# The Field Emission Current Characteristics of Carbon Nanotubes Synthesized by Thermal Chemical Vapor Deposition


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**ABSTRACT**

In this work, thermal chemical vapor deposition was utilized to grow carbon nanotubes (CNTs). Silane was the main source for carbon, and argon was used as the carrier gas. CNTs were synthesized from carbon atoms obtained from catalytic thermal decomposition of silane. In this research, we study the effect of catalyst metal thickness and deposition temperature and different catalyst on structural properties and field emission characteristics of ocarbon nanotubes (CNTs) which were synthesized by thermal chemical vapor deposition of methane. Raman spectroscopy and SEM were employed to study structural properties of CNTs, whereas field emission characteristics of CNTs were measured in high vacuum. From SEM and Raman spectroscopic studies, it is found that as catalyst nickel thickness gets thicker, the size of nickel balls formed in the nucleation period gets larger. Hence, the number of CNTs gets smaller, and the diameters of synthesized CNTs get larger. It is suspected that the supplied thermal energy at low temperature is not high enough to activate catalytic reaction to synthesize CNTs. At high temperature, thermal energy supplied has already cross the threshold for nucleation, and the diameter of CNT reach a saturation value. And CNTs were synthesized from tungsten layer is the best of different catalyst (Fe,Co,Ni). From Fowler-Nordheim tunneling analysis, it was found that the increase in nickel thickness indeed increases the work function of CNT. Hence, we arrive at the conclusion that the decrease in the number of CNT, the decrease in the field enhancement factor, and the increase in the work function of CNT are three main factors that causes the decrease in the field emission current for larger nickel metal thickness. it is found that this change in field emission current is caused not only by the change in number and diameter of CNTs, but also by the change in crystalline structure and work function of CNTs. The increase in the work function of CNTs make it difficult for electrons to emit from CNTs which can play an important role in the emission current.



Keywords : carbon nanotubes (CNTs) ; field emission ; thermal chemical vapor deposition (thermal CVD)


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## REFERENCES

1. Iijima, S. (1991). Helical microtubules of graphitic carbon. Nature, 354, 7, 56-58. 2. Radushkevich, L. V., & Lukyanovic, V. M. (1952). Zh. Fiz. Khim. 26, 88. 3. Hofer, L. J. E., Sterling, E., & MacCartney, J. T. (1955). J. Phys. Chem., 59, 6210. 4. Kroto, H. W., Heath, J. R., O ' Brian, S. C., Curl, R. F., & Smalley, R. E.(1985). C60: Buckminsterfullerene. Nature, 318 (6042), 162-163. 5. Kratschmer, W., Lamb, L. D., Fostiropoulos, K., & Huffman, D. R. (1990). Solid C60: A new form of carbon. Nature, 347, 354-358. 6. Maiti, Brabec, C. J., Roland, C., & Bernholc, J. (1995). Theory of carbon nanotube growth. Phys. Rev. B, 15; 52(20), 14850-14858. 7. Kusunoki, M., Rokkaku, M., & Suzuki, T. (1997). Epitaxial carbon nanotube film self-organized by sublimation decomposition of silicon carbide. Appl. Phys. Lett., 71(18), 2620-2622. 8. Zhang, Y., Gu, H., & Iijima, S. (1998). Single-wall carbon nanotubes synthesized by laser ablation in a nitrogen atmosphere. Appl. Phys. Lett., 73(26), 3827-3829. 9. Ebbesen, T. W. (1997). Carbon Nanotubes: Preparation and properties. CRC Press, Boca Raton, 139-162. 10. Iijima, S., & Ichihashi, T. (1993). Single-shell carbon nanotubes of 1-nm diameter. Nature, 363, 603-605. 11. Bethune, D. S., Kiang, C. H., deVries, M. S., Gorman, G., Saroy, R., Vazguez, J., & Beyers, R. (1993). Cobalt-catalyzed growth of carbon nanotubes with single-atomic-layer walls. Nature, 363, 605-607. 12. Thess, A., Lee, R., Nikolaev, P., Dai, H., Petit, P., Robert, J., Xu, C., Lee, Y. H., Kim, S. G., Rinzler, A. G., Colbert, D. T., Scuseria, G. E., Tomanek, D., Fischer, J. E., & Smalley, R. E. (1996). Crystalline ropes of metallic carbon nanotubes. Science, 273, 483-487. 13. Peter J. F. Harris, (1999). Carbon nanotubes and related structure. Cambridge University Press, Chapter 4.2: Electronic properties of nanotube. 16 – 54. 14. Charlier, J. C., & Issi, J. P. (1998). Electronic structure and quantum transport in carbon nanotubes. Applied Physics A: Materials Science & Processing, 67, 79-87. 15. Haus, M. D., Dresselhaus, G., Eklund, P., & Saito, R. (1998). Carbon nanotubes. Physics World, 11, 33-38. 16. Mintmire, J. W. & White, C. T. (1998). First-principles band structures of armchair nanotubes. Applied Physics A: Materials Science & Processing, 67, 65-69. 17. Dresselhaus, M. S., Dresselhaus, G., & Saito, R. (1995). Physics of carbon nanotubes. Carbon, 33, 883-891. 18. Jo, S. H., Tu, Y., Huang, Z. P., Carnahan, D. L., Wang, D. Z., & Ren, Z. F. (2003). Effect of length and spacing of vertically aligned carbon nanotubes on field emission properties. Appl. Phys. Lett., 82, 3520-3522. 19. Wang, Z. L., R. P. Gao, W. A. deHeer, P. Poncharal, (2002). In situ imaging of field emission from individual carbon nanotubes and their structural damage. Appl. Phys. Lett., 80, 856-858. 20. Bonard, J. M., Dean, K. A., Coll, B. F., & Klinke, C. (2002). Field emission of individual carbon nanotubes in the scanning electron microscope. Phys. Rev. Lett., 89(19), 4, 1976021-24. 21. Rinzler, A. G., Hafner, J. H., Nikolaev, P., Lou, L., Kim, S. G., Tomanek, D., Nordlander, P., Colbert, D. T., & Smalley, R. E. (1995). Unraveling nanotubes: field emission from an atomic wire. Science, 269, 1550-1553. 22. DeHeer, W. A., Chatelain, A., & Ugarte, D. (1995). A carbon nanotube field-emission electron source. Science, 270, 1179-1180. 23. Shyu, Y. M., & Hong, F. C. N. (2001). Low-temperature growth and field emission of aligned carbon nanotubes by chemical vapor deposition. Mater. Chem. Phys., 72(2), 223-227. 24. Wang, Y. H., Lin, J., & Huan, C. H. A. (2002). Macroscopic field emission properties of aligned carbon nanotubes array and randomly oriented carbon nanotubes layer. Thin Solid Films, 405(1-2), 243-247. 25. Bonard, J., Salvetat, J., Stockli, T., de Heer, W. A., Forro, L., & Chatelain, A. (1998). Field emission from single-wall carbon nanotube films. Appl. Phys. Lett., 73(7), 918-920. 26. Wang, Q. H., Corrigan, T. D., Dai, J. Y., & Chang, R. P. H. (1997). Field emission from nanotube bundle emitters at low fields. Appl. Phys. Lett., 70(24), 3308-3310. 27. Sung, S. L., Tsai, S. H., Tseng, C. H., Chiang, F. K., Liu, X. W., & Shih, H. C. (1999). Well-aligned carbon nanotubes synthesized in anodic alumina by electron cyclotorn resonance chemical vapor deposition. Appl. Phys. Lett., 74(2), 197-199. 28. Saito, Y., & Uemura, S. (2000). Field emission from carbon nanotubes and its application to electron sources. Carbon, 38(2), 169-182. 29. Yumura, M., Ohshima, S., Uchida, K., Tasaka, Y., Kuriki, Y., Ikazaki, F., Saito, Y., & Uemura, S. (1999). Synthesis and purification of multi-walledcarbon nanotubes for field emitter applications. Diamond and Related Materials, 8, 785-791. 30. Kuttel, O. M., Groning, O., Emmenegger, C., Nilsson, L., Mallard, E., Diederich, L., & Schlapbach, L. (1999). Field emission from diamond, diamond-like and nanostructured carbon films. Carbon, 37, 745. 31. 楊素華、藍慶忠 (2004)。科技發展。382期，71。 32. Saito, Y., Yoshikawa, T., Inagaki, M., Tomita, M., & Hayshi, T. (1993). Growth and structure of graphitic tubules and polyhedral particles in arc-discharge. Chemical Physics Letters, 204, 277-282. 33. Dai, H., Rinzer, A. G., Nikolaev, P., Thess, A., Colbert, D. T., & Smalley, R. E. (1996). Single-wall nanotubes produces by mental catalyzed disproportionation of carbon monoxide. Chem. Phys. Lett., 260, 471-475. 34. Lee, Y. H., Kim, S. G., & Tomanek, D. (1997). Catalytic growth of single-wall carbon nanotubes: an Ab initio study. Phys. Rev. Lett., 78, 2393-2396. 35. Endo, M., & Kroto, H. W. (1992). Formation of carbon nanofibers. Journal of Physical Chemistry, 96, 6491-6944. 36. Baker, R. T. K., & Harries, P. S. (1978). The formation of filamentous carbon. Chemistry and Physics of Carbon, New York: Marcel Deckker, 14, 83-165. 37. Baker, R. T. K., Braker, M. A., Harries, P. S., Feates, F. S., & Waite, R. J. (1972). Nucleation and growth of carbon deposits from nickel catalyzed decomposition of acetylene. Journal of Catalysis, 26, 51-62. 38. Oberlin, A., Ento, M., & Koyama, T. (1976). Filamentous growth of carbon through benzene decomposition. Journal of Crystal Growth, 32, 335-349. 39. Baird, T., & Fryer, J. R. (1974). Carbon formation on iron and. nickel foils by hydrocarbon pyrolysis reactions at 700 ° C. Carbon, 12, 591-602. 40. Oberlin, A., Ento, M., & Koyama, T. (1976). High resolution electron microscope observations of graphitized carbon fibers Carbon. Carbon, 14, 133-157. 41. Journet, C. et al., (1998). Production of carbon nanotubes. Applied Physics, .67, 1-9. 42. Alan, M. et al., (1998). Chemical vapor deposition of methane for single-walled carbon nanotubes. Chem. Phys. Lett., 292, 567-574. 43. Yacaman, M. J., Yoshida, M. M., Rendon, L., & Santiesteban, J. G. (1993). Catalytic growth of carbon. microtubules with fullerene structure. Appl. Phys. Lett., 62, 202-204. 44. Baker, R. T. K., & Chludzinski, J. J. (1980). Filamentous carbon growth on nickel – iron surfaces—effect of various oxide additives. Journal of Catalysis, 64, 464-478. 45. Baker, R. T. K., Harries, P. S., Thomas, R. B., & Waite, R. J. (1973). Formation of filamen-tous carbon from iron and chromium catalyzed decomposition of acetylene. Journal of Catalysis, 30, 86-95. 46. Baker, R. T. K., & Waite, R. J. (1975). Formation of carbonaceous

deposit from the platinum-iron catalyzed decomposition. Journal of Catalysis, 37, 101-105. 47. Jung, M., Eun, K. Y., Lee, J. K., Baik, Y. J., Lee, K. R., & Park, J. W. (2001). Growth of carbon nanotubes by chemical vapor deposition. Diamond and Related Materials, 10, 1235-1240. 48. Xie, S., Li, W., Pan, Z., Chang, B., & Sun, L. (2000). Self-assembly of shape-controlled nanocrystals and their in-situ thermodynamic properties. Materials Science and Engineering A, 286, 11-15. 49. Chen, X. H., Feng, S. Q., Ding, Y., Peng, J. C., & Chen, Z. Z. (1999). The formation conditions of carbon nanotubes array based on FeNi alloy island films. Thin Solid Films, 339, 6-9. 50. Lee, C. J., Park, J., Kang, S. Y., & Lee, J. H. (2000). Growth of well-aligned carbon nanotubes on a large area of Co-Ni co-deposited silicon oxide substrate by thermal chemical vapor deposition. Chemical Physics Letters, 323, 554-559. 51. Terrones, M. et al., (1998). Preparation of aligned carbon nanotubes catalysed by laser-etched cobalt thin films. Chemical Physics Letters, 285, 299-305. 52. Liang, Q., Li, Q., Chen, D. L., Zhou, D. R., Zhang, B. L., & Yu, Z. L. (2000). Carbon nanotube prepared in the atmosphere of partial oxidation of methane. Chemical Journal of Chinese Universities-Chineses, 21(4), 623-625. 53. Hernadi, K., Fonseca, A., Nagy, J. B., Siska, A., & Kiricsi, I. (2000). Production of nanotubes by the. catalytic decomposition of different carbon-containing compounds. .Applied Catalysis A: General, 199, 245-255. 54. Li, W. Z., Xie, S. S., Qian, L. X., Chang, B. H., Zou, B. S., Zhou, W. Y., Zhao, R. A., & Wang, G. (1996). Large-scale synthesis of aligned carbon nanotubes. Science, 274, 1701-1703. 55. Pan, Z. W., Xie, S. S., Chang, B. H., Sun, L. F., Zhou, W. Y., & Wang, G. (1999). Direct growth of aligned open carbon nanotubes by chemical vapor deposition. Chemical Physics Letters, 299, 97-102. 56. Li, A. P., Muller, F., Birner, A., Nielsch, K., & Gosele, U. (1998). Hexagonal pore arrays with a 50-420 nm interpore distance formed by self-organization in anodic alumina. J. Appl. Phys., 84, 6023-6026. 57. Masuda, H., Yamada, H., Satoh, M., & Asoh, H. (1997). Highly ordered nanochannel-array architecture in anodic alumina. Appl. Phys. Lett., 71, 2770-2772. 58. Masuda, H., & Satoh, M. (1996). Fabrication of gold nanodot array using anodic porous alumina as an evaporation mask. Jpn. J. Appl. Phys., part 2, 35, 126-129. 59. Nolan, P. E., Schabel, M. J., & Lynch, D. C. (1995). Hydrogen control of carbon deposit morphology. Carbon, 33, 79-85. 60. Pinheiro, P., Schouler, M. C., Gadelle, P., Mermoux, M., & Dooryhee, E. (2000). Effect of hydrogen on the orientation of carbon layers in deposits from the carbon monoxide disproportionation reaction over Co/Al2O3 catalysts. Carbon, 38(10), 1469-1479. 61. Khassin, A. A., Yurieva, T. M., Zaikovskii, V. I., & Parmon, V. N. (1998). Effect of metallic cobalt particles size on occurrence of CO disproportionation. Role of fluidized metallic cobalt-carbon solution in carbon nanotube formation. Reaction Kinetic and Catalysis Letter, 64, 63-71. 62. Tsai, S. H., Chao, C. W., Lee, C. L., & Shin, H. C. (1999). Bias-enhanced nucleation and growth of the aligned carbon nanotubes with open ends under microwave plasma synthesis. Appl. Phys. Lett., 74, 3462-3464. 63. Huang, Z. P., Xu, J. W., Ren, Z. F., Wang, J. H., Siegal, M. P., & Provencio, P. N. (1998). Growth of highly-oriented carbon nanotubes by plasma-enhanced hot filament chemical vapor deposition. Appl. Phys. Lett., 73, 3845-3847. 64. Ren, Z. F., Huang, Z. P., Wang, D. Z., Wen, J. G., Xu, J. W., Wang, J. H., Calvet, L. E., Chen, J., Klemic, J. F., & Reed, M. A. (1999). Growth of a single freestanding multiwall carbon nanotube on each nanonickel dot. Appl. Phys. Lett., 75, 1086-1088. 65. Fan, S., Chapline, M. G., Franklin, N. R., Tombler, T. W., Cassell, A. M., & Dai, H. (1999). Self-oriented regular arrays of carbon nanotubes and their field emission properties. Science, 283, 512-514. 66. Kwon, Y. K., Lee, Y. H., Kim, S. G., Jund, P., Tomanek, D., & Smalley, R. E. (1997). Morphology and stability of growing multiwall carbon nanotubes. Phys. Rev. Lett., 79, 2065-2068. 67. Oh, D. H., & Lee, Y. H. (1998). Stability and cap formation mechanism of single-walled carbon nanotubes. Phys. Rev. B, 58, 7407-7411. 68. Kuznetsov, V. L., Usoltseva, A. N., Chuvilin, A. L., Obraztsova, E. D. & Bonard, J. M. (2001). Thermodynamic analysis of nucleation of carbon deposits on metal particles and its implications for the growth of carbon nanotubes. Phys. Rev. B, 64, 235401-1. 69. Jacoby, S. L. S., Kowalik, J. S., & Pizzo, J. T. (1972). Iterative methods for nonlinear optimization problems. Prentice Hall, Inc., Englewood Cliffs, New Jersey, ISBN 0 – 13 – .508199 – X, 79-83. 70. Fowler, R. H., & Nordheim, L. W. (1928). Electron emission in intense electric fields. Proceedings of Royal Society of London, 119, 173-181.