經由固液固機制成長鍺奈米線

蔡耀鋒、李世鴻;蔡渙良

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

摘要

本研究在鍺基板上蒸鍍(1~9 nm)的金催化劑金屬以及3 nm的鎳催化劑金屬去成長鍺奈米線,並改變不同金催化劑厚度、不同成長溫度以及不同催化劑金屬去探討各種變數對鍺奈米線的影響。

由實驗結果可總結出以下的結論,如果將催化劑金膜厚度增大,在成核階段會形成尺寸較大的催化劑顆粒,而所析出的鍺 奈米線的直徑也會較大,而溫度對鍺奈米線的成長影響很大。在成長溫度在550°C到600°C這之間,我們觀察到隨著溫 度的增加鍺奈米線的長度會增加,但是成長溫度在625°C、650°C時因為成長溫度過高,所以鍺奈米線的數量會變少, 且會產生捲曲的鍺奈米線。鎳催化劑金屬所成長的鍺奈米線推測由於成長溫度太高所以會長出Z字型的鍺奈米線。

關鍵詞: 鍺奈米線、金鍺合金

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
中文摘要iv
ABSTRACTv
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-Solid25
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

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 鎳催化劑金屬對鍺奈米線成長的影響與討論.......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 4.6.3 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

[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. Alivisators, 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 arge-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. Tombler, 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 of 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 SiOx 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 SiOx 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. Sekiquchi, and D. Golberg, Self-assembly of SiO2 nanowires and Si microwires into hierarchiral 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-Assited 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/SiOx 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. 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 SiOx nanowires on their surface, Appl. Phys. Lett., 76, 999-1002 (2003).

[77]B. T. Park, and K. Yong, Controlled growth of core – shell Si – SiOx 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. Nanosic. 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).