

以固態-液態-固態機制成長矽奈米線及鍺奈米線

李麗英、李世鴻

E-mail: 322127@mail.dyu.edu.tw

摘要

論文中，我們利用金屬當催化劑，以SLS機制成長了矽奈米線及鍺奈米線，並且對奈米線特性及場發射的應用進行了研究。研究過程中，利用掃描式電子顯微鏡(scanning electron microscopy, SEM)及穿透式電子顯微鏡(transmission electron microscopy, TEM)觀察奈米線的表面形態及幾何結構，並使用能量散射光譜儀EDS(electron dispersive spectrometer, EDS)分析奈米線的表面結構與組成成份。此實驗中，矽奈米線以厚度5-25 nm的催化鎳膜在1000 °C的成長溫度中成功地被成長出來，並且，鍺奈米線以厚度1-9 nm的催化金膜在550 -650 °C的成長溫度中也成功地被成長出來。從量測結果得知，矽奈米線及鍺奈米線的最小平均直徑分別為38.5 nm 及45.5 nm，兩種奈米線的長度可長達數微米。比較矽奈米線和鍺奈米線的微形態及結構得知，矽奈米線比較長，因此矽奈米線會有比較大的高寬比。顯然，矽奈米線與鍺奈米線的表面型態並不相同。矽奈米線比較彎曲，而鍺奈米線比較筆直。然而，兩種奈米線的表面皆被一層氧化層所環繞，其成分結構分別為SiO_x 及GeO_x (x)

關鍵詞：矽奈米線、鍺奈米線、場發射

目錄

封面內頁 簽名頁 博碩士論文暨電子檔案上網授權書.....	iii Abstract.....iv
中文摘要.....vi Acknowledgements.....viii Table of	
Contents.....ix List of Figures.....xii List of	
Tables.....xv Chapter 1 Introduction.....1	
1.1Background.....1 1.2Purpose of Investigation.....2 1.3Outline of This	
Thesis.....3 Chapter 2 Growth Mechanisms of Nanowires.....5	
2.1Introduction.....5 2.2Vapor – Liquid – Solid (VLS) Growth Mechanism.....5 2.3Vapor-Solid	
(VS) Growth Mechanism.....7 2.4Solution-Liquid-Solid (Solution-LS) Growth Mechanism.....9 2.5Solid-Liquid-Solid	
(SLS) Growth Mechanism.....10 Chapter 3 Growth Techniques for Nanowires.....14	
3.1Introduction.....14 3.2Laser Ablation Technology.....14 3.3Molecular-Beam Epitaxy	
(MBE).....16 3.4Thermal Evaporation.....18 Chapter 4 General Preparative Methodology and	
Characterization Techniques.....23 4.1Introduction.....23 4.2Preparation	
of Metal Catalyst Film.....24 4.3Growth of Nanowires by SLS Mechanism.....25 4.4Sample	
Characterization.....26 4.4.1Scanning Electron Microscopy.....27 4.4.2Energy Dispersive X-ray	
Spectrometry.....28 4.4.3Transmission Electron Microscope (TEM).....29 4.5Field Emission Property	
Analyses.....30 Chapter 5 Synthesis and Characterization of Silicon Nanowires and Germanium	
Nanowires.....32 5.1Thickness of Catalytic Ni Layer Dependence of Morphology and Diameter of Silicon	
Nanowires Synthesized by SLS Mechanism.....32 5.1.1Introduction.....32	
5.1.2Experimental.....33 5.1.3Results and Discussion.....34	
5.1.4Conclusions.....36 5.2Temperature Dependence of Morphology and Diameter of Germanium	
Nanowires Synthesized by SLS Mechanism.....43 5.2.1Introduction.....43	
5.2.2Experimental.....43 5.2.3Results and discussion.....44	
5.2.4Conclusions.....46 5.3Thickness of Catalytic Layer Dependent Shape Transformation of Ge	
Nanostructures by the Solid-Liquid-Solid Method.....51 5.3.1Introduction.....51	
5.3.2Experimental.....51 5.3.3Results and Discussion.....51	
5.3.4Conclusions.....53 5.4The Contrast of Morphologies between SiNWs and GeNWs.....59 Chapter 6	
Enhancement of Field-Emission From Silicon Nanowires by Tetrafluoride Plasma Treatment.....61	
6.1Introduction.....61 6.2Experimental.....62 6.3Results and	
Discussion.....63 6.4Conclusions.....67 Chapter 7 Summary and	
Conclusion.....76 7.1Summary and Results.....76 7.2Recommendations for Further	
Work.....77 References.....79 Vita.....86	

參考文獻

- [1]R. Wang, G. Zhou, Y. Liu, S. Pan, H. Zhang, D. Yu, and Z. Zhang, Raman spectral study of SiNWs: High-order scattering and phonon confinement effects, *Phys. Rev. B* 61 (2000) 16827-16832.
- [2]S. C. Tsang, Y. K. Chen, P. J. F. Harris, and M. L. H. Green, A simple chemical method of opening and filling carbon nanotubes, *Nature* 372 (2002) 159 – 162.
- [3]W. K. Hsu, M. Terrones, H. Terrones, N. Grobert, A. I. Kirkland, J. P. Hare, K. Prassides, P. D. Townsend, K. W. Kroto, and D. R. M. Walton, Electrochemical formation of novel nanowires and their dynamic effects, *Chem. Phys. Lett.* 284 (1998) 177-183.
- [4]Y. Wu, R. Fan, and P. Yang, Block-by-block growth of single-crystalline Si/SiGe superlattice nanowires, *Nano Lett.* 2 (2002) 83 – 86.
- [5]R. N. Musin and X-Q. Wang, Structural and electronic properties of epitaxial core-shell nanowire heterostructures, *Phys. Rev. B* 71 (2005) 155318-155321.
- [6]Ajay Agarwal, K. Buddharaju, I. K. Lao, N. Singh, N. Balasubramanian, and D. L. Kwong, Silicon nanowire sensor array using top – down CMOS technology, *Sensors and Actuators A* 145 – 146 (2008) 207 – 213.
- [7]Inkyu Park, Zhiyong Li, Xuema Li, Albert P. Pisano, and R. Stanley Williams, Towards the silicon nanowire-based sensor for intracellular biochemical detection, *Biosens. & Bioelectron.* 22 (2007) 2065 – 2070.
- [8]M. Hofheinz, X. Jehl, M. Sanquer, G. Molas, M. Vinet, and S. Deleonibus, Simple and controlled single electron transistor based on doping modulation in silicon nanowires, *Appl. Phys. Lett.* 89 (2006) 143504-143506.
- [9]J. Zhang, Y. Yang, F. Jiang, J. Li, B. Xu, S. Wang, and X. Wang, Fabrication of semiconductor CdS hierarchical nanostructures, *J. Cryst. Growth* 293 (2006) 236 – 241.
- [10]T. Q. Jia, H. X. Chen, M. Huang, X. J. Wu, F. L. Zhao, M. Baba, M. Suzuki, H. Kuroda, J. R. Qiu, R. X. Li, and Z. Z. Xu, ZnSe nanowires grown on the crystal surface by femtosecond laser ablation in air, *Appl. Phys. Lett.* 89 (2006) 101116-101118.
- [11]J. C. Harmand, G. Patriarche, N. P?臘??Laperne, M-N. M?臘at-Combes, L. Travers, and F. Glas, Analysis of vapor – liquid – solid mechanism in Au-assisted GaAs nanowire growth, *Appl. Phys. Lett.* 87 (2005) 203101-203103.
- [12]H. D. Park, S. M. Prokes, M. E. Twigg, R. C. Cammarata, and A-C. Gaillot, Si assisted growth of InAs nanowires, *Appl. Phys. Lett.* 89 (2006) 223125-223127.
- [13]Z. G. Bai, D. P. Yu, H. Z. Zhang, Y. Ding, Y. P. Wang, X. Z. Gai, Q. L. Hang, G. C. Xiong, and S. Q. Feng, Nano-scale GeO₂ wires synthesized by physical evaporation, *Chem. Phys. Lett.* 303 (1999) 311 – 314.
- [14]H. Z. Zhang, Y. C. Kong, Y. Z. Wang, X. Du, Z. G. Bai, J. J. Wang, D. P. Yu, Y. Ding, Q. L. Hang, and S. Q. Feng, Ga₂O₃ nanowires prepared by physical evaporation, *Solid State Communications* 109 (1999) 677 – 682.
- [15]Hyun D. Park and S. M. Prokes, Study of the initial nucleation and growth of catalyst-free InAs and Ge nanowires, *Appl. Phys. Lett.* 90 (2007) 203104-1~203104-3.
- [16]Hwa Young Kim, Jeunghee Park, and Hyunik Yang, Synthesis of silicon nitride nanowires directly from the silicon substrates, *Chem. Phys. Lett.* 372 (2003) 269-274.
- [17]Bohr-Ran Huang, Jung-Fu Hsu, Chien-Sheng Huang, Yu-Tai Shih, and Kao-Sheng Lu, Silicon nanowire networks for the application of field effect phototransistor, *Mater. Sci. Eng. C* 27 (2007) 1197 – 1200.
- [18]H. C. Lin, M. H. Lee, C. J. Su, T. Y., Huang, C. C. Lee, and Y. S. Yang, A simple and low-cost method to fabricate TFTs with poly-Si nanowire channel, *IEEE Electron Device Lett.* 26 (2005) 643-645.
- [19]Q. H. Wang, A. A. Setlur, J. M. Lauerhaas, J. Y. Dai, E. W. Seeling and R. P. H. Chang, A nanotube-based field-emission flat panel display, *Appl. Phys. Lett.* 72 (1998) 2912-2913.
- [20]A. I. Klimovskaya, O. E. Raichev, A. A. Dadykin, Yu. M. Litvina, P. M. Lytvyn, I. V. Prokopenko, T. I. Kaminsc, S. Sharmac, and Yu. Moklyak, Quantized field-electron emission at 300K in self-assembled arrays of silicon nanowires, *Physica E* 37 (2007) 212 – 217.
- [21]Y. Maeda, N. Tsukamoto, Y. Yazawa, Y. Kanemitsu, and Y. Masumoto, Visible photoluminescence of Ge microcrystals embedded in SO₂ glassy matrices, *Appl. Phys. Lett.* 59 (1991) 3168.
- [22]R. S. Wagner and W. C. Ellis, Vapor-liquid-solid mechanism of single crystal growth and its application to silicon, *Appl. Phys. Lett.* 4 (1964) 89-90.
- [23]J. Westwater, D. P. Gosain, S. Tomiya, and S. Usui, Growth of silicon nanowires via gold /silane vapor-liquid-solid reaction, *J. Vac. Sci. Tech. B* 15 (1997) 554-557.
- [24]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 (2001) 803-808.
- [25]L. Dai, X. L. Chen, T. Zhou, and B. Q. Hu, Aligned silica nanofibres, *J. Phys. Condens. Matter.* 14 (2002) 473-477.
- [26]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 (2003) 625-627.
- [27]J. D. Holmes, K. P. Johnston, R. C. Doty, and B. A. Korgel, Control of thickness and orientation of solution-grown silicon nanowires, *Science*

- [28] Timothy J. Trentler, Kathleen M. Hickman, Subhash C. Goel, Ann M. Viano, Patrick C. Gibbons, and William E. Buhro, Solution-liquid-solid growth of crystalline III-V semiconductors: an analogy to vapor-liquid-solid growth, *Science* 270 (1995) 1791-1794.
- [29] 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 (2000) 224-228.
- [30] Y. J. Xing, Z. H. Xi, Z. Q. Xue, and D. P. Yu, Diameter modification of Si nanowires via catalyst size, *Chinese. Phys. Lett.* 20 (2003) 700.
- [31] 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 novel structures with SiONWs on their surfaces, *Appl. Phys. A: Mater. Sci. & Processing* 76 (2003) 999-1002.
- [32] C. Y. Wang, L. H. Chan, D. Q. Xiao, T. C. Lin, and H. C. Shih, Mechanism of solid-liquid-solid on the silicon oxide nanowire growth, *J. Vac. Sci. Technol. B* 24 (2006) 613-617.
- [33] B. T. Park and K. Yong, Controlled growth of core – shell Si – SiO_x and amorphous SiO₂ nanowires directly from NiO/Si, *Nanotechnology* 15 (2004) 365-370.
- [34] 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 (2003) 341-345.
- [35] D. P. Yu, C. S. Lee, I. Bello, G. W. Zhou, Z. G. Bai, Z. Zhang, and S. Q. Feng, Synthesis of nano-scale silicon wires by excimer laser ablation at high temperature, *Solid State Commun.* 105 (1998) 403-407.
- [36] G. Zhou, Z. Zhang, and D. P. Yu, Growth morphology and micro-structural aspects of Si nanowires synthesized by laser ablation, *J. Cryst. Growth* 197 (1999) 129-135.
- [37] Y. F. Zhang, Y. H. Tang, N. Wang, D. P. Yu, C. S. Lee, I. Bello, and S. T. Lee, Silicon nanowires prepared by laser ablation at high temperature, *Appl. Phys. Lett.* 72 (1998) 1835-1837.
- [38] Y. Q. Chen, K. Zhang, B. Miao, B. Wang, and J. G. Hou, Temperature dependence of morphology and diameter of silicon nanowires synthesized by laser ablation, *Chem. Phys. Lett.* 358 (2002) 396 – 400.
- [39] N. Fukata, T. Oshima, N. Okada, T. Kizuka, T. Tsurui, S. Ito, and K. Murakami, Phonon confinement in silicon nanowires synthesized by laser ablation, *Physica B : Condensed Matter.* 376 – 377 (2006) 864 – 867.
- [40] J. L. Liu, S. J. Cai, G. L. Jin, S. G. Thomas, and K. L. Wang, Growth of Si whiskers on Au/Si (111) substrate by gas source molecular beam epitaxy (MBE), *J. Cryst. Growth* 200 (1999) 106-111.
- [41] L. Schubert, P. Werner, N. D. Zakharov, G. Gerth, F. M. Kolb, L. Long, and U. Go sele, Silicon nanowiskers grown on (111) Si substrates by molecular-beam epitaxy, *Appl. Phys. Lett.* 84 (2004) 4968-4970.
- [42] Z. G. Bai, D. P. Yu, H. Z. Zhang, Y. Ding, Y. P. Wang, X. Z. Gai, Q. L. Hang, G. C. Xiong, and S. Q. Feng, Nano-scale GeO₂ wires synthesized by physical evaporation, *Chem. Phys. Lett.* 303 (1999) 311 – 314.
- [43] D. P. Yu, Z. G. Bai, Y. Ding, Q. L. Hang, H. Z. Zhang, J. J. Wang, Y. H. Zou, W. Qian, G. C. Xiong, H. T. Zhou, and S. Q. Feng, Nanoscale silicon wires synthesized using simple physical evaporation, *Appl. Phys. Lett.* 72 (1998) 3458-3460.
- [44] 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* 9 (2001) 305 – 309.
- [45] J. Niu, J. Sha, and D. Yang, Silicon nanowires fabricated by thermal evaporation of silicon monoxide, *Physica E* 23 (2004) 131-134.
- [46] V. Sivakov, F. Heyroth, F. Falk, G. Andra, and S. Christiansen, Silicon nanowire growth by electron beam evaporation: Kinetic and energetic contributions to the growth morphology, *J. Cryst. Growth* 300 (2007) 288 – 293 [47] 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 (2002) 1164 – 1167.
- [48] K. Q. Peng, Y. J. Yang, S. P. Gao, and J. Zhu, Dendrite-assisted growth of silicon nanowires in electroless metal deposition, *Adv. Funct. Mater.* 13 (2003) 127 – 132.
- [49] K. Q. Peng and J. Zhu, Morphological selection of electroless metal deposits on silicon in aqueous fluoride solution, *Electrochimica Acta* 49 (2004) 2563-2568.
- [50] Y. L. Chueh, L. J. Chou, S. L. Cheng, J. H. He, W. W. Wu, and L. J. Chen, Synthesis of taperlike Si nanowires with strong field emission, *Appl. Phys. Lett.* 86 (2005) 133112-1~133112-3.
- [51] Y-L. Chueh, C. N. Boswell, C-W. Yuan, S. J. Shin, K. Takei, J. C. Ho, H. Ko, Z. Fan, E. E. Haller, D. C. Chrzan, and A. Javey, Nanoscale structural engineering via phase segregation: Au-Ge System, *Nano Lett.* 10 (2010) 393-397.
- [52] N. O. V. Plank, L. Jiang, and R. Cheung, Fluorination of carbon nanotubes in CF₄ plasma, *Appl. Phys. Lett.* 83(12) (2003) 2426 – 2428.
- [53] T. C. Cheng, J. Shieh, W. J. Huang, M. C. Yang, and M. H. Cheng, Hydrogen plasma dry etching method for field emission application, *Appl. Phys. Lett.* 88 (2006) 263118-263120.
- [54] S. F. Lee, Y. P. Chang, and L.Y. Lee, Enhancement of field emission characteristics for multi-walled carbon nanotubes treated with a mixed solution of chromic trioxide and nitric acid, *Acta Physico-Chimica Sinica* 24 (2008) 1411-1416.
- [55] M. Sekine, Dielectric film etching in semiconductor device manufacturing: Development of SiO₂ etching and the next generation plasma reactor, *Appl. Surf. Sci.* 192 (2002) 270-298.

- [56] K. Ishikawa, M. Okigawa, Y. Ishikawa, S. Samukawa, and S. Yamasaki, In vacuo measurements of dangling bonds created during Ar-diluted fluorocarbon plasma etching of silicon dioxide films, *Appl. Phys. Lett.* 86 (2005) 264104-264106.
- [57] R. Kniziković, Simulation of Si and SiO₂ etching in CF₄ plasma, *Vacuum* 82 (2008) 1191 – 1193.
- [58] Chun Li, Guojia Fang, Su Sheng, Zhiqiang Chen, Jianbo Wang, Shuang Ma, Xingzhong Zhao, Raman spectroscopy and field electron emission properties of aligned silicon nanowire arrays, *Physica E* 30 (2005) 169-173.
- [59] Ha Jin Kim, In Taek Han, Young Jun Park, Jong Min Kim, Jong Bong Park, Bum Kwon Kim, and Nae Sung Lee, Synthesis of hybrid multiwall carbon nanotubes and their enhanced field emission properties, *Chem. Phys. Lett.* 396 (2004) 6 – 9.
- [60] Y-M. Shyu and F. C-N. Hong, Low-temperature growth and field emission of aligned carbon nanotubes by chemical vapor deposition, *Mater. Chem. Phys.* 73 (2001) 223-227.
- [61] 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 (1999) 1700.