

# The Field Emission Characteristics of Carbon Nanotubes Produced with Zinc Oxide Catalyst

江濬哲、李世鴻

E-mail: 9707392@mail.dyu.edu.tw

## ABSTRACT

In this study, carbon nanotubes (CNT) were synthesized on ZnO nanorods using thermal chemical vapor deposition. ZnO nanorods were coated on silicon substrates by hydrothermal process. The CNT growth temperature was maintained at 900°C at an ambient pressure. Methane and argon gases are used for the CNT synthesis. In this work, scanning electron microscopy (SEM) image was used to observe the surface morphology and side-wall structure, energy dispersive spectrometer (EDS) was used for the identification and analysis of the chemical composition on the surface of CNTs, and Raman spectroscopy was employed to investigate the CNTs structural. Our research results reveal that the carbon nanotubes grown on ZnO nanorods showed a multiwalled structure with defective graphite sheets at the wall. The SEM images showed that CNTs were quite uniform and disordered. Raman spectra show that there is larger crystallinity or little amorphous carbon than those grown on ZnO nanorods. EDS results reveal that the CNTs grown on ZnO nanorods do not need any purification process to optimize the field emission characteristics of the CNTs. The Fowler-Nordheim plot showed a good linear fit, indicating that the emission current of carbon nanotubes follows Fowler-Nordheim behavior.

Keywords : carbon nanotube ; thermal chemical vapor deposition ; field emission

## 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 . . . . .	xv 第
第一章 簡介 . . . . .	1 1.1 氧化鋅奈米柱簡介 . . . . .
1 1.2 奈米碳管簡介 . . . . .	3 1.3 奈米碳管的結構 . . . . .
5 1.4 奈米碳管的應用 . . . . .	8 1.5 研究動機 . . . . .
10 第二章 氧化鋅文獻回顧 . . . . .	12 2.1 以化學溶液法製作氧化鋅相關文獻 . . . . .
12 2.2 以氧化鋅成長奈米碳管之相關文獻 . . . . .	16 第三章 理論與研究方法 . . . . .
20 3.1 電子場發射理論 . . . . .	20 3.2 氧化鋅的製程方法 . . . . .
23 3.3 奈米碳管的成長機制 . . . . .	26 3.3.1 奈米碳管主要成長
26 3.3.2 催化劑在奈米碳管成長中扮演的角色 . . . . .	27 3.3.3 奈米碳管成長模式
分類 . . . . .	30 3.5 實驗儀器 . . . . .
28 3.4 奈米碳管的製程方法 . . . . .	37 3.5.1 热蒸鍍系統 . . . . .
沉積系統 . . . . .	37 3.5.2 热化學氣相
分析儀系統 . . . . .	40 3.5.3 掃描式電子顯微鏡系統 . . . . .
裝置系統 . . . . .	43 3.5.5 拉曼光譜儀系統 . . . . .
45 3.6 實驗流程 . . . . .	43 3.5.6 場發射量測
48 3.7.1 成長氧化鋅奈米柱和蒸鍍催化劑金屬 . . . . .	47 3.7 實驗步驟
奈米碳管 . . . . .	48 3.7.2 成長
49 3.7.3 電性量測 . . . . .	49 3.7.3 電性量測 . . . . .
實驗結果與討論 . . . . .	50 第四章 實
51 4.1 水煮時間1小時，不同濃度ZnO對奈米碳管成長之影響 . . . . .	52
4.1.1 ZnO的SEM(掃瞄式電子顯微鏡)分析 . . . . .	52 4.1.2 ZnO的EDS(能量散佈分析儀)分析 . . . . .
4.1.3 ZnO-CNT的SEM(掃描式電子顯微鏡)分析 . . . . .	57 4.1.4 ZnO-CNT的TEM(穿透式電子顯微鏡)分析 . . . . .
4.1.5 ZnO-CNT的拉曼(拉曼光譜)分析 . . . . .	59 4.1.6 ZnO-CNT的EDS(能量散佈分析儀)分析 . . . . .
4.1.7 電子場發射特性分析 . . . . .	63 4.2 改變水煮時間，固定濃度0.15M 的Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液所成長的ZnO對奈米碳管成長之影響 . . . . .
68 4.2.1 ZnO的SEM(掃瞄式電子顯微鏡)分析 . . . . .	68 4.2.1 ZnO的SEM(掃瞄式電子顯微鏡)分析 . . . . .
68 4.2.2 ZnO的EDS(能量散佈分析儀)分析 . . . . .	71 4.2.3 ZnO-CNT的SEM(掃描式電子顯微鏡)分析 . . . . .
73 4.2.4 ZnO-CNT的TEM(穿透式電子顯微鏡)分析 . . . . .	75 4.2.5 ZnO-CNT的拉曼(拉曼光譜)分析 . . . . .
76 4.2.6 ZnO-CNT的EDS(能量散佈分析儀)分析 . . . . .	77 4.2.7 電子場發射特性分析 . . . . .
79 4.3 分別以ZnO和Ni金屬成長奈米碳管之比較 . . . . .	83 4.3.1 SEM(掃描式電子顯微鏡)分析 . . . . .

83 4.3.2 拉曼(拉曼光譜)分析 . . . . .	85 4.3.3 EDS(能量散佈分析儀)分析 . . . . .
86 4.3.4 電子場發射特性分析 . . . . .	87 第五章 結論 . . . . .
90 參考文獻 . . . . .	92 圖目錄 圖1-1、氧化鋅奈米柱結構 . . . . .
2 圖1-2、多層與單層奈米碳管構造 . . . . .	4 圖1-3、石墨片捲成奈米碳管之示意圖 . . . . .
6 圖1-4、扶手椅形奈米碳管 . . . . .	7 圖1-5、鋸齒形奈米碳管 . . . . .
7 圖1-6、對掌形奈米碳管 . . . . .	8 圖1-7、無衝層所製備出的氧化鋅奈米柱 . . . . .
14 圖2-1、水熱法為溫度650C所製備出的氧化鋅奈米柱 . . . . .	14 圖2-2、水熱法為溫度700C所製備出的氧化鋅奈米柱 . . . . .
14 圖2-3、水熱法為溫度750C所製備出的氧化鋅奈米柱 . . . . .	14 圖2-4、水熱法為溫度800C所製備出的氧化鋅奈米柱 . . . . .
15 圖2-5、水熱法為溫度850C所製備出的氧化鋅奈米柱 . . . . .	15 圖2-6、為水熱法800C製備出的奈米柱側面圖 . . . . .
15 圖2-7、無衝層所製備出的氧化鋅奈米柱 . . . . .	15 圖2-8、EDS成分分析圖 . . . . .
16 圖2-9、(a)低倍、(b)高倍SEM影像圖 . . . . .	16 圖2-10、(a)低倍、(b)高倍TEM影像圖 . . . . .
18 圖2-11、奈米碳管拉曼光譜圖 . . . . .	18 圖2-12、電流密度與施加電場之(E-J)曲線圖和相對應的Fowler-Nordheim (F-N)圖 . . . . .
19 圖3-1、(a)金屬 - 真空能帶示意圖 - 未加電場 (b)金屬 - 真空能帶示意圖 - 外加高電場 . . . . .	19 圖3-2、鋅蒸氣氧化法製備氧化鋅四針狀鬚晶結構圖 . . . . .
23 圖3-3、CNT成長機制示意圖(C是碳氫化合物氣體分解後的碳源) . . . . .	24 圖3-4、碳經由催化劑表面擴散示意圖 . . . . .
30 圖3-5、底部成長模式及頂部成長模式示意圖 . . . . .	30 圖3-6、(a)弧光放電方法示意圖、(b)弧光放電法設備示意圖 . . . . .
31 圖3-7、(a)雷射剝蝕製程設備圖、(b)雷射剝蝕法儀器示意圖 . . . . .	32 圖3-8、碳氫化合物氣相熱分解法 . . . . .
34 圖3-9、燈絲熱裂解化學氣相沉積法 . . . . .	36 圖3-10、利用多孔矽基板以thermal-CVD成長具方向性排列的CNT . . . . .
36 圖3-11、電阻式蒸鍍系統 . . . . .	36 圖3-12、高溫氧化爐管(簡圖) . . . . .
39 圖3-13、場發式電子顯微鏡 . . . . .	39 圖3-14、顯微拉曼及光激光譜儀 . . . . .
44 圖3-15、電性量測(簡圖) . . . . .	46 圖3-16、場發射量測裝置系統，圖(a) ~ (f)說明於內文中 . . . . .
46 圖4-1、不同濃度Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液所成長的ZnO的上視影像圖：(a) 0.05M、(b) 0.075M、(c) 0.1M、(d) 0.125M、(e) 0.15M、(f) 0.175M。放大倍率為3千倍 . . . . .	53 圖4-2、不同濃度Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液所成長的ZnO的上視影像圖：(a) 0.05M、(b) 0.075M、(c) 0.1M、(d) 0.125M、(e) 0.15M、(f) 0.175M。放大倍率為3萬倍 . . . . .
54 圖4-3、ZnO管徑與Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液濃度之關係圖 . . . . .	54 圖4-4、ZnO沉積厚度與Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液濃度之關係圖 . . . . .
55 圖4-5、不同濃度Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液所成長的ZnO材料元素百分比分佈圖 . . . . .	56 圖4-6、不同濃度Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液所成長的ZnO-CNT的上視影像圖：(a) 0.05M、(b) 0.075M、(c) 0.1M、(d) 0.125M、(e) 0.15M、(f) 0.175M。放大倍率為3千倍 . . . . .
57 圖4-7、不同濃度Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液所成長的ZnO-CNT的上視影像圖：(a) 0.05M、(b) 0.075M、(c) 0.1M、(d) 0.125M、(e) 0.15M、(f) 0.175M。放大倍率為10萬倍 . . . . .	58 圖4-8、TEM影像圖，其中：(a) 1萬倍、(b) 4萬倍、(c) 8萬倍 . . . . .
59 圖4-9、不同濃度Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液所成長的ZnO-CNT拉曼光譜圖 . . . . .	60 圖4-10、0.05M至0.175M的Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液所成長ZnO-CNT中主要元素之百分比分佈圖 . . . . .
63 圖4-11、不同濃度Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液所成長的ZnO-CNT之電流密度與施加電場之(E-J)曲線圖 . . . . .	63 圖4-12、電場強度19V / μ m應用電場下的發射電流密度比較圖 . . . . .
66 圖4-13、不同濃度Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液所成長的ZnO-CNT之相對應的Fowler-Nordheim (F-N)圖 . . . . .	67 圖4-14、不同水煮時間所成長的ZnO的上視影像圖，其中：(a) 1小時、(b) 1.5小時、(c) 2小時、(d) 2.5小時、(e) 3小時。放大倍率為3千倍 . . . . .
67 圖4-15、不同水煮時間所成長的ZnO的上視影像圖，其中：(a) 1小時、(b) 1.5小時、(c) 2小時、(d) 2.5小時、(e) 3小時。放大倍率為3萬倍 . . . . .	69 圖4-16、ZnO管徑與水煮時間之關係圖 . . . . .
70 圖4-17、ZnO沉積厚度與水煮時間之關係圖 . . . . .	70 圖4-18、不同水煮時間所成長的ZnO材料中的元素百分比分佈圖 . . . . .
71 圖4-19、不同水煮時間所成長的ZnO-CNT的上視影像圖，其中：(a) 1小時、(b) 1.5小時、(c) 2小時、(d) 2.5小時、(e) 3小時。放大倍率為3千倍 . . . . .	72 圖4-20、不同水煮時間所成長的ZnO-CNT的上視影像圖，其中：(a) 1小時、(b) 1.5小時、(c) 2小時、(d) 2.5小時、(e) 3小時。放大倍率為10萬倍 . . . . .
74 圖4-21、TEM影像圖，其中：(a) 水煮時間1小時所成長的ZnO-CNT、1萬倍，(b) 水煮時間2小時所成長的ZnO-CNT、1萬倍，(c) 水煮時間2小時所成長的ZnO-CNT、10萬倍 . . . . .	75 圖4-22、不同水煮時間所成長的ZnO-CNT拉曼光譜圖 . . . . .
76 圖4-23、不同水煮時間所成長的ZnO-CNT材料元素百分比分佈圖 . . . . .	78 圖4-24、不同水煮時間所成長的ZnO-CNT之電流密度與施加電場之(E-J)曲線圖 . . . . .
78 圖4-25、電場強度19V / μ m應用電場下的發射電流密度比較圖 . . . . .	81 圖4-26、不同水煮時間所成長的ZnO-CNT之相對應的Fowler-Nordheim (F-N)圖 . . . . .
81 圖4-27、(a)水煮1小時所成長的ZnO-CNT、(b)水煮2小時所成長的ZnO-CNT、(c)Ni-CNT。放大倍率為3千倍 . . . . .	82 圖4-28、(a)水煮1小時所成長的ZnO-CNT、(b)水煮2小時所成長的ZnO-CNT、(c)Ni-CNT。放大倍率為3萬倍 . . . . .
84 圖4-29、水	84 圖4-29、水

煮1、2小時所成長的ZnO-CNT和Ni-CNT拉曼光譜圖	85	圖4-30、水煮1、2小時所成長的ZnO-CNT和Ni-CNT之電流密度與施加電場之(E-J)曲線圖	88
水煮1、2小時所成長的ZnO-CNT和Ni-CNT之相對應的Fowler-Nordheim (F-N)圖	89	表目錄 表4-1、不同濃度Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液所成長的ZnO材料元素百分比	56
的ZnO-CNT拉曼光譜分析之D帶強度ID與G帶強度IG之比值關係表	61	表4-2、不同濃度Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液所成長的ZnO-CNT拉曼光譜分析之D帶強度ID與G帶強度IG之比值關係表	61
至0.175M的Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液所成長ZnO-CNT材料中的元素百分比	62	表4-4、不同濃度Zn(NO <sub>3</sub> ) <sub>2</sub> 和HMT水溶液所成長的ZnO-CNT的場發射(F-N)圖所計算出的斜率 - 場增強因子	68
不同水煮時間所成長的ZnO材料元素百分比	72	表4-5、不同水煮時間所成長的ZnO-CNT拉曼光譜分析之D帶強度ID與G帶強度IG之比值關係表	77
表4-6、不同水煮時間所成長的ZnO-CNT材料元素百分比	78	表4-7、不同水煮時間所成長的ZnO-CNT的場發射(F-N)圖所計算出的斜率 - 功函數	82
表4-8、不同水煮時間所成長的ZnO-CNT和Ni-CNT拉曼光譜分析之D帶強度ID與G帶強度IG之比值關係表	86	表4-9、水煮1、2小時所成長的ZnO-CNT和Ni-CNT拉曼光譜分析之D帶強度ID與G帶強度IG之比值關係表	87
水煮1、2小時所成長的ZnO-CNT和Ni-CNT材料元素百分比	88	表4-10、水煮1、2小時所成長的ZnO-CNT和Ni-CNT的場發射(F-N)圖所計算出的斜率 - 功函數	89

## REFERENCES

- [1] Pearson ' s Handbook of Crystallographic Data, pp. 4795.
- [2] Numerical Data and Functional Relationships in Science and Technology./v.22, Subvolume a. Intrinsic Properties of Group IV Elements and III-V, II-VI and I-VII Compounds, Berlin:/Springer-Verlag (1987).
- [3] Y. Chen, D. M. Bagnall, H. Koh, K. Park, Z. Zhu, T. Yao, J. Appl. Phys., 84, pp. 3912 (1998).
- [4] <http://oxide.rlem.titech.ac.jp/kawasaki/ZnO/ZnO.htm>
- [5] D. C. Look, Material Science and Engineering, B80, pp. 383-387 (2001).
- [6] W. S. Hu, Z. G. Liu, R. X. Wu, Y.-F. Chen, W. Ji, T. Yu and D. Feng, Appl. Phys. Lett., 71, pp. 548 (1997).
- [7] S. Ezhilvalavan and T. R. N. Kutty, Appl. Phys. Lett., 69, pp. 3540 (1996).
- [8] Shigemi Kohiki, Mikihiko Nishitani, and Takahiro Wada, J. Appl. Phys. 75(4), pp. 2069-2072 (1994).
- [9] R. Wang, Laura L. H. King and Arthur W. Sleight., J. Mater. Res. 11(7), pp. 1659-1664 (1996).
- [10] B. Sang, A. Yamada, M. Konagai., Solar Energy Material and Solar Cell, 49, pp 19-26 (1997).
- [11] Kwang Joo Kim and Young Ran Park, Appl. Phys. Lett., 78, pp. 475 (2001).
- [12] M. Miyazaki, K. Sato, A. Mitsui, H. Nishimura., J. Non-Crystal Solid, 201, pp. 895 (1997).
- [13] 楊明輝 , 工業材料 , 2001年11月 [14] H. J. Ko, Y. F. Chen, S. K. Hong, H. Wenisch, T. Yao, D.C. Look, Appl. Phys. Lett., 77, pp.3761 (2000).
- [15] Kwang Joo Kim and Young Ran Park, Appl. Phys. Lett., 78, pp. 475 (2000).
- [16] W. J. Li, E. W. Shi, W. Z. Zhong, Z. W. Yin, J. Crystal. Growth, 186-196, pp. 203 (1999).
- [17] Xin-Li Guo, Hitoshi Tabata, Tomoji Kawai, Journal of Crystal Growth, pp. 237544 (2002).
- [18] Manabu Komatsu, Naoki Ohashi, Hajime Haneda, Applied Surface Science, 189, pp. 349 (2002).
- [19] R. F. Service Science, 276, pp. 895 (1997).
- [20] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature (London), 318, pp. 162, (1985).
- [21] 張自恭 , 碳六十 , 財團法人國家實驗研究院國家高速網路與計算中心 , 知識庫網頁 , NanoScience 奈米科學網 , 奈米小辭典(<http://nano.nchc.org.tw/dictionary/c60.php>) ; 張自恭 , “ C60- 碳六十(Buckminsterfullerene) ” , 機械工業雜誌 , 255 期 , pp.266 , 2004 年06月號。
- [22] S. Iijima, “ Helical microtubules of graphitic carbon ” , Nature, 354 , pp. 56 (1991).
- [23] S. Iijima and T. Ichihashi, “ Single-shell carbon nanotubes of 1-nm diameter ” , Nature 363, pp. 603-605 (1993).
- [24] <http://www.encyclopedia.thefreedictionary.com>
- [25] M. C. Bohm, J. Schulte, R. Schlogl, “ An ab initio study of the C-60 particle-hole pair C-60(12+) and C-60(12-) ” Z NATURFORSCH A 52 (4):331-334 APR (1997).
- [26] F. L. Coffman, R. Cao, P. A. Pianetta, et al. “ Near-edge x-ray absorption of carbon materials for determining bond hybridization In mixed sp<sub>2</sub>/sp<sub>3</sub> bonded materials ” , Appl. Phys. Lett. 69(4): pp. 568-570 (1996).
- [27] Y. Achiba, P. W. Fowler, D. Mitchell, et al. “ Structural predictions for the C-116 molecule ” , J. Phys. Chem. A, 102(34), pp. 6835-6841 (1998).
- [28] “ Carbon nanotubes synthesis, structure, properties, and applications ” , M. S. Dresselhaus, G. Dresselhaus, Ph. Avouris.
- [29] J. W. Ning, J. J. Zhang, Y. B. Pan, et al. “ Fabrication and thermal property of carbon nanotube/SiO<sub>2</sub> composites ” , J. Mater. Sci. Lett. 22(14), pp. 1019-1021 (2003).
- [30] P. Chen, H. B. Zhang, G. D. Lin, et al. “ Studies on structure and property of carbon-nanotubes formed catalytically from decomposition of CH<sub>4</sub> or CO ” Chem. J. Chinese U. 19(5), pp. 765-769 (1998).

- [31] O. Zhou, R. M. Fleming, D W. Murphy, C. H. Chen, R. C. Haddon, A. P. Ramirez, and S. H. Glarum, *Science*, 263 pp. 1774 (1994).
- [32] S. Amelinckx, D. Bernaerts, X. B. Zhang, G. Van Tendeloo, and J. Van Landuyt, *Science*, 267, pp. 1334 (1995).
- [33] H. Dai, E. W. Wong, and C. M. Lieber, *Science*, 272, pp. 523 (1996).
- [34] T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi, and T. Thio, *Nature*, 382, pp. 54 (1996).
- [35] "Physical Properties of Carbon Nanotubes" University of Electrocommunications, TOKYO G DRESSELHAUS & MS DRESSELHAUS
- [36] H. Yokomichi, M. Matoba, H. Sakima, et al. "Synthesis of carbon nanotubes by arc discharge in CF<sub>4</sub> gas atmosphere", *Jpn. J. Appl. Phys.* 1 37 (12A), pp. 6492-6496 (1998). site:students.chem.tue.nl nanotube.
- [37] Chuan Chen, Chia-Chang Tsai, Jian-Ming Lu, and Chi-Chuan Hwang, "Electronic properties of capped, finite-length armchair carbon nanotubes in an electric field", *The Journal of Physical Chemistry B*, 110(25): pp. 12384-12387 (2006).
- [38] <http://students.chem.tue.nl> nanotube.
- [39] P. M. Ajayan, P. Redlich, M. Ruhle, "Balance of graphite deposition and multishell carbon nanotube growth in the carbon arc discharge", *J. Mater. Res.* 12(1), pp. 244-252 (1997).
- [40] H. Folwer and L. Nordheim, *Proc. R. Soc. London, Ser A*, 119: pp. 683 (1928).
- [41] P. G. Collins and A. Zettl, *Phys. Rev. B* 55, pp. 9391 (1997).
- [42] S. Han and J. Ihm, *Phys. Rev. B*, Vol. 66, 241402; Changwook Kim, Bongsoo Kim, Seung Mi Lee, Chulsu Jo and Young Hee Lee, *Phys. Rev. B*, Vol. 65, pp. 418 (2002).
- [43] 陳盈伸，"氧化鋅奈米柱應用於染料敏化太陽能電池之研究"，國立虎尾科技大學，中華名國96年7月 [44] Yo-Sep Min, Eun Ju Bae, Un Jeong Kim, and Wanju Park, Direct growth of single-walled carbon nanotubes on conducting ZnO films and its field emission properties, *Applied Physics Letters* 89, pp. 113116 (2006).
- [45] Zuowan Zhou, Weiming Peng, Shaoying Ke, Hai Deng, *Journal of Materials Processing Technology*, 89, pp. 415 (1999).
- [46] Minoru Satoh, Norio Tanaka, Yoshikazu Ueda, Shigeo Ohshio and Hidetoshi Saitoh, *Japanese Journal of Applied Physics*, 38, L586 (1999).
- [47] Michael H. Hwang, *Science*, 292, pp. 1897 (2001).
- [48] Y. W. Wang, L. D. Zhang, G. Z. Wang, X. S. Peng, Z. Q. Chu, *Journal of Crystal Growth*, 234, pp. 171 (2002).
- [49] P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, H. -J. Choi, *Advanced Functional Materials*, 12(5), pp. 323 (2002).
- [50] Seung Chul Lyu, Ye Zhang, Hyun Ruh, Hwack-Joo Lee, Hyun-Wook Shim, Eun-Kyung Suh, Cheol Jin Lee, *Chemical Physics Letters*, 363, pp. 134 (2002) [51] Li, Seu Yi; Lee, Chia Ying; Tseng, Tseung Yuen, *Journal of Crystal Growth*, 247, pp. 357 (2003).
- [52] M. J. Zheng, L. D. Zhang, G. H. Li, W. Z. Shen, *Chemical Physics Letters*, 363, pp. 123 (2002).
- [53] Yuan-Chung Wang, *Electrochemical and Solid-State Letters*, 5, C53 (2002).
- [54] L. Vayssières, K. Keis, A. Hagfeldt, S. E. Lindquist, *Chemistry of Materials*, 13: pp. 4395 (2001).
- [55] J. Q. Hu, *Synthesis of uniform hexagonal prismatic ZnO whiskers*, 14: pp. 1216 (2002).
- [56] M. J. Zheng, L. D. Zhang, G. H. Li, W. Z. Shen, *Chemical Physics Letters*, 363, pp. 123 (2002).
- [57] Y. C. Wang, I. C. Leu, M. H. Hon, *Electrochemical and Solid-State Letters*, 5, pp. 4, C53 (2002).
- [58] H. Nagayama, H. Honda and H. Kawahara, *J. Electrochem. Soc.*, 135, pp. 2013 (1988).
- [59] S. Deki, Y. Aoi, O. Hiroi and A. Kajinami, *Chem. Lett.*, pp. 433 (1996).
- [60] Y. Saito, T. Yoshikawa, M. Inagaki, M. Tomita & T. Hayshi, Growth and structure of graphitic tubules and polyhedral particles in arc-discharge. *Chemical Physics Letters*, Vol. 204, pp. 277-282 (1993).
- [61] H. Dai, A. G. Rinzer, P. Nikolaev, A. Thess, D. T. Colbert & R. E. Smalley, Single-wall nanotubes produced by metal catalyzed disproportionation of carbon monoxide. *Chem. Phys. Lett.*, Vol. 260, pp. 471-475 (1996).
- [62] M. Endo & H. W. Kroto, Formation of carbon nanofibers. *Journal of Physical Chemistry*, Vol. 96, pp. 6491-6494 (1992).
- [63] R. T. K. Baker & P. S. Harries, *The Formation of Filamentous Carbon: Chemistry and Physics of Carbon*, New York: Marcel Dekker, Vol. 14, pp. 83-165. (1978) [64] R. T. K. Baker, M. A. Braker, P. S. Harries, F. S. Feates, & R. J. Waite, Nucleation and growth of carbon deposits from nickel catalyzed decomposition of acetylene. *Journal of Catalysis*, Vol. 26, pp. 51-62 (1972).
- [65] A. Oberlin, M. Ento, & T. Koyama, Filamentous growth of carbon through benzene decomposition. *Journal of Crystal Growth*, Vol. 32, pp. 335-349 (1976).
- [66] T. Baird & J. R. Fryer, Carbon formation on iron and nickel foils by hydrocarbon pyrolysis reactions at 700 °C. *Carbon*, Vol. 12, pp. 591-602 (1974).
- [67] A. Oberlin, M. Ento & T. Koyama, High resolution electron microscope observations of graphitized carbon fibers. *Carbon*, Vol. 14, pp. 133-157 (1976).
- [68] C. Journet, et al., Production of carbon nanotubes. *Applied Physics*, Vol. 67, pp. 1-9 (1998).
- [69] M. Alan, et al., Chemical vapor deposition of methane for single-walled carbon nanotubes. *Chem. Phys. Lett.*, Vol. 292, pp. 567-574 (1998).
- [70] M. J. Yacaman, M. M. Yoshida, L. Rendon, & J. G. Santesteban, Catalytic growth of carbon microtubules with fullerene structure. *Appl. Phys. Lett.*, Vol. 62, pp. 202-204 (1993).

- [71] R. T. K. Baker & J. J. Chludzinski, Filamentous carbon growth on nickel – iron surfaces—effect of various oxide additives. *Journal of Catalysis*, Vol. 64, pp. 464-478 (1980).
- [72] R. T. K. Baker, P. S. Harries, R. B. Thomas & R. J. Waite, Formation of filamentous carbon from iron and chromium catalyzed decomposition of acetylene. *Journal of Catalysis*, Vol. 30, pp. 86-95 (1973).
- [73] R. T. K. Baker & R. J. Waite, Formation of carbonaceous deposit from the platinum-iron catalyzed decomposition. *Journal of Catalysis*, Vol. 37, pp. 101-105 (1975).
- [74] M. Jung, K. Y. Eun, J. K. Lee, Y. J. Baik, K. R. Lee & J. W. Park, Growth of carbon nanotubes by chemical vapor deposition. *Diamond and Related Materials*, Vol. 10, pp. 1235-1240 (2001).
- [75] S. Xie, W. Li, Z. Pan, B. Chang & L. Sun, Self-assembly of shape-controlled nanocrystals and their in-situ thermodynamic properties. *Materials Science and Engineering A*, Vol. 286, pp. 11-15 (2000).
- [76] X. H. Chen, S. Q. Feng, Y. Ding, J. C. Peng & Z. Z. Chen, The formation conditions of carbon nanotubes array based on FeNi alloy island films. *Thin Solid Films*, Vol. 339, pp. 6-9 (1999).
- [77] C. J. Lee, J. Park, S. Y. Kang & J. H. Lee, 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 (2000).
- [78] M. Terrones, et al., Preparation of aligned carbon nanotubes catalysed by laser-etched cobalt thin films. *Chemical Physics Letters*, Vol. 285, pp. 299-305 (1998).
- [79] Q. Liang, Q. Li, D. L. Chen, D. R. Zhou, B. L. Zhang & Z. L. Yu, Carbon nanotube prepared in the atmosphere of partial oxidation of methane. *Chemical Journal of Chinese Universities-Chinese*, Vol. 21(4), pp. 623-625 (2000).
- [80] K. Hernadi, A. Fonseca, J. B. Nagy, A. Siska & I. Kiricsi, Production of nanotubes by the catalytic decomposition of different carbon-containing compounds. *Applied Catalysis A: General*, Vol. 199, pp. 245-255 (2000).
- [81] W. Z. Li, S. S. Xie, L. X. Qian, B. H. Chang, B. S. Zou, W. Y. Zhou, R. A. Zhao & G. Wang, Large-scale synthesis of aligned carbon nanotubes. *Science*, Vol. 274, pp. 1701-1703 (1996).
- [82] Z. W. Pan, S. S. Xie, B. H. Chang, L. F. Sun, W. Y. Zhou & G. Wang, Direct growth of aligned open carbon nanotubes by chemical vapor deposition. *Chemical Physics Letters*, Vol. 299, pp. 97-102 (1999).
- [83] A. P. Li, F. Muller, A. Birner, K. Nielsch & U. Gosele, 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 (1998).
- [84] H. Masuda, H. Yamada, M. Satoh & H. Asoh, Highly ordered nanochannel-array architecture in anodic alumina. *Appl. Phys. Lett.*, Vol. 71, pp. 2770-2772. (1997).
- [85] H. Masuda & M. Satoh, Fabrication of gold nanodot array using anodic porous alumina as an evaporation mask. *Jpn. J. Appl. Phys.*, part 2, Vol. 35, L. 126-129 (1996).
- [86] P. E. Nolan, M. J. Schabel & D. C. Lynch, Hydrogen control of carbon deposit morphology. *Carbon*, Vol. 33, pp. 79-85 (1995).
- [87] P. Pinheiro, M. C. Schouler, P. Gadelle, M. Mermoux & E. Dooryhee, Effect of hydrogen on the orientation of carbon layers in deposits from the carbon monoxide disproportionation reaction over Co/Al<sub>2</sub>O<sub>3</sub> catalysts. *Carbon*, Vol. 38(10), pp. 1469-1479 (2000).
- [88] A. A. Khassin, T. M. Yurieva, V. I. Zaikovskii & V. N. Parmon, 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 (1998).
- [89] S. H. Tsai, C. W. Chao, C. L. Lee & H. C. Shin, 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 (1999).
- [90] Z. P. Huang, J. W. Xu, Z. F. Ren, J. H. Wang, M. P. Siegal & P. N. Provencio, Growth of highly-oriented carbon nanotubes by plasma-enhanced hot filament chemical vapor deposition. *Appl. Phys. Lett.*, Vol. 73, pp. 3845-3847 (1998).
- [91] Z. F. Ren, Z. P. Huang, D. L. Wang, J. G. Wen, J. W. Xu, J. H. Wang, L. E. Calvet, J. Chen, J. F. Klemic & M. A. Reed, Growth of a single freestanding multiwall carbon nanotube on each nanonickel dot. *Appl. Phys. Lett.*, Vol. 75, pp. 1086-1088 (1999).
- [92] S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell & H. Dai, Self-oriented regular arrays of carbon nanotubes and their field emission properties. *Science*, Vol. 283, pp. 512-514 (1999).
- [93] Y. K. Kwon, Y. H. Lee, S. G. Kim, P. Jund, D. Tomanek & R. E. Smalley, Morphology and stability of growing multiwall carbon nanotubes. *Phys. Rev. Lett.*, Vol. 79, pp. 2065-2068 (1997).
- [94] D. H. Oh & Y. H. Lee, Stability and cap formation mechanism of single-walled carbon nanotubes. *Phys. Rev. B*, Vol. 58, pp. 7407-7411 (1998).
- [95] V. L. Kuznetsov, A. N. Usoltseva, A. L. Chuvilin, E. D. Obraztsova & J. M. Bonard, 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 (2001) [96] A. Chrissanthopoulos, S. Baskoutas, N. Bouropoulos, V. Dracopoulos, D. Tasis, S. N. Yannopoulos, Novel ZnO nanostructures grown on carbon nanotubes by thermal evaporation, *Thin Solid Films* 515, pp. 8524 – 8528. (2007) [97] Juntao Li, Wei Lei, Xiaobing Zhang, Xuedong Zhou, Qilong Wang, Yuning Zhang, Baoping Wang. *Applied Surface Science* 220, pp. 96 – 104 (2003) [98] S. L. S. Jacoby, J. S. Kowalik & J. T. Pizzo,

Iterative Methods for Nonlinear Optimization Problems. Prentice Hall, Inc., Englewood Cliffs, New Jersey, ISBN:0 – 13 – .508199 – X, pp. 79-83 (1972).

[99] R. H. Fowler, L. W. Nordheim, Electron emission in intense electric fields. Proceedings of Royal Society of London, 119, pp. 173-181 (1928).

[100] M. Katsura, K. Nishimaki, T. Nakagawa, T. A . Yamamoto, M. Hirota and M. Miyake. J. Nucl. Mater. 258-263, pp.839 (1998).