The Effects of Plasma Treatment on the Field Emission Characteristics of Carbon Nanotubes

許博凱、李世鴻

E-mail: 9606948@mail.dyu.edu.tw

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. CF4 gas and Ar gas plasma treatment was utilized for carbon nanotubes (CNTs) Raman spectroscopy, SEM, EDS and TEM were employed to study the structural properties of CNTs after plasma treatments. From experimental results, it is found that the shape of the tips of CNTs was modified, and amorphous carbon was removed by plasma treatment. These factors can cause an increase in the the field emission density. Observed form field emission results, after 2min of CF4 plasma treatment, the emission current density reach 9.5mA/cm2, whereas the emission current density is only 3.0mA/cm2 after 2min of Ar plasma treatment. This large difference can be attributed to the conglomeration found in the CNTs after CF4 plasma treatment which can provide lots of additional emission site.

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

Table of Contents

封面內頁 簽名頁 授權書.. iii 中文摘要....................................... iv 英文摘要... v 誌謝.. vi 目錄... vii 圖目錄.. x 表目錄....................................... xiii 第一章　簡介 1.1奈米碳管的歷史與簡介......................... 1 1.2奈米碳管的特性.............................. 4 1.3奈米碳管的應用.............................. 7 1.4研究動機...................................... 8 第二章　純化相關製程文獻回顧 2.1 H2電漿處理文獻............................. 12 2.2 CF4電漿處理文獻............................ 15 第三章　理論與研究方法 3.1電子場發射理論.............................. 18 3.2奈米碳管的成長機制.......................... 21 3.2.1 奈米碳管主要成長機制..................... 21 3.2.2 催化劑在奈米碳管成長中扮演的角色.......... 23 3.2.3 奈米碳管成長模式分類..................... 26 3.3奈米碳管的製程方法.......................... 28 3.4電漿蝕刻機制............................... 35 3.5實驗方法與步驟.............................. 36 3.5.1 熱蒸鍍系統............................... 36 3.5.2 熱化學氣相沉積系統....................... 37 3.5.3 電漿蝕刻系統............................. 39 3.5.4 掃描式電子顯微鏡系統..................... 42 3.5.5 能量散佈分析儀系統....................... 43 3.5.6 拉曼光譜儀系統........................... 45 3.5.7 場發射量測裝置統......................... 47 第四章　實驗結果與討論 4.1 CF4電漿後處理對CNT的研究與討論............. 49 4.1.1 SEM (掃瞄式電子顯微鏡)的分析及TEM(穿透式電子 顯微鏡)的分析............................ 49 4.1.2拉曼(拉曼光譜)的分析...................... 51 4.1.3 EDS(能量散佈分析儀)的分析................ 53 4.1.4電子場發射的分析.......................... 55 4.2 Ar 電漿後處理對CNT的研究與討論.............. 58 4.2.1 SEM (掃瞄式電子顯微鏡)的分析及TEM(穿透式電子 顯微鏡)的分析............................ 58 4.2.2拉曼(拉曼光譜)的分析...................... 60 4.2.3 EDS(能量散佈分析儀)的分析................ 62 4.2.4 電子場發射的分析......................... 64 4.3 不同電漿處理對CNT的研究與討論.............. 68 4.3.1 SEM、TEM表面形貌比較..................... 68 4.3.2拉曼比較.................................. 69 4.3.3 EDS比較.................................. 70 4.3.4電流密度比較.............................. 71 第五章　結論................................... 72 參考文獻....................................... 74

REFERENCES

1. Kroto, H. W., Heath, J. R., O ’ Brian, S. C., Curl, R. F., & Smalley, R. E.(1985). C60: Buckminsterfullerene. Nature, Vol. 318 (6042), pp. 162-163. 2. Kratschmer, W., Lamb, L. D., Fostiropoulos, K., & Huffman, D. R. (1990). Solid C60: A new form of carbon. Nature, Vol. 347, pp. 354-358. 3. Maiti, Brabec, C. J., Roland, C., & Bernholc, J. (1995). Theory of carbon nanotube growth. Phys. Rev. B, Nov 15; Vol. 52(20), pp. 14850-14858. 4. Iijima, S. (1991). Helical microtubules of graphitic carbon. Nature, Vol. 354, Nov. 7, pp. 56-58. 5. Iijima, S., & Ichihashi, T. (1993). Single-shell carbon nanotubes of 1-nm diameter. Nature, Vol. 363, pp. 603-605. 6. 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, Vol. 363, pp. 605-607. 7. 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, Vol. 273, pp. 483-487. 8. Dresselhaus, M. S., Dresselhaus, G., & Saito, R. (1995). Physics of carbon nanotubes. Carbon, Vol. 33, pp. 883-891. 9. Peter J. F. Harris, (1999). Carbon Nanotubes and Related Structure. Cambridge University Press, Chapter 4.2: Electronic properties of nanotube. pp. 16 – 54. 10.

Dresselhaus, M.S.; Dresselhaus, G.; Eklund, P.C. (1996) Fullerenes and Carbon Nanotubes, Academic,San Diego. 11. Charlier, J. C., & Issi, J. P. (1998). Electronic structure and quantum transport in carbon nanotubes. Applied Physics A: Materials Science & Processing, Vol. 67, pp. 79-87. 12. Haus, M. D., Dresselhaus, G., Eklund, P., & Saito, R. (1998). Carbon nanotubes. Physics World, Vol. 11, pp. 33-38. 13. Mintmire, J. W. & White, C. T. (1998). First-principles band structures of armchair nanotubes. Applied Physics A: Materials Science & Processing, Vol. 67, pp. 65-69. 14. K. Tohji, T. Goto, H. Takahashi, Y. Shinoda, N. Shimizu,B. Jeyadevan, I. Matsuoka, Y. Saito, A. Kasuya, T. Ohsuna, K. Hiraga, Y. Nishina, J. (1997) Phys. Chem. Vol.101, pp. 1974. 15. S. Bandow, A.M. Rao, K.A. Williams, A. Thess, R.E. Smalley,P.C. Eklund, J. (1997)Phys. Chem. B Vol.101 pp. 8839. 16. E. Dujardin, T.W. Ebbesen, A. Krishnan, M.M.J. Treacy, Adv.Mater. 10 (1998) pp. 1472. 17. A.G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C.B. Huffman, F.J. Rodriguez-Macias, P.J. Boul, A.H. Lu, D.T. Colbert, R.S. Lee, J.E. Fischer, A.M. Rao, P.C. Eklund, R.E. Smalley, (1998) Appl. Phys. A Vol 67 pp.29. 18. K.B. Shelmov, R.O. Esenaliev, A.G. Rinzler, C.B. Huffman,R.E. Smalley, (1998)Chem. Phys. Lett. Vol 282 pp. 429. 19. A.C. Dillon, T. Gennett, K.M. Jones, J.L. Alleman, P.A. Parilla, M.J. Heben, Adv. Mater. 11 (1999) , pp.1354. 20. Z. Shi, Y. Lian, F. Liao, X. Zhou, Z. Gu, Y. Zhang, S. Iijima, (1999)Solid State Commun. 112 , pp.35. 21. I.W. Chiang, B.E. Brinson, R.E. Smalley, J.E. Margrave, R.H. Hauge, J. (2001)Phys. Chem. B 105, pp.1157. 22. J.M. Moon, K.H. An, Y.H. Lee, Y.S. Park, D.J. Bae, G.S. Park, J. (2001)Phys. Chem. B 105, pp.5677. 23. S. Niyogi, H. Hu, M.A. Hamon, P. Bhowmik, B. Zhao, S.M. Rozenzhak, J. Chen, M.E. Itkis, M.S. Meier, R.C. Haddon, J. Am. Chem. Soc. 123 (2001) , pp.733. 24. A.R. Harutyunyan, B.K. Pradhan, J.P. Chang, G.G. Chen, P.C. Eklund, J. Phys. Chem. B 106 (2002) , pp.8671. 25. M.T. Mart? ’ nez, M.A. Callejas, A.M. Benito, W.K. Maser, M. Cochet, J.M. Andre ’ s, J. Schreiber, O. Chauvet, J.L.G. Fierro, Chem. Commun. (2002); , pp.1000. 26. E. Va ’ zquez, V. Georgakilas, M. Prato, Chem. Commun. 2002; 230 Jo, S. H., Y. Tu, Z. P. Huang, D. L. Carnahan, D.Z. Wang and Z. F. Ren (2003) Effect of length and spacing of vertically aligned carbon nanotubes on field emission properties. Applied Physics Letters, 82(20), , pp.3520-3522. 27. Shelimov, K.B.; Esenaliev, R.O.; Rinzler, A.G.; Huffman, C. B.; Smalley, R.E. Chem. Phys. Lett., 282, (1998)429. 28. Z. Shi, Y. Lian, F. Liao, X. Zhou, Z. Gu, Y. Zhang, S. Iijima. Solid State Communications, Vol.112, (1999) , pp.35-37. 29. .Duesberg, G.S.; Burghard, M.; Muster, J.; Philipp, J.; Roth, S. Chem. Commun., 1998, (1998) , pp.435. 30. S. H. Jo, Y. Tu, Z. P. Huang, D. L. Carnahan, D. Z. Wang, Z. F. Ren, Appl. Phys. Lett. 82 (2003) 3520. 31. Z. L. Wang, R. P. Gao, W.A. de Heer, P. Poncharal, Appl. Phys. Lett. 80 (2002) 856. 32. J. M. Bonard, K. A. Dean, B. F. Coll, C. Klinke, Phys. Rev. Lett. 89 (2002) 197602. 33. H. Folwer and L. Nordheim , (1928) Proc. R. Soc. London, Ser A, Vol.119, pp.683 34. P.G. Collins and A.Zettl, (1997) Phys. Rev. B 55, pp.9391 35. S. Han and J. Ihm, Phys. Rev. B, Vol.66, 241402 (2002); Changwook Kim, Bongsoo Kim, Seung Mi Lee, Chulsu Jo and Young Hee Lee, Phys. Rev. B, Vol.65, pp.418, 36. V.I.Trefilov,D.V.Schur,B.P.Tarasov,Yu.M.Shul'ga,A.V.Chernogorenko, .K.Pishuk, S.Yu.Zaginaichenko. Fullerenes is a basis of materials for future?. Kiev, 2001, pp.148. 37. E.G.Rakov. Uzpekhi Khim., (2000), Vol. 69, N 1, pp.41. 38. Terrones M., Hsu W.K., Kroto H.W., Walter D.R. (1999) Top. Curr. Chem., Vol 199, pp. 189. 39. Journet C., Bernier P. (1998) 1 Appl. Phys. A: Mater. Sci. Process, A67(1),. 40. Ajayan P. M.. Chem. Rev., (1999)1787. 41. S. Ijima,; Ichihashi, (1993) T. Nature, Vol 363,pp. 603. 42. A. Wadhawan, R.R. Stallcup, J.M. Perez, (2001) Appl. Phys. Vol.78 ,pp. 108. 43. Q.H. Wang, T.D. Corrigan, J.Y. Dai, R.P.H. Chang, A.R. Krauss, Appl. Phys. Lett. 70 (1997) 3308. 44. C.Y. Zhi, X.D. Bai, E.G. Wang, Appl. Phys. Lett. 81 (2002) 1690. 45. H. Burbert, S. Haiber, W. Brandl, G. Marginean, M. Heintze, V. Bru··ser, (2003)Diamond Relat. Mater, Vol.12 ,pp. 811. 46. Ke Yu, Ziqiang Zhu, Yongsheng Zhang, Qiong Li, Weiming Wang, Laiqiang Luo, Xianwen Yu, Honglei Ma, Zhenwen Li, Tao Feng (2004). Change of surface morphology and field emission property of carbon nanotube films treated using a hydrogen plasma. Applied Surface Science, Vol. 225, pp. 380 – 388. 47. Y. W. Zhu, F. C. Cheong, T. Yu , X. J. Xu, C. T. Lim, J. T. L. Thong, Z. X. Shen, C. K. Ong, Y.J. Liu, A.T.S. Wee, C. H. Sow (2005). Effects of CF4 plasma on the field emission properties of aligned multi-wall carbon nanotube films. Carbon, Vol. 43, pp. 395-400. 48. 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, Vol. 204, pp. 277-282. 49. 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., Vol. 260, pp. 471-475. 50. Lee, Y. H., Kim, S. G., & Tomanek, D. (1997). Catalytic growth of single-wall carbon nanotubes: an ab initio study. Phys. Rev. Lett., Vol. 78, pp. 2393-2396. 51. Endo, M., & Kroto, H. W. (1992). Formation of carbon nanofibers. Journal of Physical Chemistry, Vol. 96, pp. 6491-6944. 52. Baker, R. T. K., & Harries, P. S. (1978). The formation of filamentous carbon. Chemistry and Physics of Carbon, New York: Marcel Deckker, Vol. 14, pp. 83-165. 53. 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, Vol. 26, pp. 51-62. 54. Oberlin, A., Ento, M., & Koyama, T. (1976). Filamentous growth of carbon through benzene decomposition. Journal of Crystal Growth, Vol. 32, pp. 335-349. 55. Baird, T., & Fryer, J. R. (1974). Carbon formation on iron and. nickel foils by hydrocarbon pyrolysis reactions at 700 ° C. Carbon, Vol. 12, pp. 591-602. 56. Oberlin, A., Ento, M., & Koyama, T. (1976). High resolution electron microscope observations of graphitized carbon fibers. Carbon, Vol. 14, pp. 133-157. 57. Journet, C. et al., (1998). Production of carbon nanotubes. Applied Physics, Vol.67, pp. 1-9. 58. Alan, M. et al., (1998). Chemical vapor deposition of methane for single-walled carbon nanotubes. Chem. Phys. Lett., Vol. 292, pp. 567-574. 59. Yacaman, M. J., Yoshida, M. M., Rendon, L., & Santiesteban, J. G. (1993). Catalytic growth of carbon. microtubules with fullerene structure. Appl. Phys. Lett., Vol. 62, pp. 202-204. 60. Baker, R. T. K., & Chludzinski, J. J. (1980). Filamentous carbon growth on nickel – iron surfaces—effect of various oxide additives. Journal of Catalysis, Vol. 64, pp. 464-478. 61. 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, Vol. 30, pp. 86-95. 62. Baker, R. T. K., & Waite, R. J. (1975). Formation of carbonaceous deposit from the platinum-iron catalyzed decomposition. Journal of Catalysis, Vol. 37, pp. 101-105. 63. 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, Vol. 10, pp.1235-1240. 64. 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, Vol. 286, pp. 11-15. 65. 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, Vol. 339, pp. 6-9. 66. 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, Vol. 323, pp. 554-559. 67. Terrones, M. et al., (1998). Preparation of aligned carbon nanotubes catalysed by laser-etched cobalt thin films. Chemical Physics Letters, Vol. 285, pp. 299-305. 68. 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, Vol. 21(4), pp. 623-625. 69. 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, Vol. 199, pp. 245-255. 70. 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, Vol. 274, pp. 1701-1703. 71. 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, Vol. 299, pp. 97-102. 72. 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., Vol. 84, pp. 6023-6026. 73. Masuda, H., Yamada, H., Satoh, M., & Asoh, H. (1997). Highly ordered nanochannel-array architecture in anodic alumina. Appl. Phys. Lett., Vol. 71, pp. 2770-2772. 74. Masuda, H., & Satoh, M. (1996). Fabrication of gold nanodot array using anodic porous alumina as an evaporation mask. Jpn. J. Appl. Phys., part 2, Vol. 35, L. 126-129. 75. Nolan, P. E., Schabel, M. J., & Lynch, D. C. (1995). Hydrogen control of carbon deposit morphology. Carbon, Vol. 33, pp. 79-85. 76. 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, Vol. 38(10), pp. 1469-1479. 77. 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, Vol. 64, pp. 63-71. 78. 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., Vol. 74, pp. 3462-3464. 79. 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., Vol. 73, pp. 3845-3847. 80. 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., Vol. 75, pp. 1086-1088. 81. 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, Vol. 283, pp. 512-514. 82. 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., Vol. 79, pp. 2065-2068. 83. Oh, D. H., & Lee, Y. H. (1998). Stability and cap formation mechanism of single-walled carbon nanotubes. Phys. Rev. B, Vol. 58, pp. 7407-7411. 84. 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, Vol. 64, pp. 235401-1. 85. Lieberman, M. A., and A. J. Lichtenberg, " Principles of plasma discharges and materials processing, " John Wiley & Sons Inc., 1994. 86. Xiao, H. (2001). " Introduction to semiconductor manufacturing technology, " Prentice Hall Inc..