熱退火處理對熱化學氣相沉積奈米碳管表面結構及場發射特性影響

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摘 要

本實驗利用化學氣相沉積法來成長奈米碳管(CNT)。主要的碳原子來源為甲烷(CH4)，並以氬氣(Ar)作為載氣使用。利用觸媒熱分解效應將CH4分解成碳原子並成長出典型的CNT。之後，將所成長的CNT在氬氣氛圍中進行熱退火處理。我們也用掃瞄式電子顯微鏡(SEM)、能量散佈分析儀(EDS)、拉曼光譜來分析熱退火處理對於CNT性質之影響。由實驗數據得知，CNT的表面形態、結構、及場發射特性都是由所採用的熱退火處理溫度及時間所決定的。只有在適當溫度(200℃)下進行特定時間(10至20分鐘)的退火處理才能使CNT的場發射特性增強。這種場發射電流的增強主要是由於碳管表面的缺陷修補以及原本座落在碳管表面的非晶質碳的再結晶所造成的。這會導致碳管尖端的石墨層裸露，因而使發射電流增大。超乎這個溫度及時間範圍的高溫處理只會造成碳管結構的破壞，進而使CNT的場發射電流因而衰減。

關鍵詞 : 奈米碳管 ; 熱退火 ; 場發射 ; 化學氣相沉積法

目錄

參考文獻

1. Radushkevich, L. V., & Lukyanovic, V. M. (1952). Zh. Fiz. Khim. 26, 88. 2. Hofer, L. J. E., Sterling, E., & MacCartney, J. T. (1955). J. Phys. Chem., 59, 6210. 3. Kroto, H. W., Heath, J. R., O’Brian, S. C., Curl, R. F., & Smalley, R. E.(1985). C60: Buckminsterfullerene. Nature, 318 (6042), 162-163. 4. Kratschmer, W., Lamb, L. D., Fostiropoulos, K., & Huffman, D. R. (1990). Solid C60: A new form of carbon. Nature, 347, 354-358. 5. Maiti, Brabec, C. J., Roland, C., & Bernholc, J. (1995). Theory of carbon nanotube growth. Phys. Rev. B, 15; 52(20), 14850-14858. 6. Iijima, S. (1991). Helical microtubules of graphitic carbon. Nature, 354, 7, 56-58. 7. Iijima, S., & Ichihashi, T. (1993). Single-shell carbon nanotubes of 1-nm diameter. Nature, 363, 603-605. 8. 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. 9. 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. 10. Peter J. F. Harris, (1999). Carbon nanotubes and related structure. Cambridge University Press, Chapter 4.2: Electronic properties of nanotube. 16 – 54. 11. Charlier, J. C., & Issi, J. P. (1998). Electronic structure and quantum transport in carbon nanotubes. Applied Physics A: Materials Science & Processing, 67, 79-87. 12. Haus, M. D., Dresselhaus, G., Eklund, P., & Saito, R. (1998). Carbon nanotubes. Physics World, 11, 33-38. 13. Mintmire, J. W. & White, C. T. (1998). First-principles band structures of armchair nanotubes. Applied Physics A: Materials Science & Processing, 67, 65-69. 14. Dresselhaus, M. S., Dresselhaus, G., & Saito, R. (1995). Physics of carbon nanotubes. Carbon, 33, 883-891. 15. 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. 16. 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. 17. 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. 18. Endo, M., & Kroto, H. W. (1992). Formation of carbon nanofibers. Journal of Physical Chemistry, 96, 6491-6944. 19. 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. 20. 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. 21. Oberlin, A., Ento, M., & Koyama, T. (1976). Filamentous growth of carbon through benzene decomposition. Journal of Crystal Growth, 32, 335-349. 22. Baird, T., & Fryer, J. R. (1974). Carbon formation on iron and. nickel foils by hydrocarbon pyrolysis reactions at 700 ° C. Carbon, 12, 591-602. 23. Oberlin, A., Ento, M., & Koyama, T. (1976). High resolution electron microscope observations of graphitized carbon fibers Carbon. Carbon, 14, 133-157. 24. Journet, C. et al., (1998). Production of carbon nanotubes. Applied Physics, .67, 1-9. 25. Alan, M. et al., (1998). Chemical vapor deposition of methane for single-walled carbon nanotubes. Chem. Phys. Lett., 292, 567-574. 26. 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. 27. 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. 28. 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. 29. Baker, R. T. K., & Waite, R. J. (1975). Formation of carbonaceous deposit from the platinum-iron catalyzed decomposition. Journal of Catalysis, 37, 101-105. 30. 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. 31. 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. 32. 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. 33. 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. 34. Terrones, M. et al., (1998). Preparation of aligned carbon nanotubes catalysed by laser-etched cobalt thin films. Chemical Physics Letters, 285, 299-305. 35. 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. 36. 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. 37. 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. 38. 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. 39. 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. 40. Masuda, H., Yamada, H., Satoh, M., & Asoh, H. (1997). Highly ordered nanochannel-array architecture in anodic alumina. Appl. Phys. Lett., 71, 2770-2772. 41. 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. 42. Nolan, P. E., Schabel, M. J., & Lynch, D. C. (1995). Hydrogen control of carbon deposit morphology. Carbon, 33, 79-85. 43. 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. 44. 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. 45. 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. 46. 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. 47. 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. 48. 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. 49. 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. 50. Oh, D. H., & Lee, Y. H. (1998). Stability and cap formation mechanism of single-walled carbon nanotubes. Phys. Rev. B, 58, 7407-7411. 51. 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. 52. 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. 53. 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. 54. 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.