

催化劑電漿前處理對熱化學氣相沉積奈米碳管表面型態與場發射特性之影響

葉國輝、李世鴻

E-mail: 9607638@mail.dyu.edu.tw

摘要

本實驗利用四氯化碳(CF₄)及氮氣(N₂)兩種氣體之電漿分別對鍍薄膜催化劑進行電漿前處理，以研究其對於所成長奈米碳管的表面形態及場發射特性之影響。本研究的奈米碳管是利用熱化學氣相沉積(thermal chemical vapor deposition)法來成長的。甲烷(CH₄)氣體是主要的碳原子來源，而氬氣(Ar)則作為載氣使用。甲烷被觸媒熱分解來獲得碳原子，並從而成長出奈米碳管。我們使用拉曼光譜(Raman spectroscopy)、電子顯微鏡(SEM)、能量散佈分析儀(EDS)來分析經過電漿處理後的奈米碳管特性。從實驗數據得知，隨著電漿前處理時間的增大，所成長出的奈米碳管管徑會變小及碳管數目會變多，因而增強了奈米碳管的場發射特性。另外，從場發射的分析，經過CF₄電漿處理4分鐘所成長的奈米碳管的場發射電流會達到1.67mA/cm²，而經過N₂電漿處理4分鐘後場發射電流只有0.908 mA/cm²。因此，使用CF₄氣體電漿前處理會比N₂氣體電漿前處理對奈米碳管場發射特性會有更顯著的增強效果。

關鍵詞：奈米碳管；場發射；熱化學氣相沉積

目錄

目錄封面內頁簽名頁授權書	iii
中文摘要	iii
英文摘要	iv
誌謝	v
目錄	vii
圖目錄	x
表目錄	x
第一章 簡介	xiv
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	4
1.4. 研究動機	7
第二章 催化劑電漿前處理文獻回顧	11
2.1. 氬氣對催化劑電漿前處理文獻	13
第三章 理論與研究方法	17
3.1. 電子場發射理論	17
3.2. 奈米碳管的成長機制	20
3.2.1. 奈米碳管主要成長機制	20
3.2.2. 催化劑在奈米碳管成長中扮演的角色	22
3.2.3. 奈米碳管成長模式分類	25
3.3. 奈米碳管的製程方法	27
3.4. 電漿蝕刻機制	34
3.5. 實驗儀器與實驗步驟	35
3.5.1. 實驗流程	35
3.5.2. 熱蒸鍍系統	36
3.5.3. 熱化學氣相沉積系統	37
3.5.4. 電漿蝕刻系統	39
3.5.5. 掃描式電子顯微鏡系統	41
3.5.6. 能量散佈分析儀系統	42
3.5.7. 拉曼光譜儀系統	44
3.5.8. 場發射量測裝置系統	46
第四章 實驗結果與討論	48
4.1. 不同時間CF ₄ 電漿前處理對奈米碳管成長之影響	48
4.1.1. SEM(掃描式電子顯微鏡)的分析	48
4.1.2. Raman(拉曼光譜)分析	52
4.1.3. EDS(能量散佈分析儀)的分析	55
4.1.4. 電子場發射特性分析	56
4.2. 不同時間N ₂ 電漿前處理對奈米碳管成長之影響	60
4.2.1. SEM(掃描式電子顯微鏡)的分析	60
4.2.2. Raman(拉曼光譜)分析	64
4.2.3. EDS(能量散佈分析儀)的分析	66
4.2.4. 電子場發射特性分析	67
4.3. 不同電漿前處理對奈米碳管的研究與討論	71
4.3.1. 不同電漿前處理SEM表面結構比較	71
4.3.2. 不同電漿前處理拉曼比較	72
4.3.3. 不同電漿前處理EDS比較	73
4.3.4. 不同電漿前處理場發射特性比較	74
第五章 結論	76
參考文獻	78

參考文獻

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., Vazquez, 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. Matsuoaka, 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. Martinez, 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. Vazquez, V. Georgakilas, M. Prato, *Chem. Commun.* 2002; 230. 27. 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. L. Nilsson, O. Groening, C. Emmenegger, et al., *Appl. Phys. Lett.* 79 (2001) 1534. 37. Z.P. Huang, D.Z. Wang, J.G. Wen, M. Sennett, H. Gibson, Z.F. Ren, *Appl. Phys. A: Mater. Sci. Process* 74 (2002) 387. 38. K.B.K. Teo, M. Chhowalla, G.A.J. Amaratunga, et al., *Appl. Phys. Lett.* 79 (2001) 1534. 39. Z.F. Ren, Z.P. Huang, D.Z. Wang, et al., *Appl. Phys. Lett.* 75 (1999) 1086. 40. H. Murakami, M. Hirakawa, C. Tanaka, H. Yamakawa, *Appl. Phys. Lett.* 76 (2000) 1776. 41. Y. Tu, Z.P. Huang, D.Z. Wang, J.G. Wen, Z.F. Ren, *Appl. Phys. Lett.* 80 (2002) 4018. 42. Z.F. Ren, Z.P. Huang, J.W. Xu, P.N. Provencio, *Science* 282 (1998) 1105. 43. C.J. Lee, J. Park, S.Y. Kang, J.H. Lee, *Chem. Phys. Lett.* 323 (2000) 554. 44. M. Jung, K.Y. Eun, J.-K. Lee, Y.-J. Baik, K.-R. Lee and J.W. 45. Z.F. Ren, Z.P. Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegel, et al., *Science* 282 (1998) 1105. 46. C.J. Lee, D.W. Kim, T.J. Lee, Y.C. Choi, Y.S. Park, Y.H. Lee, et al., *Chem. Phys. Lett.* 312 (1999) 461. 47. M. Jung, K.Y. Eun, J.K. Lee, Y.T. Baik, K.R. Lee, J.W. Park, al., *Science* 273 (1996) 483. 48. K.S. Choi, Y.S. Cho, S.Y. Hong, J.B. Park, D.J. Kim, *J. Eur. Ceram. Soc.* 21 (2001) 2095. 49. G.S. Choi, Y.S. Cho, S.Y. Hong, J.B. Park, K.H. Son, D.J. Kima, *J. Appl. Phys.* 91 (2002) 3847. 50. M. Jung, K.Y. Eun, Y.J. Baik, K.R. Lee, J.K. Shin, S.T. Kim, *Thin Solid Films* 398 – 399 (2001) 150. 51. C.J. Lee, D.W. Kim, T.J. Lee, Y.C. Choi, Y.S. Park, Y.H. Lee, et al., *Chem. Phys. Lett.* 312 (1999) 461. 52. Jong Hyung Choi , Tae Young Lee , Sun Hong Choi , Jae-Hee Han , Ji-Beom Yoo , Chong-Yun Park , Taewon Jung , Se Gi Yu , Whikun Yi , In-Taek Han , J.M. Kim. “ Control of carbon nanotubes density through Ni nanoparticle formation using thermal and NH3 plasma treatment ” , *Diamond and Related Materials* 12 (2003) 794 – 798. 53. Jae-Hee Han , Chong Hyun Lee , Duk-Young Jung , Chul-Woong Yang , Ji-Beom Yoo * , Chong Yun Park , Ha Jin Kim , SeGi Yu , Whikun Yi , Gyeong Su Park , I.T. Han , N.S. Lee , J.M. Kim. “ NH3 effect on the growth of carbon nanotubes on glass substrate in plasma enhanced chemical vapor deposition ” *Thin Solid Films* 409 (2002) 120 – 125. 54. Saito, Y., Yoshikawa, T., Inagaki, M., Tomita, M., & Hayashi, T. (1993). Growth and structure of graphitic tubules and polyhedral particles in arc-discharge. *Chemical Physics Letters*, Vol. 204, pp. 277-282. 55. Dai, H., Rinzler, A. G., Nikolaev, P., Thess, A., Colbert, D. T., & Smalley, R. E. (1996). Single-wall nanotubes produced by metal catalyzed disproportionation of carbon monoxide. *Chem. Phys. Lett.*, Vol. 260, pp. 471-475. 56. 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. 57. Endo, M., & Krotov, H. W. (1992). Formation of carbon nanofibers. *Journal of Physical Chemistry*, Vol. 96, pp. 6491-6944. 58. Baker, R. T. K., & Harries, P. S. (1978). The formation of filamentous carbon. *Chemistry and Physics of Carbon*, New York: Marcel Dekker, Vol. 14, pp. 83-165. 59. 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. 60. Oberlin, A., Ento, M., & Koyama, T. (1976). Filamentous growth of carbon through benzene decomposition. *Journal of Crystal Growth*, Vol. 32, pp. 335-349. 61. 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. 62. Oberlin, A., Ento, M., & Koyama, T. (1976). High resolution electron microscope observations of

graphitized carbon fibers. *Carbon*, Vol. 14, pp. 133-157. 63. Journet, C. et al., (1998). Production of carbon nanotubes. *Applied Physics*, Vol.67, pp. 1-9. 64. Alan, M. et al., (1998). Chemical vapor deposition of methane for single-walled carbon nanotubes. *Chem. Phys. Lett.*, Vol. 292, pp. 567-574. 65. 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. 66. 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. 67. Baker, R. T. K., Harries, P. S., Thomas, R. B., & Waite, R. J. (1973). Formation of filamentous carbon from iron and chromium catalyzed decomposition of acetylene. *Journal of Catalysis*, Vol. 30, pp. 86-95. 68. 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. 69. 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. 70. 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. 71. 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. 72. 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. 73. 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. 74. 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-Chinese*, Vol. 21(4), pp. 623-625. 75. 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. 76. 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. 77. 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. 78. 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. 79. 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. 80. 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. 81. Nolan, P. E., Schabel, M. J., & Lynch, D. C. (1995). Hydrogen control of carbon deposit morphology. *Carbon*, Vol. 33, pp. 79-85. 82. 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. 83. 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. 84. 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. 85. 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. 86. 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. 87. Fan, S., Chapline, M. G., Franklin, N. R., Tomblor, 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. 88. 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. 89. 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. 90. 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. 91. Lieberman, M. A., and A. J. Lichtenberg, " Principles of plasma discharges and materials processing, " John Wiley & Sons Inc., 1994. 92. Xiao, H. (2001). " Introduction to semiconductor manufacturing technology, " Prentice Hall Inc.. 93. A. Maiti. C.J. Brabec and J. Bernholc: *Phys. Rev. B* 55 (1997) R6097. 94. 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. 95. Fowler, R. H., & Nordheim, L. W. (1928). Electron emission in intense electric fields. *Proceedings of Royal Society of London*, 119, 173-181.