

Growth of chromium carbide capped–carbon nanotip using bias-assisted microwave plasma chemical vapor deposition

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Abstract

Chromium carbide capped–carbon nanotips were synthesized using bias-assisted microwave plasma chemical vapor deposition. Such a material grew up to several hundreds of nanometer long and tens of nanometer in diameter. The applied bias voltage is a significant parameter in the growth process whereas the higher bias voltage is effective in increasing the growth rate. However, the higher bias voltage also contributes to a rapid formation of chromium carbide which leads to a shorter length of carbon nanotip at the same time. Higher ion energies also vary the tip diameter due to strong ion bombardment which is a competitor to the deposition process. Our investigations revealed that the growth of chromium carbide capped–carbon nanotips reaches a limit due to the full carburization of chromium.

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1. Introduction

Since the first observation and characterization of carbon nanotubes structure [1], extensive researches on nanoscale materials have been approached in the last decade. These elongated nanotubes consist of carbon hexagons arranged in a concentric manner with ends of tubes normally capped by metallic catalyst. In fact, carbon can exist in similar forms such as carbon nanofiber [2] or carbon nanotips [3]. In addition to carbon nanotubes, these nanomaterials also show superior capabilities, for example, controlled orientation [4], selective growth [5], and ultra-sharpness [3], which make them the suitable candidates for practical field emission [6] and scanning microscope probe [7] applications.

Approaches have been made to aligned carbon nanotubes [8–10]. In particular, we have recently synthesized a new material [11] using bias-assisted microwave plasma chemical vapor deposition, which grow just perpendicular to the substrate with amazing uniformity. The growth and the

appearance of the chromium carbide capped–carbon nanotip are quite different from the carbon-related nanomaterial reported before [12]. This new composite material combines nanocrystalline chromium carbide with carbon nanotips. Here, we demonstrate that the surface morphology is greatly controlled by the applied bias voltages and the nanotip is grown by the catalyst-cap growth.

2. Experimental details

Mirror-polished n-type, (100) oriented Si wafers with resistivity of 4.5–5.5 Ω/cm were cleaned by RCA cleaning process to remove contaminations. Wet oxidation was then carried out using a high-temperature furnace system (model ASM LB-45). After that, a 200-Å-thick Cr film was deposited on SiO_2 using an E-Gun Evaporator (model ULVAC EBX-10C, Japan). Then the substrates underwent bias-assisted microwave plasma chemical vapor deposition to grow the chromium carbide capped–carbon nanotip.

The microwave power was maintained at 400 W with an external negative DC voltage supplied to the substrate. A two-step process was taken for the synthesis of chromium

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carbide capped–carbon nanotip. The substrate was first treated under hydrogen plasma for 10 min in order to activate the surface of the deposited film. The total pressure in the chamber was kept at 2000 Pa and the hydrogen flow rate was 200 sccm. Followed by the pretreatment procedure, reactive gas of a mixture with $H_2/CH_4=20/10$ was admitted to the quartz chamber. The synthesis temperature was about $700^\circ C$, as measured with an IR thermometer (Minolta TR-630).

After deposition, the synthesized chromium carbide capped–carbon nanotip was characterized using scanning electron microscope (SEM; Hitachi S-4000) with an acceleration voltage of 25 kV to observe the surface morphology. High-resolution transmission electron microscopy (HR-TEM; Philips Tecnai 20) operating at 200 kV was used to observe the nanostructure of the nanotubes.

3. Results and discussion

Fig. 1a shows the surface morphology of chromium carbide capped–carbon nanotips from the edge part of the silicon substrate. The specimen was grown with a bias

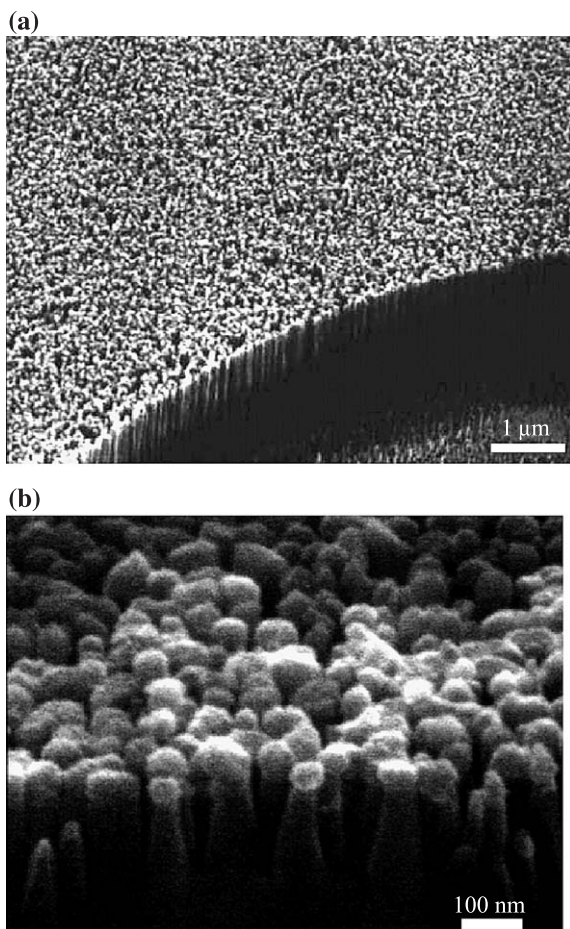


Fig. 1. (a) Low-magnification SEM image showing the uniformity of the vertical aligned chromium carbide capped–carbon nanotips. (b) SEM image at higher magnification.

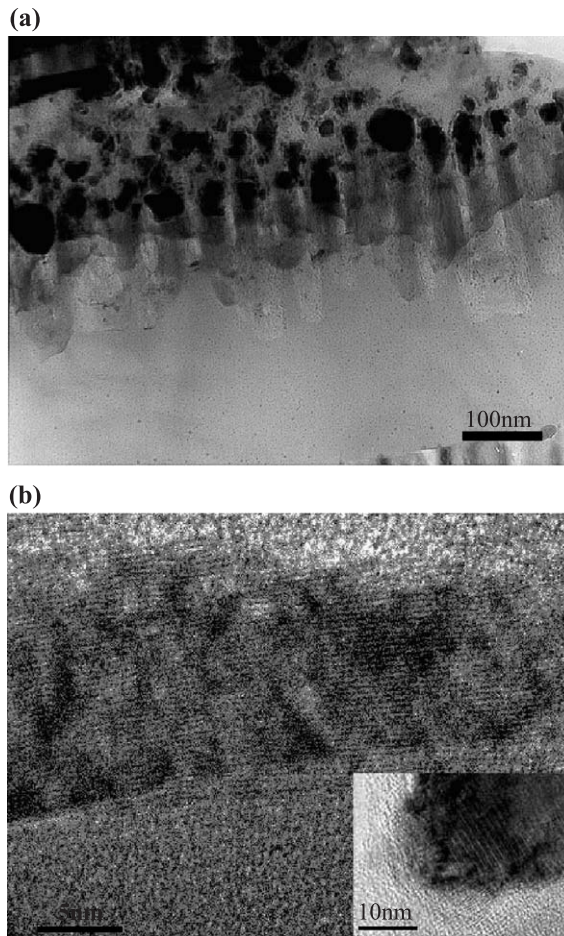


Fig. 2. TEM images showing (a) the cross-section view of chromium carbide capped–carbon nanotips and, (b) high-magnification view of an individual carbon nanotip and the inset shows the chromium carbide head.

voltage of -150 V for 30 min. The image demonstrates the great uniformity and the chromium carbide capped process also indicates the selective growth of the nanotips, which both are important issues in field emission applications. Though this material shows such a good property [11], models such as microscopy electron transport behavior [13] between the dielectric chromium carbide and the graphitic layer still need to be understood. Fig. 1b shows the magnified view of the nanotips. It has to be noticed that there are white spots on top of each nanotip and the root of their tip-like structure is connected to each other. The average size of the nanoparticle on the tip is 50 nm with its neck, the as-grown carbon nanotip of 40 nm and increasing its diameter to the root part.

Fig. 2a shows the cross-section TEM image of the chromium carbide capped–carbon nanotip. It is also found that the dark spots exist only on top of the nanotips without any residual at the bottom, this is quite distinct from carbon nanotubes where tip growth model and base growth model co-exist [14]. X-ray diffraction spectra show that the crystal structure is Cr_7C_3 . Fig. 2b shows individual crystalline chromium carbide embedded on a carbon nanotip with lots of defects such as twins or stacking faults. This phenom-

enon is attributed to the low-temperature process and the rapid formation of chromium carbide relative to typical high-temperature processes and long time for hard coatings of Cr_7C_3 [15]. The inset shows the lateral cross section of the carbon nanotips with tip end pointing to the right. It shows the parallel graphitic layers stretched along the growth direction just like carbon nanofibers [16] but accompanied with decreasing shorter layers around them.

Fig. 3a represents schematic diagram of the growth mechanism of chromium carbide capped carbon nanotips. The substrate was first treated with hydrogen plasma to remove the passive layer such as chromium oxide or other contaminations and created certain roughness. Then the reaction gas mixtures flowed into the chamber to start the deposition process. The chromium layer act as catalyst for the precipitation of carbon atoms, which may be a vapor–liquid–solid growth mechanism similar to the growth of carbon nanotubes [12] or carbon nanofiber [16]. The chromium did carburize during deposition, which made the carbide very stable. This suggests that surface diffusion [17] becomes the main process step for the growth. The carbon nanotips also increase their diameter during growth by vapor–solid process which means that the carbon species are deposited directly onto the tip body. The applied bias voltage of more than -100 V is essential for the growth of chromium carbide capped carbon nanotips. This is probably because the bias voltage provides a higher reactant concentration around the chromium with relatively high ion energies, and also the sharpness of the tips induces high electrical field strength to attract positive ions. The high activation energy for the carbon diffusion in chromium also leads to the growth of carbon nanotubes using chromium as a catalyst that has been rarely seen.

Interestingly, the application of a bias voltage helps to grow the tips, but destroys it, too. The growth of the nanotips is accompanied by ion bombardment due to the strong field applied by the negative DC bias [18]. The growth of chromium carbide capped carbon nanotip is a

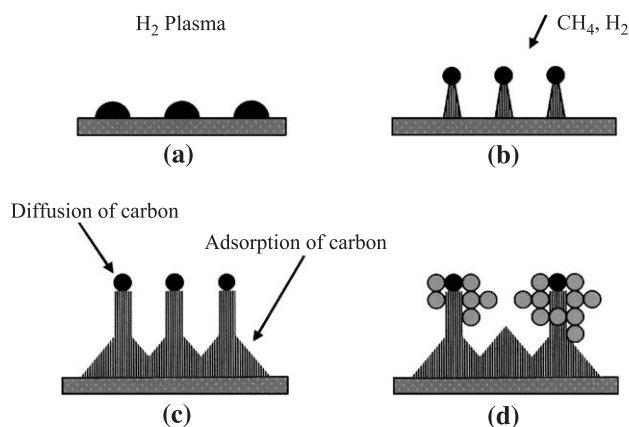


Fig. 3. Schematic diagram of the proposed growth model. (a) Formation of the nucleation process; (b) cap growth; (c) deposition of carbon; (d) asparagus-like structure forms.

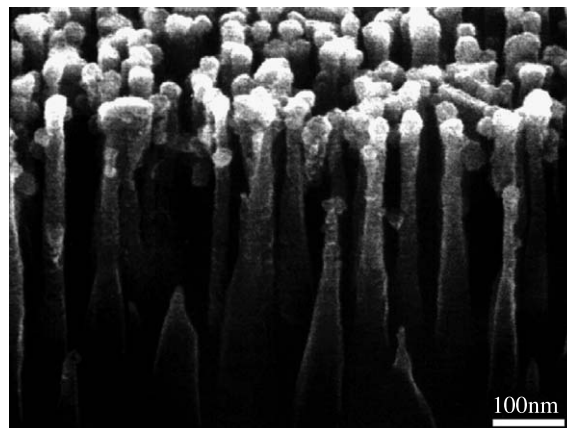


Fig. 4. Chromium carbide capped carbon nanotip grown under a bias voltage of -300 V for 30 min.

competition between carbon deposition and ion bombardment. Under bias of -150 V, the diameter of the carbon nanotips increases from the as-grown diameter of 40 nm with increasing time. But under high bias voltages of -300 V, the diameter of the nanotips maintains at about 40 nm or less and some even breakdown from its neck, which is revealed in Fig. 4. This is also a direct evidence that the chromium carbide is efficiently resistant to ion bombardment and shields the carbon nanotip, which might indicate a way to improve field emission for lifetime applications. Unlike the growth of carbon nanotubes or carbon nanofibers, a length limit exists. This might be due to the full carburization of chromium that leads to the deficiency in diffusing carbon. Application of bias in microwave plasma chemical vapor deposition increases the deposition rate in most cases [19]. The higher bias voltage contributes to a faster formation of chromium carbide that limits the length of the nanotip. The following carbon thus starts to deposit around the chromium carbide, where the high field induced by the tip sharpness and a higher carbon supplement becomes the preferential sites for the carbon and makes them look like asparagus.

In fact, some similar phenomenon were been observed for other elemental catalyst. In this way, from the Fowler–Nordheim model [20], the work function ϕ can be easily tuned for further improvement in field emission applications or the specific property of the material can be used in some special applications.

4. Conclusions

In summary, chromium can be used as a catalyst to grow chromium carbide capped carbon nanotip with size of several tens of nanometers. Surface diffusion is believed to be the main mechanism for the growth of carbon nanotip. The applied bias voltage plays an important role that either assists the growth or etches the carbon away during growth. In other words, the dimension of the chromium carbide

capped-carbon nanotip can be controlled. And there exists a length limit which is due to the full carburization of chromium. By supplying a sufficient high bias voltage, an asparagus-like structure forms.

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References

- [1] S. Iijima, *Nature* 354 (1991) 56.
- [2] L.R. Baylor, V.I. Merkulov, E.D. Ellis, M.A. Guillorn, D.H. Lowndes, A.V. Melechko, M.L. Simpson, J.H. Wheaton, *J. Appl. Phys.* 91 (2002) 4602.
- [3] C.L. Tsai, C.F. Chen, L.K. Wu, *Appl. Phys. Lett.* 81 (2002) 721.
- [4] Vladimir I. Merkulov, A.V. Melechko, M.A. Guillorn, M.L. Simpson, *Appl. Phys. Lett.* 80 (2002) 4816.
- [5] M.A. Guillorn, A.V. Melechko, V.I. Merkulov, D.K. Hensley, M.L. Simpson, D.H. Lowndes, *Appl. Phys. Lett.* 81 (2002) 3660.
- [6] C.L. Tsai, C.F. Chen, C.L. Lin, *Appl. Phys. Lett.* 80 (2002) 1821.
- [7] H. Dai, J.H. Hafner, A.G. Rinzler, D.T. Colbert, R.E. Smalley, *Nature* 384 (1996) 147.
- [8] Z.F. Ren, Z.P. Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal, P.N. Provencio, *Science* 282 (1998) 1105.
- [9] W.Z. Li, S.S. Xie, L.X. Qian, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao, G. Wang, *Science* 274 (1996) 1701.
- [10] S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tomblor, A.M. Casell, H. Dai, *Science* 283 (1999) 512.
- [11] C.L. Tsai, J.H. Hsu, C.F. Chen, *Appl. Phys. Lett.* 82 (2003) 4337.
- [12] E.F. Kukovitsky, S.G. L'vov, N.A. Sainov, *Chem. Phys. Lett.* 317 (2000) 65.
- [13] Kevin L. Jensen, Patrick G. O'Shea, Donald W. Feldman, *Appl. Phys. Lett.* 81 (2002) 3867.
- [14] L.C. Chen, C.Y. Wen, C.H. Lian, W.K. Hong, K.J. Chen, H.C. Chen, C.S. Shen, C.T. Wu, K.H. Chen, *Adv. Funct. Mater.* 12 (2002) 687.
- [15] P.K. Rajagopalan, T.S. Krishnan, D.K. Bose, *J. Alloys Compd.* 297 (2002) L1.
- [16] C.F. Chen, C.L. Lin, C.M. Wang, *Appl. Phys. Lett.* 82 (2003) 2515.
- [17] D.B. Hash, M. Meyyappan, *J. Appl. Phys.* 93 (2003) 750.
- [18] D.A. Carla, D.W. Hess, M.A. Lieberman, T.D. Nguyen, R. Gronsky, *J. Appl. Phys. Lett.* 70 (1991) 3301.
- [19] C.L. Tsai, C.F. Chen, *Diamond Relat. Mater.* 12 (2003) 1615.
- [20] R.H. Fowler, L.W. Nordheim, *Proc. R. Soc. London, Ser. A* 119 (1928) 173.