Direct synthesis, characterization and modification of SiC nanowires

Kijung Yong, Yonghwan Ryu, Youngjo Tak
Surface Chemistry Lab. Of Electronic Materials, Department of Chemical Engineering, Pohang University of Science and Technology, San 31, Hyoja-dong, Nam-gu, Pohang, Kyungbuk 790-784, Korea

It is well known that nanostructures with the sharp tip are promising materials for the applications as the cold cathode field emission devices [1-7]. Various types of nanomaterials have attracted much attention as electron emitters for field emission display (FED) applications, including carbon nanotubes [1,2], tungsten/tungsten oxide nanowires [3], molybdenium/ molybdenium oxide nanowires [4], zinc oxide nanoneedles [5], silicon [6] and silicon carbide nanowires [7], etc. Among these materials, recent field emission measurements on the SiC nanowires suggest that the SiC nanowires are potential candidates for the cold cathode FED because of their unique electrical, chemical, and mechanical properties [8]. Various synthesis methods have been explored to produce SiC nanowires including laser ablation [9], physical evaporation [10], and chemical vapor deposition (CVD) [11]. Most previous methods required vacuum environment and silicon/carbon source materials to grow SiC nanowires on the substrate. Basically in those methods, silicon/carbon source vapors are delivered onto the substrate to grow SiC nanostructures. In this work we report a simple, direct synthesis of the crystalline SiC nanowires achieved by heating the Si substrate in Ar-ambient atmosphere without using any additional silicon source materials. Si substrates were used as a Si source material and WO_3/C carbothermal reduction provided carbon source to grow SiC nanowires.

The growth of the crystalline SiC nanowires cladded with the amorphous SiO_x was carried out in a tube furnace. The substrates used in our experiments were 0.003 Ω-cm n-type Si (100) wafers (3×5 cm^2). The silicon substrates were dipped in the $Ni(NO_3)_2$/ethanol solution after being cleaned in an ultrasonic acetone bath for 20 min. After drying in the air, the substrates were put in a long quartz tube and purged by 1000 sccm Ar (high-purity argon, 99.99%) flow for 1 h. The nanowires were synthesized in the temperature range of 1000-1100 °C for 3 h under a constant 500 sccm Ar flow. To synthesize the core-shell

nanowires, the WO_3 and graphite mixed powders were used to provide reductive environment. A carbothermal reduction of WO_3 by C produces CO/CO_2 reducing agents [12] and also carbon sources. After cooling down to room temperature, the surface of the Si substrate was covered with a white colored deposit. To remove the SiO_x shell layer from the core-shell nanowires, a dilute HF acid solution was used. The field emission measurements were carried out in a vacuum chamber at a pressure of ~ 1.0×10^{-4} torr at room temperature. The n-type silicon substrate was used as the cathode and a glass plate pre-coated with the indium tin oxide (ITO, 100 nm, polished) was used as the anode. The cathode was connected to a 700kΩ resistor. The edges of silicon substrate cathode were covered with scotch tapes to minimize edge effects. The scotch tapes also separated anode from cathode as spacers with thickness of 200 μm. The electric field was estimated by the applied voltage per the anode-cathode separation (*V/d*). The emission current density was calculated from the obtained emission current and the cathode surface area (6.46 cm^2). The current density–electric field curve was obtained after sweeping the voltage several times.

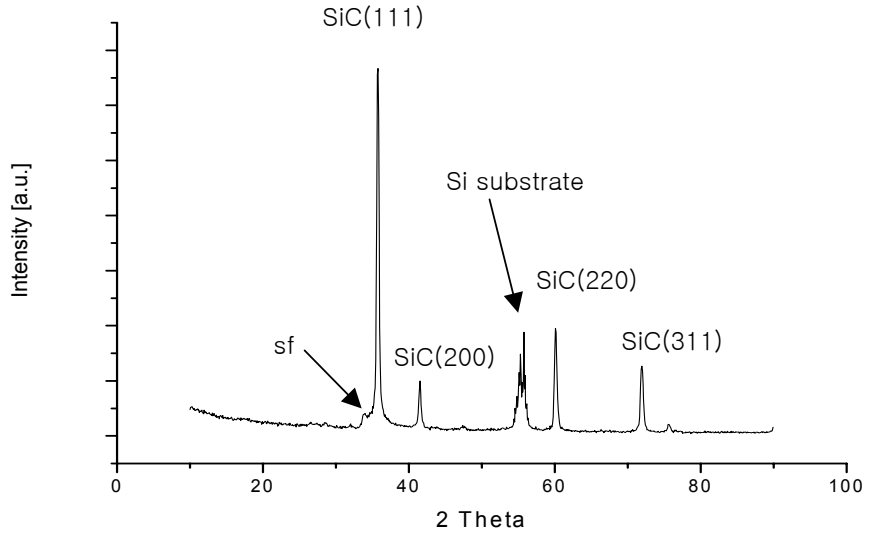

Figure 1. XRD pattern of the carbon-coated SiC nanowires. The crystal phases (111), (200), (220), and (311) of SiC are denoted, and *sf* indicates a diffraction peak due to the stacking faults in the SiC crystal. A XRD peak from the bare Si substrate is also shown.

The crystallinity of nanowires was investigated using X-ray diffraction (XRD). The XRD pattern of the nanowires is shown in figure 1. It shows a typical XRD pattern of the β-SiC crystal, which was obtained from SiC nanowires

directly grown on the Si substrate. Peaks corresponding to the Si substrate and the stacking faults (sf) of SiC were also found. Figure 2 shows SEM image of the HF treated nanowires. SEM image clearly reveals a uniform diameter distribution in the range 20 ~ 50 nm. The surface of nanowires was clean without any particles. The internal structure of nanowires was investigated using high-resolution transmission electron microscopy (HRTEM). Figure 3 is a typical image of the synthesized nanowires. The atomic arrangements of the SiC core-nanowire were clearly seen in the HRTEM image. It shows the (111) fringes perpendicular to the wire axis are on average separated by 0.25 nm, indicating the crystalline SiC nanowire growth along the [111] direction.

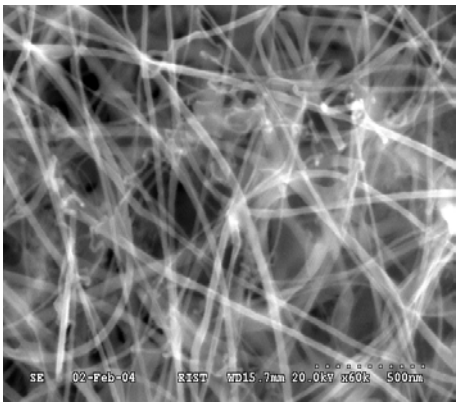

Figure 2. High-magnification SEM image of the SiC nanowires.

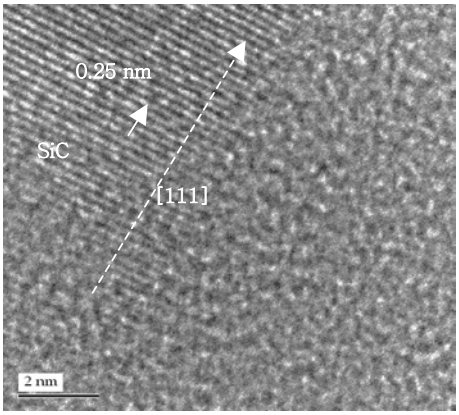

Figure 3. HRTEM image of SiC nanowires. The core SiC nanowire shows the (111) planes perpendicular to the wire axis with an average spacing of 0.25 nm.

The field emission current density SiC nanowires directly grown from Si was presented in figure 4. It shows the field emission current density as a

function of the applied electric field. The current density–electric field curve was obtained after sweeping the voltage several times. The E_{to} (turn on electric field) of our SiC nanowires was about 4.0 V/μm in the current density vs. electric field graph.

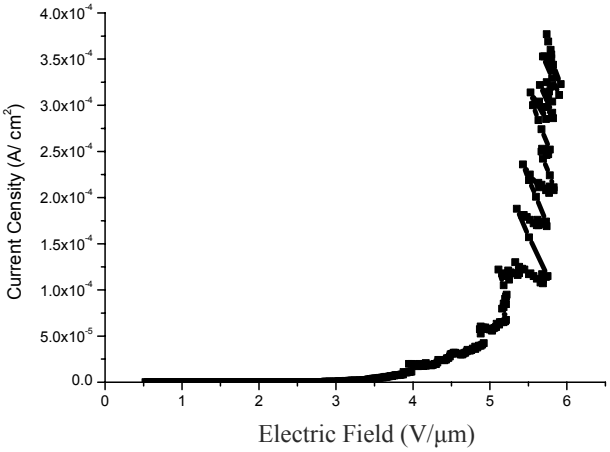

Figure 4. Current density (A/cm^2)-electric field (V/μm) characteristics of the SiC nanowire emitters. The turn-on field was 4.0 V/μm to generate emission current density of 10 $\mu A/cm^2$.

A hetero-junction of SiC-ZnO nanowires was also produced using vapor-solid method. This interesting hetero-junction of nanowires has potential applications in fabrication of nano-devices.

References

[1] Shoushan Fan, Michael G, Chapline, Nathan R. Franklin, Thomas W. Tombler, Alan M. Cassell. Hongjie Dai 1999 *Science* **283** 512.

[2] Juntao Li, Wei Lei, Xiaobing Zhang, Xuedong Zhou, Qilong Wang, Yuning Zhang, Baoping Wang 2003 *Appl. Surf. Sci.* **220** 96

[3] Yubao Li, Yoshio Bando, Dmitri Golberg 2003 *Adv. Mater.***15** 1294.

[4] Jun Zhou, Ning-Sheng Xu, Shao-Zhi Deng, Jun Chen, Jun-Cong She, Zhong-Lin Wang 2003 *Adv. Mater.* **15** 1835.

[5] Y. B. Li, Y. Bando, D. Golberg 2004 *Appl. Phys. Lett.* **84** 3603.

[6] Frerderic C. K. Au, K. W. Wong, Y. H. Tang, Y. F. Zhang, I. Bello, S. T. Lee 1999 *Appl. Phys. Lett.* **75** 1700

[7] Z. S. Wu, S. Z. Deng, N.S. Xu, Jian Chen, J. Zhou, Jun Chen 2002 *Appl. Phys. Lett.* **80** 3829

[8] Robert F. Davis, J. W. Palmour, J. A. Edmond 1992 *Diamond and Related Materials* **1** 109

[9] W. Shi, Y. Zheng, H. Peng, N. Wang, C. S. Lee and S. T. Lee 2000 *J. Am. Chem. Soc.* **83** 3228

[10] Z. S. Wu, S. Z. Deng, J. Chen and J. Zhou 2002 *Appl. Phys. Lett.* **80** 3829

[11] H. F. Zhang, C. M. Wang and S. L. Wang 2002 *Nano Lett.* **2** 941

[12] X. H. Sun, S. D. Wang, N. B. Wong, D.D.D. Ma, S. T. Lee and B. K. 2003 Teo, *Inorg. Chem.* **42**, 2398