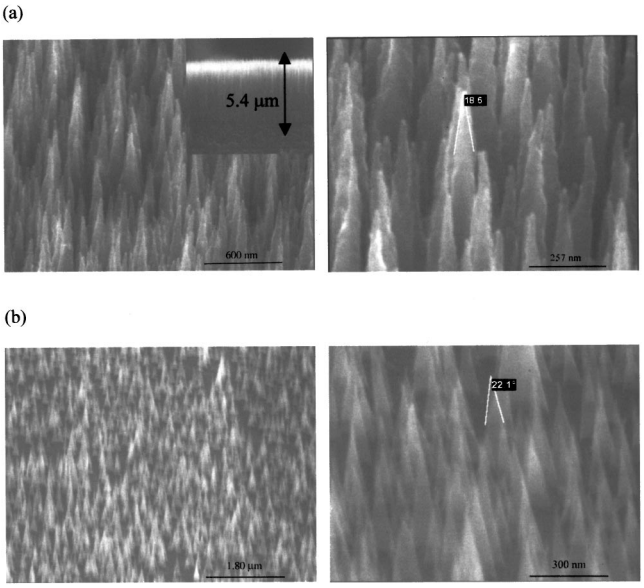


FIG. 2. SEM photographs of carbon nanotips grown under −120 V on (a) Pt and (b) Si.

characteristics for field emission. Figure 1(b), however, indicates that tips will grow to a submicrometer diameter under a higher bias (more negative than −120 V), revealing that bias can enhance the growth of carbon nanotips on Pt films. Hence, the optimal bias for growing carbon nanotips on Pt films is −120 V.

Figure 2(b) also shows good results of carbon nanotips grown on Si under −120 V, but the deposition time is shorter than those grown on Pt films. This is due to the fact that it is easier to form carbon materials on Si than on Pt.[9]

Figure 3(a) displays the transmission electron microscopy (TEM) images of an end section of an individual nanotip grown under −120 V. Unlike hollow carbon nanotubes, carbon nanotips are solid. The main feature of note is the tip's somewhat irregular shape, with one primary protrusion. The diffraction pattern (DP) indicates that the end section is graphite. Moreover, Fig. 3(b) displays the lateral section of the same tip, showing a well-organized microcrystalline graphite section. The DP of Fig. 3(b) also confirms the existence of well-organized microcrystalline graphite, proving that the carbon nanotips are made of graphite.

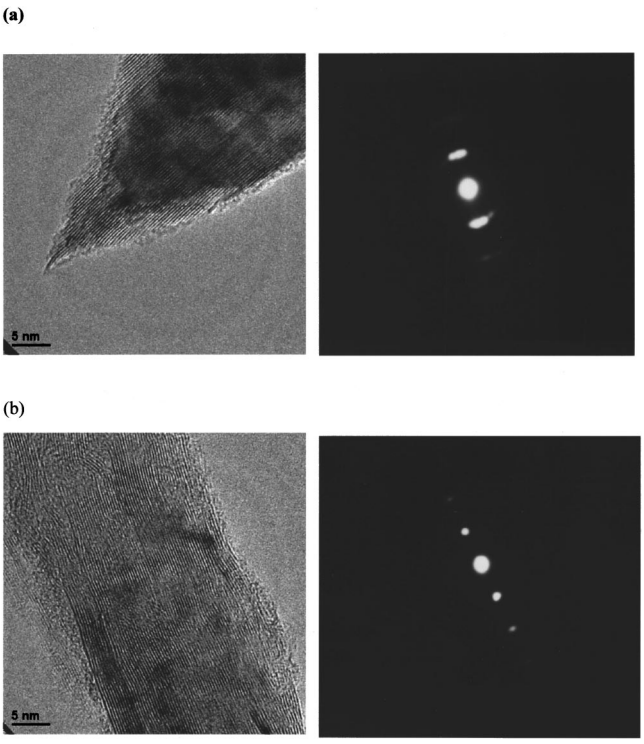


FIG. 3. TEM images and diffraction pattern of (a) the end section and (b) lateral section of an individual tip.

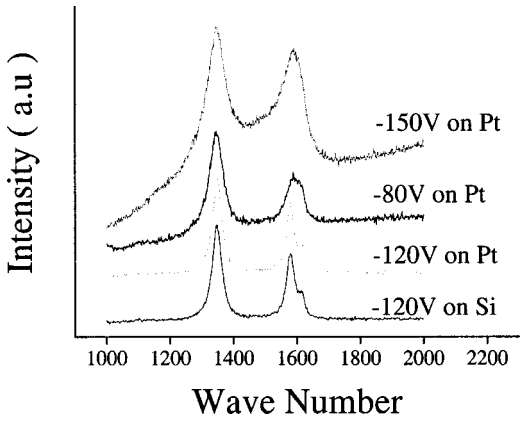


FIG. 4. Raman spectra of carbon nanotips grown under various biases and substrates.

Figure 4 exhibits the Raman spectra of carbon nanotips grown under various biases and substrates. All of them have two sharp peaks located on about 1345 and 1580 cm^{-1}, respectively. The first-order Raman spectrum of aligned carbon nanotips shows strong sharp peaks at 1581 cm^{-1} (G line), which is the high-frequency E_{2g} first-order mode and 1350 cm^{-1} (roughly corresponding to the D line associated with disorder-allowed zone-edge modes of graphite). The peaks

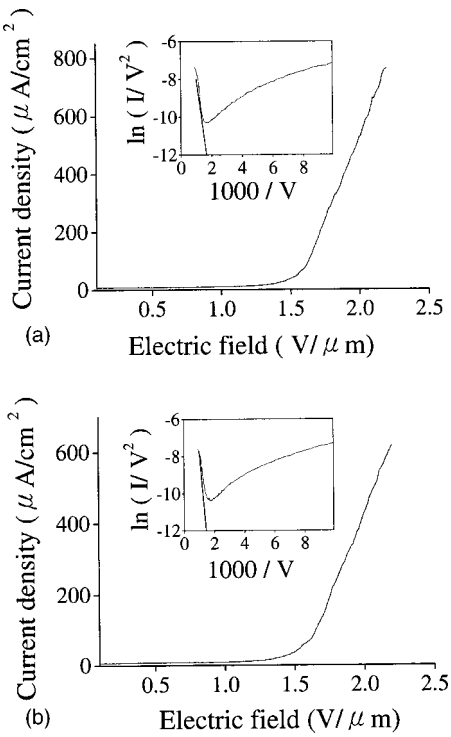


FIG. 5. The current density vs electric field and FN plot of carbon nanotips grown under −120 V on (a) Pt and (b) Si.

imply that the nanotips are characteristic of microcrystalline graphite. The relative intensities of the two peaks depend on the type of graphitic material. Normally, the intensity of the 1350 cm^{-1} peak increases (i) with an increase in the amount of unorganized carbon in the samples and (ii) with a decrease in the graphite crystal size.[10]

The most conspicuous feature of carbon nanotips (grown under -120 V) is that their Raman spectra show an additional weak peak at about 1618 cm^{-1} (D' line). The origin of the D and D' lines in other forms of carbon materials has been explained as disorder-induced features, caused by the finite particle size effect or lattice distortion.[11–13] Besides, a sample grown under -120 V with a narrow bandwidth of the G line and the D line has well-organized carbon. The previous TEM image clearly displays the existence of well-organized graphite in the sample.

The field emission tests are performed on a diode structure, in which the carbon nanotips are separated from the anode, indium-tin-oxide glass, using 500 μm glass as spacers. The current–voltage ($I-V$) properties are measured and analyzed through the Fowler–Nordheim (FN) model, via the $\ln(I/V^2)$ vs $1/V$ plot. Figure 5 characterizes carbon nanotips grown under -120 V on Si and Pt. The current densities at 2.2 V/μm of nanotips under -120 V grown on Pt and Si are 761 and 617 $\mu A/cm^2$, respectively. The threshold voltage (V_T) is defined as the intersection of the slope of FN plots with abscissa. According to the FN analysis, the emission behavior of the sample grown on the Pt films is better than that grown on Si (lower turn-on field$=1.5$ V/μm). It is attributed to the presence of Pt layers, which provide a good conduction path for electron transport from the cathode to the emission sites.[14]

The authors would like to thank the National Science Council of the Republic of China for financially supporting this research under Contract No. NSC 90-2216-E-009-036.

[1] S. Iijima, Nature (London) **354**, 56 (1991).
[2] *Characterization of Nanophase Materials*, edited by Z. L. Wang (Wiley-VCH, New York, 1999), pp. 1.
[3] C. Bower, O. Zhou, W. Zhu, D. J. Werder, and S. Jin, Appl. Phys. Lett. **77**, 2767 (2000).
[4] J. Kim, K. No, and C. J. Lee, J. Appl. Phys. **90**, 2591 (2001).
[5] J. I. Sohn, S. Lee, Y. H. Song, S. Y. Choi, K. L. Cho, and K. S. Nam, Appl. Phys. Lett. **78**, 901 (2001).
[6] S. Yugo, T. Kanai, T. Kimura, and T. Muto, Appl. Phys. Lett. **58**, 1036 (1991).
[7] J. T. Huang, W. Y. Yeh, J. Hwang, and H. Chang, Thin Solid Films **315**, 35 (1998).
[8] R. Stöckel, K. Janischowsky, S. Rohmfeld, J. Ristein, M. Hundhausen, and L. Ley, Diamond Relat. Mater. **5**, 321 (1996).
[9] T. Tachibana, Y. Yokota, K. Hayashi, K. Miyata, K. Kobashi, and Y. Shintani, Diamond Relat. Mater. **9**, 251 (2000).
[10] F. Tuinstra and J. L. Koenig, J. Chem. Phys. **53**, 1126 (1970).
[11] G. Vitali, M. Rossi, M. L. Terranova, and V. Sessa, J. Appl. Phys. **77**, 4307 (1995).
[12] D. G. McCulloch, S. Prawer, and A. Hoffman, Phys. Rev. B **50**, 5905 (1994).
[13] V. Barbarossa, F. Galluzzi, R. Tomaciello, and A. Zanobi, Chem. Phys. Lett. **185**, 53 (1991).
[14] J. S. Lee, K. S. Liu, and I. N. Lin, Appl. Phys. Lett. **71**, 554 (1997).