Electronic Supplementary Information

Current Emission from P-doped SiC Nanowires with Ultralow Turn-on Fields

Shanliang Chen, Minghui Shang, Zuobao Yang, Jinju Zheng, Lin Wang, Qiao Liu,

Fengmei Gao and Weiyou Yang**

Institute of Materials, Ningbo University of Technology, Ningbo City, 315016, P.R. China.

Corresponding Author:

E-mail: fmgao@163.com (F. Gao) and weiyouyang@tsinghua.org.cn (W. Yang)

Tel: +86-574-87080966, ***Fax:*** +86-574-87081221

*Corresponding authors. E-mails: fmgao@163.com (F. Gao) and weiyouyang@tsinghua.org.cn (W. Yang)

Tel: +86-574-87080966, Fax: +86-574-87081221.

Mechanism for the Growth of P-doped SiC Nanowires

The growth of P-doped SiCNWs with high aspect ratio *via* the pyrolysis of polysilazane (PSN) precursors should undergo a typical vapor-liquild-solid (VLS) mechanism, which performs the typical process as followings: i) The PSN polymeric precursors are converted into metastable SiCN amorphous ceramics when heated up to 1000°C[1] and the vapor phases such as SiO and CO are released as the temperature continues to rise.[2] ii) With the further increase of the temperatures, the vapor phases would react with the molten catalyst, leading to the formation of Co catalyst alloy droplets on the substrate surface; iii) During the decrease of the temperatures, the continuous dissolution and precipitation of vapor phases within the liquid catalytic droplets would initiate the nucleation and growth of SiC nanowires by Reaction (1). Meanwhile, the P atoms coming form the decomposition of $FePO_4 \cdot H_2O$ power would undergo the similar dissolution and precipitation process, which leads to the incorporation of P into the crystal lattice *via* the formations of substitutional solid solutions.[3]

$$SiO_{(g)} + 3CO_{(g)} = SiC_{(s)} + CO_{2(g)} \quad \text{(1)}$$

The just-formed SiC nucleus during the initiate cooling process should be a two-dimensional (111) seed disc on the graphite paper substrate surface to maintain the minimum surface energy of the crystal,[4,5] which will be the first (111) plane of a subsequent SiC nanowire. More (111) plane piled up on the just-formed nucleus as the temperature continues to decrease, resulting the growth of the 1D SiC nanowires with the [111] direction and high aspect ratio.

For the growth of 1D SiC nanostructures based on the VLS process, the catalyst droplets cannot be considered as an adiabatic or isothermal system, because of the radiative losses and conductive heat transfer between the droplets and surrounding vapors.[6] The Ar pyrolysis atmosphere with a low thermal

conductivity (0.01795 $W(m \cdot k)^{-1}$) around the catalyst droplets would obstacle the heat transfer and make the droplet temperature drops slower, which allows the droplet temperature higher than that of the furnace, thus facilitate the thermal evaporation of droplet and resulting in the grown SiC nanowires with a small catalyst droplet and body diameter.[7] The other case driving the growth of the SiCNNW with high aspect ratio could be ascribed to the fixed cooling rate. Compared with the previous reports,[8-10] the cooling rate (25°C/min) in the present work is much slower, which facilitate the growth of nanowires and the thermal evaporation of droplet, and lead to the SiC nanowires present large lengths. In a brief word, the low thermal conductivity of pyrolysis atmosphere and low cooling rate finally make the growth of P-doped SiC nanowires with high aspect ratio and clear tips.

Table S1 The field emission current densities of typical SiC and other nanowire systems.

Emitters	Field emission current density, test time, current fluctuations	Ref.
N-doped SiC nanoneedles	1138 μA/cm^2, 1 h, 8.1%	11
Well-aligned SiC nanowires	693.3 μA/cm^2, 4 h, 3.8%	12
Amorphous carbon coated SiC nanowires	2.0 *m*A/cm^2, 2 h, ＜5%	13
B-doped SiC nanoneedle arrays	512.9-514.5 μA/cm^2, 8 h, 6.5-7.8%	14
N-doped SiC nanoneedles	~1100 μA/cm^2, 1 h, 7.7%-14.1%	15
B-doped 3*C*-SiC nanowires	~85 μA/cm^2, 10 h, 11-14%	16
n-type SiC nanoneedles	1.7 *m*A/cm^2, 30 min, --	17
Aligned SiC porous nanowires	570 μA/cm^2, 20 h, --	18
Nonaligned SiC nanowires	60 μA/cm^2, 2 h , ±15%	19
P-doped SiC nanowires	~770-960 μA/cm^2, 5 h, ~±4.1-±4.5%	this work
Al nanoparticles decorated carbon nanotubes	~700-850 μA/cm^2, ~4000 s, --	20
Regular arrays of carbon nanotubes	~0.5 *m*A/cm^2, 20, --	21
ZnO nanowires-on-nanoplate structures	~530 μA/cm^2, 1000 min, ＜9.4%	22
Layered VS_2/ZnO nanocomposite	0.4 *m*A/cm^2, 4 h, --	23
Single-crystalline PrB_6 nanorods	~25 μA/cm^2, 1000 min, ＜10%	24
Single-crystalline LaB_6 nanowires	~0.5 *m*A/cm^2, 1000 min, ＜6.0%	25
Oriented CuO nanoknife arrays	1.15 *m*A/cm^2, ~1.5 h, ~5%	26
SnO_2 nanowires	~1 *m*A/cm^2, 40 h, --	27
Branched ZnS nanotube-in nanowires structures	~0.3 *m*A/cm^2, 3 h, --	28
Ordered CdS nanostructure arrays	~0.1 *m*A/cm^2, 5 h, --	29
Tungsten oxide nanowires	5.25 *m*A/cm^2, 1 h, ~5%	30

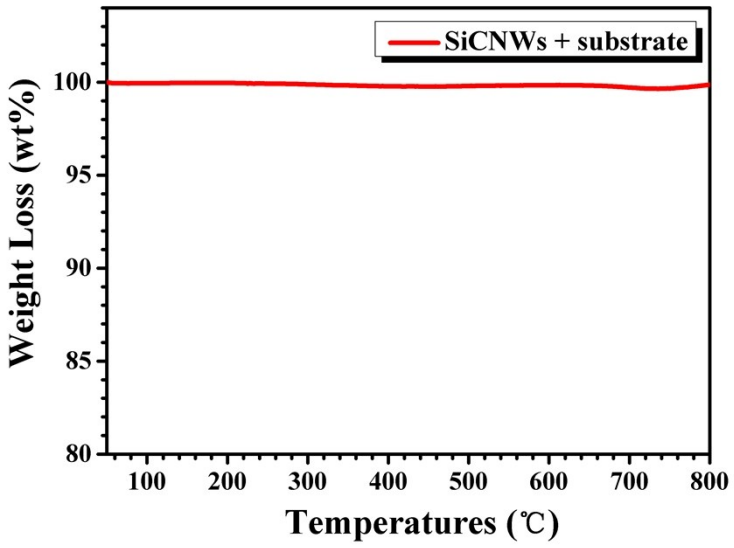

Fig. S1 The thermal stability of as-synthesized P-doped SiCNWs.

References

1 A. Dhamne, W. Xu, B. Fookes, Y. Fan, L. Zhang, S. Burton, J. Hu, J. Ford and L. An, *J. Am. Ceram. Soc.*, 2005, **88**, 2415.

2 Y. Li, Y. Liang and Z. Hu, *Ceram. Int.*, 1995, **21**, 59.

3 S. Chen, M. Shang, F. Gao, L. Wang, P. Ying, W. Yang and X. Fang, *Adv. Sci.*, 2016, **3**, 1500256.

4 R. Wu, K. Zhou, J. Wei, Y. Huang, F. Su, J. Chen and L. Wang, *J. Phys. Chem. C*, 2012, **116**, 12940.

5 G. Yang, H. Cui, Y. Sun, L. Gong, J. Chen, D. Jiang and C. Wang, *J. Phys. Chem. C*, 2009, **113**, 15969.

6 D. Zhang, A. Alkhateeb, H. Han, H. Mahmood, D. McIlroy and M. Norton, *Nano Lett.*, 2003, **3**, 983.

7 S. Chen, P. Ying, L. Wang, F. Gao, G. Wei, J. Zheng, Z. Xie and W. Yang, *RSC Adv.*, 2014, **4**, 8376.

8 S. Chen, P. Ying, L. Wang, G. Wei, J. Zheng, F. Gao, S. Su and W. Yang, *J. Mater. Chem. C*, 2013, **1**, 4779.

9 G. Wei, H. Liu, C. Shi, F. Gao, J. Zheng, G. Wei and W. Yang, *J. Phys. Chem. C*, 2011, **115**, 13063.

10 X. Zhang, Y. Chen, Z. Xie and W. Yang, *J. Phys. Chem. C*, 2010, **114**, 8251.

11 S. Chen, P. Ying, L. Wang, G. Wei, F. Gao, J. Zheng, M. Shang, Z. Yang, W. Yang and T. Wu, *NPG Asia Mater.*, 2015, **7**, e157.

12 L. Wang, C. Li, Y. Yang, S. Chen, F. Gao, G. Wei and W. Yang, *ACS Appl. Mater. Inter.*, 2015, **7**, 526.

13 M. Zhang, Z. Li, J. Zhao, L. Gong, A. Meng, X. Liu, X. Fan and X. Qi, *J. Mater. Chem. C*, 2015, **3**, 658.

14 L. Wang, G. Wei, F. Gao, C. Li and W. Yang, *Nanoscale*, 2015, **7**, 7585.

15 S. Chen, P. Ying, L. Wang, G. Wei and W. Yang, *Appl. Phys. Lett.*, 2014, **105**, 133106.

16 Y. Yang, H. Yang, G. Wei, L. Wang, M. Shang, Z. Yang, B. Tang and W. Yang, *J. Mater. Chem. C*, 2014, **2**, 4515.

17 X. Zhang, Y. Chen, W. Liu, W. Xue, J. Li and Z. Xie, *J. Mater. Chem. C*, 2013, **1**, 6479.

18 Y. Yang, G. Meng, X. Liu, L. Zhang, Z. Hu, C. He and Y. Hu, *J. Phys. Chem. C*, 2008, **112**, 20126.

19 W. Zhou, Y. Wu, E. Kong, F. Zhu, Z. Hou and Y. Zhang, *Appl. Surf. Sci.*, 2006, **253**, 2056.

20 S. Sridhar, C. Tiwary, S. Vinod, J. Taha-Tijerina, S. Sridhar, K. Kalaga, B. Sirota, A. Hart, S. Ozden and R. Sinha, *ACS Nano*, 2014, **8**, 7763.

21 S. Fan, M. Chapline, N. Franklin, T. Tombler, A. Cassell and H. Dai, *Science*, 1999, **283**, 512.

22 J. Song, S. Kulinich, J. Yan, Z. Li, J. He, C. Kan and H. Zeng, *Adv. Mater.*, 2013, **25**, 5750.

23 C. Song, K. Yu, H. Yin, H. Fu, Z. Zhang, N. Zhang and Z. Zhu, *J. Mater. Chem. C*, 2014, **2**, 4196.

24 Q. Zhang, J. Xu, Y. Zhao, X. Ji and S. Lau, *Adv. Funct. Mater.*, 2009, **19**, 742.

25 J. Xu, G. Hou, H. Li, T. Zhai, B. Dong, H. Yan, Y. Wang, B. Yu, Y. Bando and D. Golberg, *NPG Asia Mater.*, 2013, **5**, e53.

26 S. Das, S. Saha, D. Sen, U. Ghorai, D. Banerjee and K. Chattopadhyay, *J. Mater. Chem. C*, 2014, **2**, 1321.

27 X. Fang, J. Yan, L. Hu, H. Liu and P. Lee, *Adv. Funct. Mater.*, 2012, **22**, 1613.

28 U. Gautam, X. Fang, Y. Bando, J. Zhan and D. Golberg, *ACS Nano*, 2008, **2**, 1015.

29 T. Zhai, X. Fang, Y. Bando, Q. Liao, X. Xu, H. Zeng, Y. Ma, J. Yao and D. Golberg, *ACS Nano*, 2009, **3**, 949.

30 X. Zhang, L. Gong, K. Liu, Y. Cao, X. Xiao, W. Sun, X. Hu, Y. Gao, J. Chen and J. Zhou, *Adv.*

Mater., 2010, **22**, 5292.