

Growth of Germanium Nanowires via a Solid - Liquid - Solid Mechanism

蔡耀鋒、李世鴻；蔡渙良

E-mail: 9806471@mail.dyu.edu.tw

ABSTRACT

In this study, thin layers of Au and Ni were evaporated onto the germanium substrate as the metal catalyst for germanium nanowires growth. The thickness of Au film is ranged from 1 nm to 9 nm and the thickness of Ni film is 3 nm. In this experiment, different parameters of synthesis condition were varied for nanowires growth, including the thickness of metal layer and growth temperature. The effects of the various parameters on the growth of germanium nanowires were investigated in detail.

In the period of nucleation, the size of catalyst droplet increases with the increasing thickness of metal layer, so is the diameter of germanium nanowires. The influence of growth temperature on the morphology of germanium nanowires is dramatic. The length of nanowire increases with the growth temperature ranging from 550 °C~600 °C. Nevertheless, the quantity of grown nanowire decreases with the growth temperature ranging from 625 °C to 650 °C. It is found that the temperatures 625 °C and 650 °C are too high to grow nanowires appropriately and result in the z-shaped nanowires.

Keywords : germanium nanowire、Au-Ge alloy

Table of Contents

封面內頁

簽名頁

博碩士論文暨電子檔案上網授權書.....iii

中文摘要.....iv

ABSTRACT.....v

誌謝.....vi

目錄.....vii

圖目錄.....x

表目錄.....xv

第一章、緒論.....1

1.1 奈米與科技.....1

1.2 奈米材料.....1

1.3 奈米線簡介.....4

1.4 奈米材料的應用.....5

第二章、文獻回顧.....9

2.1 鍺粉末成長二氧化鍺奈米線文獻.....9

2.2 GeO₂奈米線的原位熱氧化製備與發光性質.....15

2.3 研究動機.....18

第三章、理論與研究方法.....20

3.1 奈米線的成長機制.....20

3.1.1 Vapor-Liquid-Solid(VLS).....20

3.1.2 氧化物輔助生長(Oxide-Assisted Growth, OAG)..22

3.1.3 Vapor-Solid(VS).....24

3.1.4 Solution-Liquid-Solid.....25

3.1.5 Solid-Liquid-Solid(SLS).....27

3.1.6 Solid-Solid transformation(SS).....29

3.2 實驗儀器原理.....30

3.2.1 熱蒸鍍系統.....30

3.2.2 高溫爐管系統.....32

3.2.3 掃描式電子顯微鏡系統.....33

3.2.4 能量散佈分析儀系統.....	34
3.2.5 高解析穿透式電子顯微鏡(TEM).....	36
3.3 實驗步驟.....	37
3.3.1 蒸鍍.....	37
3.3.2 成長鍺奈米線.....	38
第四章、實驗結果與討論.....	40
4.1 不同厚度的金催化劑金屬對鍺奈米線成長的影響與討論.....	40
4.2 不同溫度對鍺奈米線成長的影響與討論.....	51
4.3 不同成長溫度下鍺試片的能量散佈分析儀 (EDS) 分析和比較.....	58
4.4 金催化劑金屬成長的鍺奈米線穿透式電子顯微鏡(TEM)分析.....	62
4.5 鍺催化劑金屬對鍺奈米線成長的影響與討論.....	63
4.5.1 掃描式電子顯微鏡(SEM)的分析比較.....	63
4.5.2 能量散佈分析儀 (EDS) 的成份分析和比較.....	67
4.5.3 穿透式電子顯微鏡(TEM)分析.....	67
4.6 不同催化劑金屬對鍺奈米線成長的比較.....	69
4.6.1 掃描式電子顯微鏡(SEM)的分析比較.....	70
4.6.2 能量散佈分析儀(EDS)的分析比較.....	71
4.6.3 穿透式電子顯微鏡(TEM)的分析比較.....	72
第五章、結論.....	74
參考文獻.....	76

REFERENCES

- [1]N. W. Ashcroft and N. D. Nmermin, *Solid State Physics*, 2nd Edition, Harcourt (1976).
- [2]S. Veprek, Electronic and mechanical properties of nanocrystalline composites when approaching molecular size, *Thin Solid Films*, 279(1-2), 145-153 (1997).
- [3]A. P. Alivisatos, Semiconductor clusters, nanocrystals, and quantum dots, *Science*, 271, 933-937 (1996).
- [4]L. T. Canham, Silicon quantum wire array fabrication by electro-chemical and chemical dissolution of wafers, *Appl. Phys. Lett.*, 57, 1046-1048 (1990).
- [5]H. W. Pollack, *Materials Science and Metallurgy*, 4th Edition, Prentice-Hall, Englewood Cliffs, N. J. (1998).
- [6]R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, Visible-light photocatalysis in nitrogen-doped titanium oxides, *Science*, 293, 269-271 (2001).
- [7]尹邦躍。納米時代—實現與夢想。中國輕工業出版社，2001年。
- [8]M. C. Daniel and D. Astruc, Nanoparticles: Assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology, *Chem. Rev.*, 104(1), 293-346. (2004).
- [9]R. M. Crooks, M. Zhao, L. Sun, V. Chechik, and L. K. Yeung, Dendrimer-encapsulated metal nanoparticles: Synthesis, characterization, and applications to catalysis, *Acc. Chem. Res.*, 34(3), 181-190. (2001).
- [10]L.-S. Li, J. Walda, L. Manna, and A. P. Alivisatos, Semiconductor nanorod liquid crystals, *Nano Lett.*, 2(6), 557-560 (2002).
- [11]J. Hu, T. W. Odom, and C. M. Lieber, Chemistry and physics in one dimension: Synthesis and properties of nanowires and nanotubes, *Acc. Chem. Res.*, 32(5), 435-445 (1999).
- [12]P. M. Ajayan, Nanotubes from carbon, *Chem. Rev.*, 99(7), 1787-1800 (1999).
- [13]M. S. Arnold, P. Avouris, Z. W. Pan, and Z. L. Wang, Field-effect transistors based on single semiconducting oxide nanobelts, *J. Phys. Chem. B*, 107(3), 659-663. (2003)[14]A. P. Alivisatos, Semiconductor clusters, nanocrystals, and quantum dots, *Science*. 271, 933-937. (1996).
- [15]R. S. Wagner and W. C. Ellis, Vapor-liquid-solid mechanism of single crystal growth, *Appl. Phys. Lett.*, 4, 89-90 (1964).
- [16]E. I. Givargizov, Fundamental aspects of VLS growth, *J. Crystal Growth*, 31, 20-30 (1975).
- [17]L. T. Canham, Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers, *Appl. Phys. Lett.*, 57, 1046-1048 (1990).
- [18]S. Iijima, Helical microtubules of graphitic carbon, *Nature*, 354, 7, 56-58 (1991).
- [19]A. M. Morales and C. M. Lieber, A laser ablation method for the synthesis of crystalline semiconductor nanowires, *Science*, 279, 208-211. (1998).
- [20]H. F. Yan, Y. J. Xing, Q. L. Hang, D. P. Yu, Y. P. Wang, J. Xu, Z. H. Xi, and S. Q. Feng, Growth of amorphous silicon nanowires via a solid – liquid – solid mechanism, *Chem. Phys. Lett.*, 323, 224 – 228 (2000).
- [21]D. P. Yu, Y. J. Xing, Q. L. Hang, H. F. Yan, J. Xu, Z. H. Xi, and S. Q. Feng, Controlled growth of oriented amorphous silicon nanowires via

a solid – liquid – solid (SLS) mechanism, *Physica E*, 34, 305-309 (2001).

- [22] X. Chen, Y. Xing, J. Xu, J. Xiang, and D. Yu, Rational growth of highly oriented amorphous silicon nanowire films, *Chem. Phys. Lett.*, 374, 626-630. (2003).
- [23] K.-Q. Peng, Y.-J. Yang, S.-P. Gao, and J. Zhu, Synthesis of large-area silicon nanowire arrays via self-assembling nanoelectrochemistry, *Adv. Mater.*, 14(16), 1164-1167 (2002).
- [24] T. C. Cheng, A. J. Shieh, W. J. Huang, M. C. Yang, M. H. Cheng, H. M. Lin, and M. N. Chang, Hydrogen plasma dry etching method for field emission application, *App. Phys. Lett.*, 88, 263118-1 - 263118-3 (2006).
- [25] D. Whang, S. Jin, Y. Wu, and C. M. Lieber, Large-scale hierarchical organization of nanowire arrays for integrated nanosystems, *Nano Lett.*, 3, 1255-1259 (2003).
- [26] J. Xiang, W. Lu, Y. Hu, Y. Wu, H. Yan, and C. M. Lieber, Ge/Si nanowire heterostructures as high performance field-effect transistors, *Nature*, 441, 498-493 (2006).
- [27] F. C. K. Au, K. W. Wong, Y. H. Tang, Y. F. Zhang, I. Bello, and S. T. Lee, Electron field emission from silicon nanowires, *Appl. Phys. Lett.*, 75, 1700-1702 (1999).
- [28] S. T. Purcell, V. T. Binh, and N. Garcia, 64 meV measured energy dispersion from cold field emission nanotips, *Appl. Phys. Lett.*, 67, 436-438 (1995).
- [29] W. A. Deheer, A. Chatelain, and D. Ugarte, A carbon nanotube field-emission electron source, *Science*, 270, 1179-1180 (1995).
- [30] Yong Su, Xuemei Liang, Sen Li, Yiqing Chen, Qingtao Zhou, Song Yin, Xia Meng, Mingguang Kong, Self-catalytic VLS growth and optical properties of single-crystalline GeO₂ nanowire arrays, *Materials Letters*, 62, 1010-1013 (2008).
- [31] C. B. Li, K. Usami, T. Muraki, H. Mizuta, and S. Oda, The impacts of surface conditions on the vapor-liquid-solid growth of germanium nanowires on Si (100) substrate, *Appl. Phys. Lett.*, 93, 041917-1 - 041917-3 (2008).
- [32] Hemant Adhikari and Paul C. McIntyre, Conditions for subeutectic growth of Ge nanowires by the vapor-liquid-solid mechanism, *Appl. Phys. Lett.*, 102, 094311-1 - 094311-5 (2007).
- [33] L. Z. Pei, H. S. Zhao, W. Tan, and Q. F. Zhang, Facile hydrothermal preparation and characterizations of single crystalline Ge dioxide nanowires, *Appl. Phys. Lett.*, 105, 054313-1 - 054313-5 (2009).
- [34] K. Das, A. K. Chakraborty, M. L. NandaGoswami, R. K. Shingha, A. Dhar, K. S. Coleman, S. K. Ray, Temperature dependent shape transformation of Ge nanostructures by the vapor-liquid-solid method, *Appl. Phys. Lett.*, 101, 074307-1 - 074307-4 (2007).
- [35] Chuanbo Li, Kouichi Usami, Gento Yamahata, Yoshishige Tsuchiya, Hiroshi Mizuta, and Shunri Oda, Position-Controllable Ge Nanowires Growth on Patterned Au Catalyst Substrate, *Appl. Phys. E.*, 2 015004-1 - 015004-3 (2009).
- [36] H. W. Kim and J. W. Lee, GeO₂ nanostructures fabricated by heating of Ge powders: Pt-catalyzed growth, structure, and photoluminescence, *Physica E*, 40(7), 2499-2503 (2007).
- [37] 陳曉波, 揚合情, 張瑞剛, 楊瑞麗, 董紅星, 尹文艷, 宋玉哲, 陳迪春. GeO₂奈米線的原位熱氧化製備與發光性質. *中國科學E輯: 技術科學*, 第38卷, 第1期, 24-35頁, 2008年.
- [38] S. S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tomblor, A. M. Cassell, and H. J. Dai, Self-oriented regular arrays of carbon nanotubes and their field emission properties, *Science*, 283, 512-514 (1999).
- [39] D. M. Christie, and J. R. Chelikowsky, Electronic and structural properties germania polymorphs, *Phys. Rev. B*, 62(22), 14703-14711 (2000).
- [40] C. N. R. Rao, F. L. Deepak, G. Gundiah, and A. Gorindarj, Inorganic nanowires, *Prog. Solid State Chem.*, 31, 5-147 (2003).
- [41] Y. Wu and P. Yang, Direct observation of vapor-liquid-solid nanowire growth, *Science*, 123, 3165-3166 (2001).
- [42] Y. W. Wang, C. H. Liang, G. W. Meng, X. S. Peng, and L. D. Zhang, Synthesis and photoluminescence properties of amorphous SiO_x nanowires, *J. Matter. Chem.*, 12, 651-653 (2002).
- [43] D. P. Yu, Q. L. Hang, Y. Ding, H. Z. Zhang, Z. G. Bai, J. J. Wang, Y. H. Zou, W. Qian, G. C. Xiong, and S. Q. Feng, Amorphous silica nanowires: Intensive blue light emitters, *Appl. Phys. Lett.*, 73, 3076-3078 (1998).
- [44] H. F. Zhang, C. M. Wang, E. C. Buck, and L. S. Wang, Synthesis, characterization, and manipulation of helical SiO₂ nanosprings, *Nano Lett.*, 3, 577-580 (2003).
- [45] X. C. Wu, W. H. Song, K. Y. Wang, T. Hu, B. Zhao, Y. P. Sun, and J. J. Du, Preparation and photoluminescence properties of amorphous silica nanowires, *Chem. Phys. Lett.*, 336, 53-56 (2001).
- [46] Y. J. Chen, J. B. Li, Y. S. Han, Q. M. Wei, and J. H. Dai, A novel morphology of SiO_x nanowires with a modified, *App. Phys. Lett.*, 74, 433-435 (2002).
- [47] J. C. Wang, C. Z. Zhan, and F. G. Li, The synthesis of silica nanowire arrays, *Solid State Commun.*, 125, 629-631 (2003).
- [48] Z. W. Pan, Z. R. Dai, C. Ma, and Z. L. Wang, Molten Gallium as A Catalyst for the Large-Scale Growth of Highly Aligned Silica Nanowires, *J. Am. Chem. Soc.*, 124, 1817-1822 (2002).
- [49] S. H. Sun, G. W. Meng, M. G. Zhang, Y. T. Tian, T. Xie, and L. D. Zhang, Preparation and characterization of oriented silica nanowires, *Solid State Commun.*, 128, 287-290 (2003).
- [50] J. Hu, Y. Bando, J. Zhan, X. Yuan, T. Sekiuchi, and D. Golberg, Self-assembly of SiO₂ nanowires and Si microwires into hierarchical

heterostructures on a large scale, *Adv. Matter.*, 17, 971-975 (2005).

[51] S. T. Lee, N. Wang, Y. F. Zhang, and Y. H. Tang, Oxide-assisted semiconductor nanowire growth, *MRS Bull.*, 24, 36-42 (1999).

[52] S. T. Lee, Y. F. Zhang, N. Wang, Y. H. Tang, I. Bello, C. S. Lee, Y. W. Chung, and Y. W. Chung, Semiconductor nanowires from oxides, *J. Mater. Res.*, 14, 4503-4507 (1999).

[53] N. Wang, Y. H. Tang, Y. F. Zhang, C. S. Lee, and S. T. Lee, Nucleation and growth of Si nanowires from silicon oxide, *Phys. Rev.*, 58, R16024-R16026 (1998).

[54] T. S. Chu, R. Q. Zhang, and H. F. Cheung, Geometric and electronic structures of silicon oxide clusters, *J. Phys. Chem.*, 105, 1705-1709 (2001).

[55] R. Q. Zhang, Y. Lifshitz, and S. T. Lee, Oxide-Assisted Growth of Semiconducting Nanowires, *Adv. Mater.*, 15, 635-640 (2003).

[56] X. M. Meng, J. Q. Hu, Y. Jiang, C. S. Lee, and S. T. Lee, Oxide-assisted growth and characterization of Ge/SiO_x nanocables, *App. Phys. Lett.*, 83, 2241-2243 (2003).

[57] Y. Cui, L. J. Lauhon, M. S. Gudiksen, J. F. Wang, and C. M. Lieber, Diameter-controlled synthesis of single-crystal silicon nanowires, *App. Phys. Lett.*, 78, 2214-2216 (2001).

[58] G. W. Zhou, H. Li, H. P. Sun, D. P. Yu, Y. Q. Wang, X. J. Huang, L. Q. Chen, and Z. Zhang, Controlled Li doping of Si nanowires by electrochemical insertion method, *App. Phys. Lett.*, 75, 2447-2449 (1999).

[59] D. D. Ma, C. S. Lee, F. C. K. Au, S. Y. Tong, and S. T. Lee, Small-diameter silicon nanowire surfaces, *Science*, 299, 1874-1877 (2003).

[60] Y. F. Zhang, Y. H. Tang, N. Wang, C. S. Lee, I. Bello, and S. T. Lee, Germanium nanowires sheathed with an oxide layer, *Phys. Rev.*, 61, 4518-4521 (2000).

[61] W. S. Shi, Y. F. Zheng, N. Wang, C. S. Lee, and S. T. Lee, Microstructures of gallium nitride nanowires synthesized by oxide-assisted method, *Chem. Phys. Lett.*, 345, 377-380 (2001).

[62] H. Y. Peng, X. T. Zhou, N. Wang, Y. F. Zheng, L. S. Liao, W. S. Shi, C. S. Lee, and S. T. Lee, Bulk-quantity GaN nanowires synthesized from hot filament CVD, *Chem. Phys. Lett.*, 327, 263-270 (2000).

[63] W. S. Shi, Y. F. Zheng, N. Wang, C. S. Lee, and S. T. Lee, A general synthetic route to III-V compound semiconductor nanowires, *Adv. Mater.*, 13, 591-594 (2001).

[64] W. S. Shi, Y. F. Zheng, N. Wang, C. S. Lee, and S. T. Lee, Oxide-assisted growth and optical characterization of gallium-arsenide nanowires, *App. Phys. Lett.*, 78, 3304-3306 (2001).

[65] W. S. Shi, Y. F. Zheng, N. Wang, C. S. Lee, and S. T. Lee, Synthesis and microstructure of gallium phosphide nanowires, *J. Vac. Sci. Technol. B*, 19, 1115-1118 (2001).

[66] J. Q. Hu, X. L. Ma, Z. Y. Xie, N. B. Wong, C. S. Lee, I. Bello, and S. T. Lee, Characterization of zinc oxide crystal whiskers grown by thermal evaporation, *Chem. Phys. Lett.*, 344, 97-100 (2001).

[67] Y. H. Tang, N. Wang, Y. F. Zhang, C. S. Lee, I. Bello, and S. T. Lee, Synthesis and characterization of amorphous carbon nanowires, *Appl. Phys. Lett.*, 75, 2921-2923 (1999).

[68] K. H. Lee, S. W. Lee, R. R. Vanflee, and W. Sigmund, Amorphous silica nanowires grown by the vapor-solid mechanism, *Chem. Phys. Lett.*, 376, 498-503 (2003).

[69] Y. Zhang, N. Wang, R. He, J. Liu, X. Zhang, and J. Zhu, A simple method to synthesize Si₃N₄ and SiO₂ nanowires from Si or Si/SiO₂ mixture, *J. Cryst. Growth*, 233, 803-808 (2001).

[70] L. Dai, X. L. Chen, T. Zhou, and B. Q. Hu, Aligned silica nanofibres, *J. Phys.: Condens. Matter.*, 14, L473-L477. (2002).

[71] L. Dai, X. L. Chen, J. K. Jian, W. J. Wang, T. Zhou, and B. Q. Hu, Strong blue photoluminescence from aligned silica nanofibers, *Appl. Phys. Lett.*, 76, 625-627 (2003).

[72] T. J. Trentler, K. M. Hickman, S. C. Goel, A. M. Viano, P. C. Gibbons, and W. E. Buhro, Solution-liquid-solid growth of crystalline III-V semiconductors: An analogy to vapor-liquid-solid growth, *Science*, 270, 1791-1974 (1995).

[73] X. Lu, T. Hanrath, K. P. Johnston, and B. A. Korgel, Growth of single crystal silicon nanowires in supercritical solution from tethered gold particles on a silicon substrate, *Nano Lett.*, 3, 93-99 (2003).

[74] Y. J. Xing, Z. H. Xi, Z. Q. Xue, and D. P. Yu, Diameter modification of Si nanowires via catalyst size, *Chin. Phys. Lett.*, 20, 700-702 (2003).

[75] Y. J. Xing, Z. H. Xi, D. P. Yu, Q. L. Hang, H. F. Yan, S. Q. Feng, and Z. Q. Xue, Growth of silicon nanowires by heating Si substrate, *Chin. Phys. Lett.*, 19, 240-242 (2002).

[76] S. H. Sun, G. W. Meng, T. Gao, M. G. Zhang, Y. T. Tian, X. S. Peng, Y. X. Jin and L. D. Zhang, Micrometer-sized Si-Sn-O structures with SiO_x nanowires on their surface, *Appl. Phys. Lett.*, 76, 999-1002 (2003).

[77] B. T. Park, and K. Yong, Controlled growth of core – shell Si – SiO_x and amorphous SiO₂ nanowires directly from NiO/Si, *Nanotechnology*, 15, S365-S370 (2004).

[78] M. Paulose, O. K. Varghese, and C. A. Grimes, Synthesis of gold-silica composite nanowires through solid-liquid-solid phase growth, *J. Nanosci. Nanotech.*, 3, 341-346 (2003).

[79] K. H. Lee, H. S. Yang, K. H. Baik, J. Bang, R. R. Vanfleet, and W. Sigmund, Direct growth of amorphous silica nanowires by solid state

transformation of SiO₂ films, Chem. Phys. Lett., 383, 380-384 (2004).

[80]H. Hanamura, H. Itoh, Y. Shimogaki, J. Aoyama, T. Yoshimi, J. Ueda, and H. Komiyama, Structural change of TiN/Ti/SiO₂ multilayers by N₂ annealing, Thin Solid Films, 320, 31-34 (1998).

[81]Ung-Fu Hsu, and Bohr-Ran Huang, The growth of silicon nanowires by electroless plating technique of Ni catalysts on silicon substrate, Thin Solid Films, 514, 20-24 (2006).

[82]Liang Li, Xiaosheng Fang, Han Guan Chew, Fei Zheng, Tze Haw Liew, Xijin Xu, Yunxia Zhang, Shusheng Pan, Guanghai Li, and Lide Zhang, Crystallinity-Controlled Germanium Nanowire Arrays: Potential Field Emitters, Adv. Funct. Mater., 18, 1080 – 1088 (2008).