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# A simple catalyst-free route for large-scale synthesis of SiC nanowires

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## ABSTRACT

A large number of SiC nanowires were fabricated by a simple catalyst-free method using silicon powders and expandable graphite as raw materials. Digital camera, X-ray diffractometer, Fourier transform infrared spectrometer, field-emission scanning electron microscopy and transmission electron microscopy demonstrate that a large number of loose products were obtained in graphite crucible. The products are composed of single crystalline 3C-SiC nanowires with lengths up to several tens of micrometers and diameters of 20–60 nm. The vapor–solid mechanism was proposed to interpret the growth procedure of SiC nanowires. The expandable graphite as carbon source can provide enough growth space for nanowires, which is helpful to improve the yield of SiC nanowires. The simple method provides a promising candidate for industrial fabrication of SiC nanowires.

## 1. Introduction

SiC is a new generation semiconductor with a wide band gap that can be used in high-temperature, high-frequency, and high-power environment. One-dimensional (1D) SiC nanomaterials have attracted much attention because of their versatile electrical, optical and mechanical properties compared to their bulk counterparts [1–3]. These unique properties make 1D SiC nanomaterials suitable for various applications in electronic nanodevices [4,5], optoelectronic nanodevices [5,6], field-emission devices [7,8], nanocomposites [1,9], photocatalysts [10], hydrogen storage [11], and hydrophobic devices [12].

Motivated by these applications of 1D SiC nanomaterials, a variety of techniques have been reported for the synthesis of SiC nanowires, including chemical vapor deposition [13,14], thermal evaporation [15,16], carbothermal reduction [17,18], laser ablation [19], arc-discharge [20], carbon nanotubes confined reaction [21,22], and catalyst-assisted [23,24]. In most of these methods, expensive raw materials, catalysts, and sophisticated techniques were used. These drawbacks may limit the massive fabrication and application of SiC nanowires. It is still a challenge for scientists and industrials to synthesize large-scale SiC nanowires by using a simple and rapid method. Researchers often focused on seeking some special techniques to realize the massive synthesis of SiC nanowires. For example, Wang et al. [25] synthesized SiC nanowires by heating a mixture of SiO powder and arc-discharge plasma pretreated carbon black with porous and loose structures in a high frequency induction furnace. The total heating-up and reaction time was less than 1 h, and more than 200 g products can be obtained per day. The formation of the loose and porous structures may be the key factor for the high yield of SiC nanowires.

In this work, we fabricated SiC nanowires in large scale by using a special carbon source with porous and loose structures. Expandable graphite (EG) is a graphite intercalation compound in which some oxidants, such as sulfuric acid, potassium permanganate, are inserted between the carbon layers of the graphite. EG expands hundred times larger than its original volume when heated [26]. Therefore, EG can form porous structure and has excellent absorptive capacity for reactant gas after expansion. In our experiment, the mixture of EG and silicon powders was used as raw materials to prepare SiC nanowires by a simple heating method. The work demonstrated that large-scale loose products were obtained in graphite crucible. The growth mechanism of SiC nanowires was discussed and the simple method provides a promising candidate for industrial fabrication of SiC nanowires.

## 2. Experimental

### 2.1. Synthesis of SiC nanowires

Silicon powders (6000 mesh, Juyuan Silicon Co., Fuzhou, China) and EG (Tianhe Graphite Co., Qingdao, China) were mixed together by a muller for 2 h keeping the mixing of silicon and EG. The mixture (6 g) was then placed in a graphite crucible

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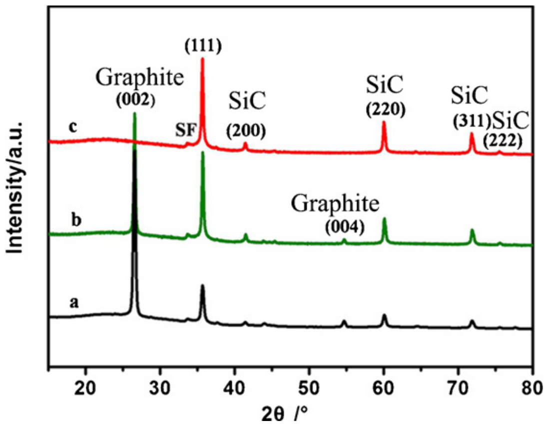

**Fig. 1.** X-ray diffraction spectra of as-synthesized products grown from mixtures with different mixing ratios of silicon:EG of (a) 1:2, (b) 1:1, (c) 2:1.

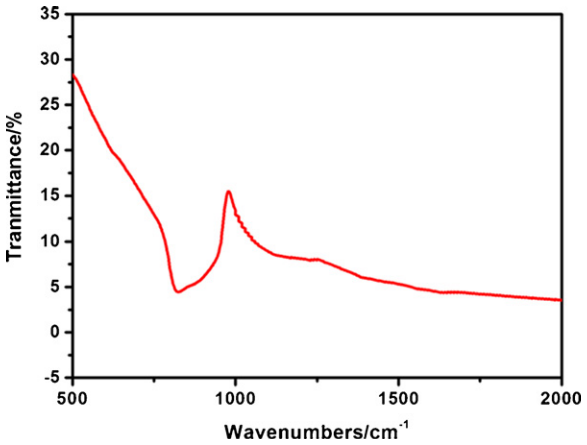

**Fig. 2.** FT-IR transmittance spectrum of the obtained products.

(Ø60 mm × 60 mm) with a graphite top covered. The crucible was put in the center of a vertical furnace. Before heating, the furnace was initially evacuated to $10^4$ Pa by a rotary pump, and then argon gas (99.99%) was introduced into the furnace with a pressure of $2 \times 10^4$ Pa. The process was conducted twice and the pressure remained under 1 atm during the experiment. The furnace was first heated up at 8 °C/min to 900 °C, and was then further heated up at 3 °C/min to 1500 °C and maintained for 7 h. Ar gas was keep static during heating. The fast cooling was then followed by turning power off and leaving cooling water on. After cooling to room temperature, gray colored loose products were found in the graphite crucible. The EG expands when heated, and volume of the products was ten times larger than that of the total raw materials.

### 2.2. Characterization of as-synthesized products

The products collected from the graphite crucible were directly investigated by X-ray diffraction (XRD, Rigaku, D/max-γA and Cu-Kα radiation). IR absorbance spectrum was characterized by Fourier transform infrared spectroscopy (FT-IR, Nicolet 5700) using KBr pallet method. The morphology and detailed microstructure information were characterized by digital camera, field-emission scanning electron microscopy (FE-SEM, FEI-SIRION100) and transmission electron microscopy (TEM, JEM-2100). The specimens for the TEM analyses were dispersed in ethanol by ultrasonication (KQ-100 DB) for 5 min and a drop of the suspension containing the products was dropped on copper grids with an amorphous carbon supporting film.

## 3. Results and discussion

### 3.1. Structure and morphology characterizations

The XRD patterns of the obtained products are shown in Fig. 1. Patterns (a), (b), and (c) represent the products synthesized by the mixtures with different mixing molar ratios of silicon:carbon (EG) of 1:2, 1:1 and 2:1, respectively. Fig. 1(a) and (b) reveals that, besides crystalline 3C-SiC, the diffraction peaks of residual graphite are also observed. Moreover, the peak intensity of residual graphite decreases with the silicon fraction. Five sharp peaks at 35.7°, 41.5°, 60.1°, 71. 9° and 75.6° can be indexed as (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes of 3C-SiC, respectively (JCPDS Card No. 29-1129). The low shoulder peak at $2\theta = 33.7°$ (marked with "SF") is typically observed in XRD spectra of 3C-SiC, which is usually ascribed to stacking faults within the crystals [27]. The peaks at 26.6° and 54.8° can be indexed as the (0 0 2) and (0 0 4) diffraction of residual graphite (JCPDS Card No. 41-1487). As shown in Fig. 1(c), with no noticeable diffraction peaks of other impurities in the pattern, we believe that the as-produced material is only single-crystalline 3C-SiC. A broad peak at $2\theta = 24°$ can be attributed to amorphous $SiO_2$. According to the three XRD patterns, the peak intensity of 3C-SiC increase with the silicon fraction. Fig. 2 is the FT-IR transmittance spectrum of the sample synthesized by mixing ratio of silicon:EG of 2:1. The strong peak centered at 820 $cm^{-1}$ corresponds to the transverse optical (TO) photon vibration mode of the Si–C bonds [28–30]. The low intensity broad band at 1250 $cm^{-1}$ is assigned to the presence of a small fraction of silica.

Fig. 3(a) shows the digital camera photograph of the products directly grown in graphite crucible from mixing ratio of silicon:EG of 2:1; it reveals explicitly that a mass of gray products have been achieved in graphite crucible. The volume of products is over ten times larger than that of the previous mixed raw materials. To evaluate the yield of the products, an electronic balance is used to weigh the sample, which shows the yield of the products is about 3.5 g. Though few SiC particles are found in the sample (shown in Fig. 3(b)), we thought the high yield of SiC nanowires was obtained (the weight of the mixed raw materials is 6 g). The FE-SEM images of the products are shown in Fig. 3(b) and (c). Fig. 3(b) reveals a representative low-magnification FE-SEM image of the SiC products, which suggests that the products consist of a large number of nanowires and few particles. The nanowires are dense and twisted with lengths up to several tens of micrometers. High-magnification FE-SEM image displays that the nanowires have different morphologies, such as straight and curved nanowires, and the diameters of these nanowires are ranging from 20 to 60 nm.

Fig. 4 shows the TEM images and selected-area electron diffraction (SAED) pattern of the SiC nanostructures. As is obviously shown in Fig. 4(a) and (b), nanowires with various morphologies and few particles have been obtained. The diameters and lengths of the nanowires are not uniform. Fig. 4(c) reveals a single nanowire and the corresponding SAED pattern (inset). The diameter of the nanowire is about 40 nm, and it is wrapped by a thin amorphous $SiO_2$ shell with a thickness of 1–2 nm. Moreover, a high density of striations can be observed in the nanowire. The striations indicate lots of planar defects, stacking faults perpendicular to the nanowire axis. The inset of Fig. 4(c) is the SAED pattern of the nanowire. The diffraction spots can be indexed based on 3C-SiC crystal, and the zone axis is determined to be $[\bar{1}\,2\,2]$.

### 3.2. Growth mechanism

The vapor–solid (VS) mechanism reported by our previous research [31,32] was proposed to explain the growth of SiC nanowires. The proposed growth process was also illustrated in Fig. 5. When temperature is up to 200 °C, the EG begins to expand and generates a porous and loose structure. In our experiment, the argon used in this study is 99.99% pure with oxygen of 10 ppm, i.e. the partial pressure of oxygen is about 1 Pa when the pressure of argon in the vertical furnace is $10^5$ Pa. Moreover, the vapor is hard to be expelled from the graphite crucible

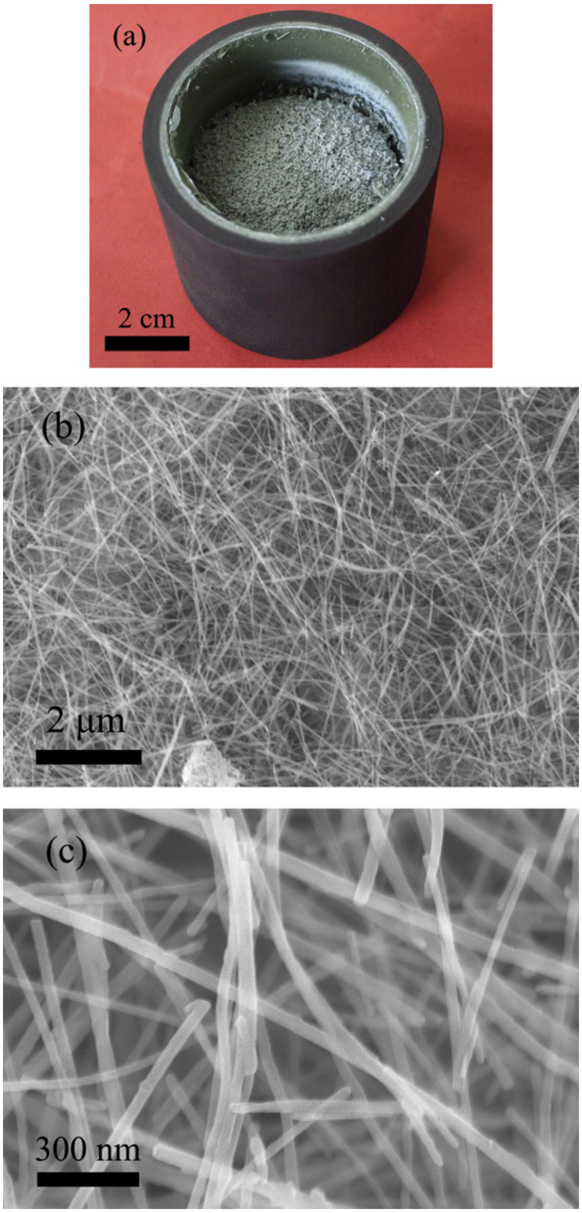

**Fig. 3.** (a) Digital camera photograph of the products synthesized in graphite crucible; (b) Low-magnification FE-SEM image of the SiC nanowires; (c) High-magnification FE-SEM image.

by rotary pump before argon was introduced to experimental setup, so the partial pressure of the residual oxygen in the furnace is more than 1 Pa. Oxygen in the furnace can react with silicon and carbon to produce SiO and CO for the Gibbs energy of reactions (1) and (2) are all very negative [32].

$$2\mathrm{Si(s)} + \mathrm{O_2(g)} \rightarrow 2\mathrm{SiO(g)} \tag{1}$$

$$2\mathrm{C(s)} + \mathrm{O_2(g)} \rightarrow 2\mathrm{CO(g)} \tag{2}$$

SiO and CO gas was formed according to the reaction (1) and (2). The gas infiltrated into the porous structure of EG (Process a in Fig. 5). This provides more chance for the reaction with carbon and SiC embryos can be formed by heterogeneous nucleation according to reaction (3) (Process b in Fig. 5).

$$\mathrm{SiO(g)} + 2\mathrm{C(s)} \rightarrow \mathrm{SiC(s)} + \mathrm{CO(g)} \tag{3}$$

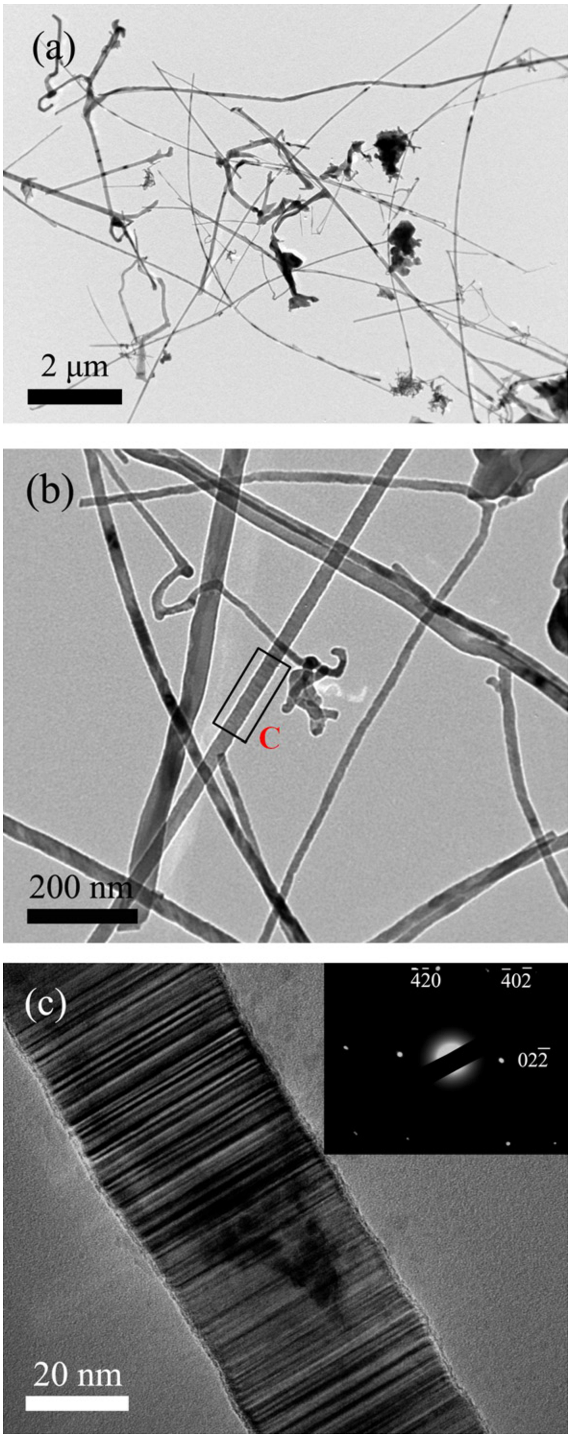

**Fig. 4.** (a) and (b) Low-magnification TEM image of the SiC nanowires; (c) High-magnification TEM image from the framed domain marked as "C" and the corresponding SAED pattern (inset).

The growth of SiC nanowires is believed to undergo a SiO gas and CO gas interaction in reactions (4) and (5). The newly formed SiC nucleus deposits on the top of SiC nanowires to form the long SiC nanowires (Process c in Fig. 5). Reaction (4) can only occur under a supersaturated condition of CO at higher temperature (the temperature holding stage) [33]. But during the cooling stage (lower temperature), when SiO vapor is prevail, reaction (5) will occur. With temperature decreasing, the reaction leads to a decrease in

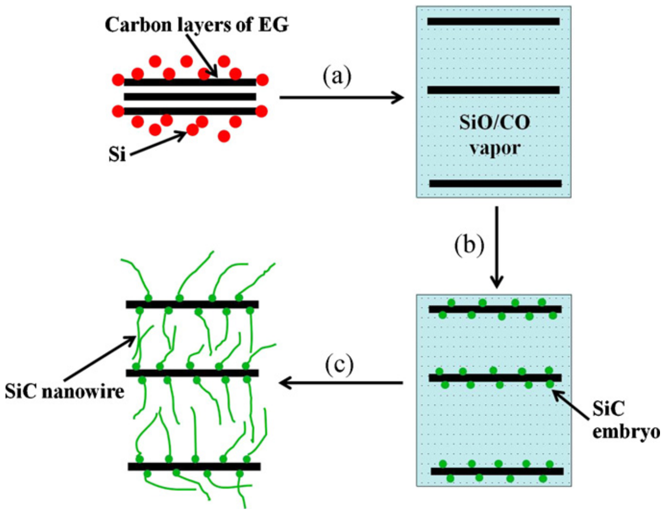

**Fig. 5.** Mechanistic process of β-SiC nanowires: (a) Expandable graphite expands and SiO/CO vapor is formed; (b) SiC embryos are produced by heterogeneous nucleation; (c) Long SiC nanowires grow along the (1 1 1) direction.

enthalpy and Gibbs energy [34–36], which is thermodynamically favorable at low temperature. Therefore, $SiO_2$ is formed on the surface of the SiC nanowires by the reaction (5).

$$SiO(g) + 3CO(g) \rightarrow SiC(s) + 2CO_2(g) \quad (4)$$

$$3SiO(g) + CO(g) \rightarrow SiC(s) + 2SiO_2(s) \quad (5)$$

The new produced $CO_2$ will be consumed immediately by carbon to form CO to promote the reaction (4).

$$CO_2(g) + C(s) \rightarrow 2CO(g) \quad (6)$$

The porous structure of the EG can provide enough growth space for SiC nanowires, which is helpful to improve the yield of SiC nanowires.

## 4. Conclusions

In summary, 3C-SiC nanowires have been synthesized in large scale by a simple carbothermal reduction method. Straight and curved nanowires can be found and their diameters are ranging from 20 nm to 60 nm. The transmission electron microscopy images show the nanowires are single-crystalline structure with a high density of stacking faults. Vapor–solid mechanism is employed to interpret the growth procedure of SiC nanowires. This simple method using EG as carbon source provides a promising candidate for industrial fabrication of SiC nanowires.

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## References

[1] E.W. Wong, P.E. Sheehan, C.M. Lieber, Science 277 (1997) 1971.
[2] H.W. Shim, J.D. Kuppers, H. Huang, J. Nanosci. Nanotech. 8 (2008) 3999.
[3] W.M. Zhou, X. Liu, Y.F. Zhang, Appl. Phys. Lett. 89 (2006) 223124.
[4] C.O. Jang, T.H. Kim, S.Y. Lee, D.J. Kim, S.K. Lee, Nanotechnology 19 (2008) 345203.
[5] H.K. Seong, H.J. Choi, S.K. Lee, J.I. Lee, D.J. Choi, Appl. Phys. Lett. 85 (2004) 1256.
[6] L.G. Zhang, W.Y. Yang, H. Jin, Z.H. Zheng, Z.P. Xie, H.Z. Miao, L.N. An, Appl. Phys. Lett. 89 (2006) 143101.
[7] Z.W. Pan, H.L. Lai, C.K. Frederick, X.F. Duan, W.Y. Zhou, W.S. Shi, N. Wang, C.S. Lee, N.B. Wong, S.T. Lee, S.S. Xie, Adv. Mater. 12 (2000) 1186.
[8] D.W. Kim, Y.J. Choi, K.J. Choi, J.G. Park, J.H. Park, S.M. Pimenov, V.D. Frolov, N.P. Abanshin, B.I. Gorfinkel, N.M. Rossukanyi, A.I. Rukovishnikov, Nanotechnology 19 (2008) 225706.
[9] W. Yang, H. Araki, C. Tang, S. Thaveethavorn, A. Kohyama, H. Suzuki, T. Noda, Adv. Mater. 17 (2005) 1519.
[10] W.M. Zhou, L.J. Yan, Y. Wang, Y.F. Zhang, Appl. Phys. Lett. 89 (2006) 013105.
[11] G. Mpourmpakis, G.E. Froudakis, G.P. Lithoxoos, J. Samios, Nano Lett. 6 (2006) 1581.
[12] J.J. Niu, J.N. Wang, J. Phys. Chem. B 113 (2009) 2909.
[13] G.Y. Li, X.D. Li, Z.D. Chen, J. Wang, H. Wang, R.C. Che, J. Phys. Chem. C 113 (2009) 17655.
[14] Z.J. Li, W.D. Gao, A. Meng, Z.D. Geng, L. Gao, J. Phys. Chem. C 113 (2009) 91.
[15] W. Khongwong, K. Yoshida, T. Yano, Mater. Sci. Eng. B 173 (2010) 117.
[16] K.Y. Cheong, Z. Lockman, J. Nanomater. 2009 (2009) 572865.
[17] G. Attolini, F. Rossi, M. Bosi, B.E. Watts, G. Salviati, J. Non-Cryst. Solids 354 (2008) 5227.
[18] J. Zhu, H. Wu, H.T. Chen, X.L. Wu, X. Xiong, Phys. Lett. A 373 (2009) 1697.
[19] W. Shi, Y. Zheng, H. Peng, N. Wang, C.S. Lee, S.T. Lee, J. Am. Ceram. Soc. 83 (2000) 3228.
[20] X.M. Liu, K.F. Yao, Nanotechnology 16 (2005) 2932.
[21] S.C. Chiu, Y.Y. Li, J. Cryst. Growth 311 (2009) 1036.
[22] J. Zhu, S.S. Fan, J. Mater. Res. 14 (1999) 1175.
[23] C.H. Liang, G.W. Meng, L.D. Zhang, Y.C. Wu, Z. Cui, Chem. Phys. Lett. 329 (2000) 323.
[24] J.J. Niu, J.N. Wang, J. Phys. Chem. B 111 (2007) 4368.
[25] F.L. Wang, L.Y. Zhang, Y.F. Zhang, Nanoscale Res. Lett. 4 (2009) 153.
[26] L. Shi, Z.M. Li, W. Yang, M.B. Yang, Q.M. Zhou, R. Huang, Powder Technol. 170 (2006) 178.
[27] K. Koumoto, S. Takeda, C.H. Pai, T. Sato, H.J. Yanagida, J. Am. Ceram. Soc. 72 (1989) 1985.
[28] L.S. Liao, X.M. Bao, Z.F. Yang, N.B. Min, Appl. Phys. Lett. 66 (1995) 2383.
[29] T. Li, L.Q. Xu, L.C. Wang, L.S. Yang, Y.T. Qian, J. Alloys Compd. 484 (2009) 342.
[30] Q.L. Pang, L.Q. Xu, Z.C. Ju, Z. Xing, L.S. Yang, Q. Hao, Y.T. Qian, J. Alloys Compd. 501 (2010) 61.
[31] J.J. Chen, Y. Pan, W.H. Tang, Q. Shi, Nano-Micro Lett. 2 (2010) 15.
[32] R.B. Wu, B.S. Li, M.X. Gao, J.J. Chen, Q.M. Zhu, Y. Pan, Nanotechnology 19 (2008) 335602.
[33] W.Q. Han, S.S. Fan, Q.Q. Li, W.J. Liang, B.L. Gu, D.P. Yu, Chem. Phys. Lett. 265 (1997) 374.
[34] G.Y. Yang, R.B. Wu, J.J. Chen, Y. Pan, R. Zhai, L.L. Wu, J. Lin, Nanotechnology 18 (2007) 155601.
[35] B.S. Li, R.B. Wu, Y. Pan, L.L. Wu, G.Y. Yang, J.J. Chen, Q.M. Zhu, J. Alloys Compd. 462 (2008) 449.
[36] X.W. Du, X. Zhao, S.L. Jia, Y.W. Lu, J.J. Li, N.Q. Zhao, Mater. Sci. Eng. B 136 (2007) 76.