Influence of raw powder size, reaction temperature, and soaking time on synthesis of SiC/SiO₂ coaxial nanowires via thermal evaporation

Wasana KHONGWONG,[†] Masamitsu IMAI, Katsumi YOSHIDA and Toyohiko YANO

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8550

High-yield SiC/SiO₂ core-shell nanowires were synthesized without adding metal catalysts from outside through a simple thermal evaporation of silicon powders during decomposition of methane gas. The influence of three parameters, size of Si raw powder (50 nm and 5 μ m), reaction temperature (1573, 1623 and 1673 K), and soaking time (1, 3 and 6 h), was investigated. The typical synthesized nanowires from different conditions possess the diameter of no thicker than 100 nm with several tens micrometers in length. It was addressed that the condition using the smaller size Si powder, which contained the highest amount of oxygen, at higher temperature lead to more complete reaction to obtain a large quantity of nanowires. The synthesized nanowires at higher reaction temperature and longer soaking time possessed larger core than those nanowires prepared at lower reaction temperature and shorter soaking time. Oxidation of larger size Si powder improved yield of nanowires. Based on these results, it was suggested that the typical nanowires should be grown via the oxide-assisted growth mechanism.

©2009 The Ceramic Society of Japan. All rights reserved.

Key-words : SiC nanowire, Core/shell structure, Reaction condition, Thermal evaporation, CH₄ gas, Oxide-assisted growth

[Received November 21, 2008; Accepted February 19, 2009]

1. Introduction

In recent years, the variety of morphologies of quasi-one-dimensional (1D) nanoscale structures such as wires, rods, tubes, springs, ribbons, and etc. has been researched intensively because of their potential applications as interconnects or functional components in nanoscale electronic, nanocomposites and nanodevices including field-effect transistors.^{1)–3)} It is well known that silicon carbide (SiC) has excellent properties, such as high mechanical strength, high thermal conductivity, high thermal stability, and large band gap.^{4)–6)} Wong et al.⁷⁾ reported that SiC nanowires could act as reinforcement materials for ceramic matrix composites to improve strength and toughness, owing to their very high bending strength and Young's modulus (53.4 and 610–660 GPa, respectively) over their bulk-counterparts. Therefore, great efforts have been made on the synthesis of SiC nanorods/nanowires,^{8)–10)} nanotubes,¹¹⁾ nanocables,¹²⁾ and nano-springs.¹³⁾

SiC/SiO₂ coaxial nanowires were first synthesized through laser ablation in 1998, and they were expected to be an ideal semiconductor-insulator heterojunctions in the radial direction.¹⁴⁾ Moreover, SiC/SiO₂ core-shell nanowires are anticipated to substitute for large-sized SiO₂ that act as the reinforcing phase in the rubber. The nanowire will enhance the interfacial bonding strength of rubber and reinforcement.¹⁵⁾ In addition, coaxial SiC/SiO_x nanowires may be used as a good light emitting material since it can emit stable and strong intense blue-green¹⁶⁾ or violet-blue¹⁷⁾ light. Therefore, synthesis and properties of SiC/SiO₂ core-shell nanowires, including the effect of reaction conditions, should be attractive research fields.

Many approaches have been applied to synthesize SiC/SiO₂

core-shell nanowires, such as using a one-step direct heating of Si powders and multiwall carbon nanotubes,¹⁸⁾ chemical vapor reaction via mixture of milled Si and SiO₂ powders and C₃H₆,¹⁵⁾ reaction of SiO vapor and activated carbon fibers by high frequency induction heating,^{19),20)} and so on. However, the effect of important reaction parameters on synthesis SiC/SiO₂ core-shell nanowires has rarely been reported. In a previous work, we succeeded in producing a large quantity of β -SiC/SiO₂ core-shell nanowires by heating up the Si nanopowder under flowing CH₄ gas at 1623 K for 1 h.²¹⁾ In that report, effect of synthesis parameters was not studied yet.

In this work, we focus on the effects of size of raw powder, reaction temperature, and soaking time on growth of β -SiC/SiO₂ core-shell nanowires which were synthesized through simple thermal evaporation of Si powders among flowing CH₄ gas.

2. Experimental procedure

Two types of silicon powder, SM (average particle size $\approx$ 5 μ m, dark gray, 99% nominal purity, Kojundo Chemical Laboratory Co., Ltd., Japan) and SN (average particle size $\approx$ 50 nm, brown-yellow, 99% nominal purity, Hefei Kaier Nanometer Technology & Development Co., Ltd., China) were used as raw powders. To study the effect of oxygen content in Si starting material, therefore, the SM powder was oxidized in air at different temperature of 873 or 1073 K for 1 h before using as the raw powder. Oxygen content in Si raw powders was detected by TC-436 Nitrogen/Oxygen determinator (LECO Co., USA). The oxygen content in each Si raw powder is shown in **Table 1**.

The synthesis of nanowires was conducted in a horizontal mullite tube furnace, the same as mentioned before.²¹⁾ First, a small amount of silicon raw powder was put in the mullite boat which was then covered with a thin sheet of alumina fiber net (Nextel™ Woven Fabric 610 style, Sumitomo 3M Ltd., Japan). After placing the whole set into the center of the furnace, the

[†] Corresponding author: W. Khongwong; E-mail: khongwong.w.aa@m.titech.ac.jp

Table 2. Experimental Conditions and Corresponding Products

Specimen code	Type of Si raw powder			Reaction temperature, K (°C)	Soaking time, h	Product*
	SN	SM	Oxidized temperature of SM, K			
			873 1073			
SM-1351		○		1623 (1350)	1	small amount of A
SMO6-1351			○	1623 (1350)	1	small amount of B
SMO8-1351			○	1623 (1350)	1	B
SN-1301	○			1573 (1300)	1	C + small amount of B at inner wall of boat
SN-1351	○			1623 (1350)	1	B
SN-1353	○			1623 (1350)	3	B
SN-1356	○			1623 (1350)	6	B
SN-1401	○			1673 (1400)	1	D

Remark: *Product A = soft bright gray part on Si surface

B = white-blue wool-like product on Si surface

C = black-blue wool-like product on Si surface

D = white-blue wool-like product on Si surface and alumina fiber net sheet

Table 1. Oxygen Content in Raw Materials

Type of Si raw powder	Oxygen content (mass%)
SM	0.3
SMO6*	0.9
SMO8**	4.5
SN	23.4

Remark: *Oxidized SM at 873 K, **Oxidized SM at 1073 K

chamber was initially evacuated to a pressure below 1.33 Pa by a rotary pump. Ar gas (purity: 99.9995%) was then applied at a flow rate of 0.6 dm³/min into the tube to maintain an inert atmosphere. The furnace was first ramped to 1473 K at 600 K/h and then continued to heat but 300 K/h to a preset target temperature of 1573, 1623 or 1673 K. At the maximum temperature, H₂ (purity: 99.999%) at a flow rate of 20 sccm (standard cubic centimeter per minute) was introduced for 2 min before flowing of CH₄ gas (purity: 99.99%) at a flow rate of 10 sccm for 30, 90 and 180 min in batch for soaking time of 1, 3 and 6 h, respectively. Then, the furnace was allowed to cool down to room temperature in Ar atmosphere and the mullite boat containing as-grown SiC nanowires was moved out of the furnace.

After reaction at different conditions, different products were obtained in the boat. The experimental conditions, specimen codes and corresponding products are shown in **Table 2**. X-ray diffractometry (XRD; Cu K α , PW 1700, Philips, Holland), scanning electron microscopy (FE-SEM; field-emission type, S-4800, Hitachi, Ltd., Japan), transmission electron microscopy (TEM; H-9000, Hitachi, Ltd., Japan), and scanning TEM (STEM) were used to characterize the synthesized products. Specimen preparation for TEM observation was described elsewhere.²¹⁾

3. Results and discussion

3.1 Effect of particle size of Si raw powder

Figure 1 shows a photograph of SN-1351 specimen (upper one) and SM-1351 specimen (lower one). Obviously, white-blue

Fig. 1. Photograph of products from SN-1351 (upper side) and SM-1351 (lower side) specimen. The left figures are FE-SEM images of white-blue wool-like product (upper side) and soft bright gray part (lower side).

wool-like products occurred on the SN raw powder surface, whereas color of the SM powder surface only changed from dark gray to bright gray on some area. However, FE-SEM observation indicated bright gray part composed of randomly distributed wire-shaped products (hereafter: nanowire). The white-blue wool-like product from the SN-1351 specimen consisted of a large quantity of curved, straight, kinked, randomly oriented nanowires (see upper left image of Fig. 1). Since a small amount of wires can be observed at inter-space between raw particles in the bright gray part (see lower left image of Fig. 1) in the SM-1351 specimen, it is very interesting that the mere existence of wire-like nanostructures indicating this synthetic condition was close to a critical point of nanowires growth.

The XRD patterns of the SN-1351 and the SM-1351 specimens are shown in **Figs. 2(a)** and **(b)**, respectively. Four main diffraction peaks of the SN-1351 specimen could be identified as the (111), (200), (220), and (311) reflections of β -SiC. Moreover, Si and C peaks with low intensity were also detected. Appearance of Si peaks was attributed to attachment of Si raw powder under wool-like product. However, XRD peaks from the prod-

Fig. 2. XRD pattern of as-grown product from; (a) SN-1351 specimen (b) SM-1351 specimen.

ucts at bright gray part of the SM-1351 specimen indicated that it contained a small amount of β -SiC along with Si as a dominant phase, due to difficulty to separate as-synthesized products from Si raw powder. From these results, it can be confirmed that the as-grown nanowires should be SiC nanowires, as confirmed previously by EDX and FT-IR.²¹⁾

According to the above results, it was suggested that the Si raw powder with smaller size could produce larger amount of nanowires. One reason may be attributed for the difference in amount of oxygen content in the Si raw materials. Analyses of both Si raw powders before experiment indicated that the SN powder contained extremely higher oxygen content than that of the SM powder as shown in Table 1. It is supposed that the rate of the production of SiO vapor, which is a key factor of nanowires formation,^{22,23)} in the present experiment with using the SN powder was much higher than those using the SM powder.

To confirm the effect of oxygen content in the Si raw materials, the SM powder was oxidized in air and was used as a raw powder. Figures 3(a) and (b) show TEM images of typical nanowires synthesized at 1623 K for 1 h using the SN powder and the SM powder oxidized at 1073 K, respectively. The diameter of wires was distributed in the range from 10–35 nm and 10–60 nm for synthesized wires from the SN powder and the SM powder oxidized at 1073 K, respectively. The amount of as-grown nanowires increased with increasing oxidation temperature from 873 to 1073 K. The oxidation of SM powder increased amount of oxygen content (see in Table 1) as surface SiO₂, which should

Fig. 3. TEM images of typical nanowires synthesized at 1623 K for 1 h by using (a) SN and (b) oxidized SM at 1073 K.

be source to produce SiO in the system. The detailed mechanism will be mentioned in latter section. Moreover, it is fortunate that we can use large-sized Si powder as a raw material to synthesize SiC nanowires, leading to low-cost production and easy to scale-up in the future.

3.2 Effect of reaction temperature

The as-synthesized products after processing at 1573, 1623 and 1673 K using the SN powder are listed in Table 2. The yield of white-blue wool-like product increased with increasing temperature. The XRD analysis indicated that each of the as-synthesized product consisted of β -SiC, even through in the black-blue wool-like product on Si surface from the SN-1301 powder (process temperature: 1573 K). FE-SEM observation exhibited that the wool-like product from every specimen was nanowires. Lengths of the typical nanowires were up to several tens micrometers and diameter ranging from 5–30, 10–35 and 10–65 nm for SN-1301, SN-1351 and SN-1401, respectively. As an example, the typical FE-SEM image of nanowires from the SN-1401 specimen is shown in Fig. 4. The product composed of large amount of straight, curved, haphazardly distributed nanowires. The upper left inset of Fig. 4 is a high magnification TEM photograph of a typical nanowire, clearly revealing that the nanowire consisted of a dark-contrasted inner core and a light-contrasted outer shell, and the dark core was positioned at the middle of the wire.

The EDX spectrum obtained during STEM observation (not shown here) showed that the wires contained Si, C, and O, thus, we roughly deduced that the wires were the composite of carbide and oxide of silicon. Figure 5(a) disclosed the typical HREM image of an individual nanowire synthesized at 1623 K using the

Fig. 4. FE-SEM image of white-blue wool-like product from SN-1401 specimen and (inset) TEM image of a nanowire at high magnification.

SN raw material. This image revealed that the core of nanowire was crystalline and that the distance between two adjacent lattice planes was about 0.25 nm, which well corresponded to {111} planes of the cubic 3C-SiC. In addition, the [111] direction was parallel to the fiber axis of the nanowire, indicating that the growth direction of the nanowire was [111].²¹⁾ Figures 5(b) and (c) is the selected-area electron diffraction (SAD) pattern of the wire core and the shell layer, respectively. It could be indexed that core was the β -SiC crystal with twins and stacking disorder. Stacking fault into {111} planes is a typical fault characteristic in 1 D SiC nanostructures.^{24)–26)} Shell layer of this wire was amorphous.

Table 3 is showing morphology of typical SiC/SiO₂ core-shell nanowires from different experiment conditions, observed by TEM photographs of more than 50 nanowires. These data indicated that the higher reaction temperature was, the thicker nanowires were, whereas core thickness showed more different thickness than those shell thickness. Particularly, difference of reaction temperature between 1573 K, 1623 K, and 1673 K was significant. Distribution of core thickness of nanowires from the SN-1351 specimen was, for example, shown in Fig. 6(a). The average thickness of core/shell of typical nanowires from the SN-1301, SN-1351 and SN-1401 specimen was 11.7/4.1, 12.5/4.2 and 36.0/9.1 nm, respectively. No clear relation between core thickness and shell thickness was observed as show in Fig. 6(b).

3.3 Effect of soaking time

SiC nanowires were fabricated at 1623 K with soaking times of 1, 3 and 6 h (see in Table 2). After reaction, the white-blue wool-like product covered on the Si raw powder surface was formed in the boat. Although it was expected that extension of the soaking time increased amount of product, the yield of prepared product by increasing soaking time of 3 h to 6 h was not significantly different. However, the color of Si raw powder under the white-blue wool-like product more changed from brown-yellow to gray with increasing soaking time.

FE-SEM observation indicated that the as-grown products which were synthesized at 1623 K for the duration of 1, 3 and 6 h consisted from large quantities of nanowires. Lengths of the nanowires were up to several tens of micrometers and diameter less than 100 nm. Morphologies of typical nanowires from the SN-1351, SN-1353 and SN-1356 specimen are also shown in Table 3. Core thickness increased with longer soaking time. Average core thickness was 12.5, 17.2 and 20.2 nm for SN-1351,

Fig. 5. (a) HREM image of an individual nanowire (The [111]-growth direction is indicated by arrow), (b) The corresponding SAD pattern of the wire core, (c) The corresponding SAD pattern of the shell layer.

Table 3. Morphology of Typical Nanowires of Each Synthetic Condition

Specimen code	Average core thickness* (nm)	Average shell thickness* (nm)	Average diameter of nanowire* (nm)
SN-1301	11.7	4.1	19.9
SN-1351	12.5	4.2	21.0
SN-1353	17.2	5.9	28.9
SN-1356	20.2	**	20.2
SN-1401	36.0	9.1	54.2

Remark: *measured from 50 nanowires

**shell thickness was very thin, almost completely disappeared

Fig. 6. Distribution of core thickness (a) and relation between core thickness and shell thickness (b) of SN-1351 specimen.

SN-1353 and SN-1356 specimen, respectively. Interestingly, after reaction for 6 h, shell thickness became very thin. Disappearance of the outer shell layer after extended soaking time is mentioned in the next section.

3.4 Formation mechanism of nanowire

As mentioned before,²¹⁾ nanowires with cap were rarely observed in the products. The cap contained high concentration of Fe, which should come from the impurity in the raw powder. In this case, the growth mechanism should be VLS (Vapor-Liquid-Solid) mechanism. However, in the case of the typical nanowires without cap should not be formed by traditional metal-catalyzed VLS growth mechanism. One possible mechanism of typical nanowire formation without cap may be a process similar to the oxide-assisted growth.²⁷⁾ Although the detailed growth mechanism of β -SiC/SiO₂ coaxial nanowires is not completely understood yet, we infer that the overall reactions of nanowire formation can be written as following reactions (1)–(4).

$$(\Delta G = -61.971 \text{ kJ/mol at } 1623 \text{ K})$$

$$(\Delta G = -512.673 \text{ kJ/mol at } 1623 \text{ K})$$

$$(\Delta G = -229.135 \text{ kJ/mol at } 1623 \text{ K})$$

$$(\Delta G = -330.068 \text{ kJ/mol at } 1623 \text{ K})$$

where s and g in the brackets refer to solid and gas state, respectively. In fact, Si is very easy to oxidize to silica. Therefore, it is not questionable that its surface was covered with silica. As the temperature increases, SiO vapor is generated from not only the reaction of SiO₂ and Si (reaction (1)), but also is supplied from the experimental set up such as mullite tube and boat at high temperature. The effect of oxide boat for the nanowire formation was confirmed experimentally using a BN boat instead of the mullite boat.²¹⁾ Dense SiO smoke is deposited first near Si powder surface. Subsequently, when the furnace is heated up till close to the melting point of Si (1687 K), evaporation of Si also happens.

The SiC nanonuclei may be formed from the reactions of SiO vapor and CH₄ gas, and evaporated Si and CH₄ gas simultaneously (reaction (2)). The cluster of nuclei acts as reservoir to absorb both CH₄ gas and SiO vapor. The nanowires in a preferred orientation grow fast as more SiO vapor and CH₄ gas are absorbed into the clusters. Finally, the formation of SiO₂ outer layer may occur by oxidation of remained SiO vapor and/or as-grown SiC nanowires by H₂O, which is a by-product of the reaction (2), according to the reactions (3) and (4), respectively.

Considering size difference of the raw powders, the SN powder occupies ultra-fine particle size (≈ 50 nm), very high surface area and high oxygen content (23.4 mass%) than that of the SM powder. Therefore, using the SN powder or the oxidized SM powder caused to create more SiO, resulted in formation of higher amount of final products than that using the SM powder as reported in the first section.

At 1673 K, this temperature is just below the melting point of Si, therefore high rate of Si evaporation occurs, resulted in increasing the nuclei of SiC. Also at higher temperature oxidation rate should be higher than that at lower temperatures. The synthesized SN-1401 nanowires, therefore, showed the largest SiC core diameter and thickest amorphous shell layer. If reaction still proceeding for longer time, length of nanowires may increase, but it was difficult to confirm the length change of wires in this experiment. Otherwise, increase in the thickness of shell part was observed for longer soaking time specimen from 1 to 3 h. It supported the oxidation of nanowires. However, if as-grown products were kept for longer time such as 6 h, SiO₂ may react with evaporated Si to produce SiO (g) as shown in reaction (1), since during latter soaking period, CH₄ gas was not fed into the furnace, therefore the reaction (2) should not occur. Then, oxidation by the reactions (3) and/or (4) also does not proceed.

Kang et al.²⁸⁾ presented that the width and length of synthesized β -SiC nanowires by metalorganic chemical vapor deposition (MOCVD) method were mainly controlled by the depositing temperature. Q. G. Fu et al.²⁹⁾ afterwards reported that as the increasing of deposition temperature, or as the increasing of concentration of CH₃SiCl₃ (MTS), the SiC crystal dimensions increased and the morphologies of the as-grown SiC crystal changed from nanowires to grain. More recently, K. F. Cai et al.³⁰⁾ confirmed the influence of cooling time on morphologies of SiC/SiO_x nanocables, and prolongation of cooling time increased the diameter of nanocable core. Here, we showed that higher reaction temperature and longer soaking time (not more than for about 3 h) resulted in larger diameter of nanowires.

According to above, the SiC/SiO₂ core-shell nanowires should be formed through the reaction of SiO and methane. It seems that

SiO is important precursor for nanowire growth. Thereby, this mechanism can be classified into the oxide-assisted growth (OAG) mechanism.^{20),27)}

4. Conclusions

Based on the experimental results of the current work, the conclusions can be written as follows. The high yield of very long SiC/SiO₂ core-shell nanowires with diameter not more than 100 nm are fabricated by the simple evaporation method through the oxide-assisted growth mechanism. The yield of as-synthesized products increased with synthesis using smaller size of Si raw powder or oxidized Si (very high oxygen content) as a raw powder at higher reaction temperature. The synthesized nanowires at higher reaction temperature and longer soaking time possessed larger core than those nanowires prepared at lower reaction temperature and shorter soaking time. It was clarified that larger size Si instead of nanopowder, can be applied as a raw material for nanowire growth after proper heat-treatment.

References

- 1) P. D. Yang and C. M. Lieber, *Science*, **273**, 1836–1840 (1996).
- 2) A. M. Morales and C. M. Lieber, *Science*, **279**, 208–211 (1998).
- 3) H. K. Seong, H. J. Choi, S. K. Lee, J. I. Lee and D. J. Choi, *Appl. Phys. Lett.*, **85**, 1256–1258 (2004).
- 4) J. D. Holmes, K. P. Johnston, R. C. Doty and B. A. Korgel, *Science*, **287**, 1471–1473 (2000).
- 5) I. A. Salama, N. R. Quick and A. Kar, *J. Appl. Phys.*, **93**, 9275–9281 (2003).
- 6) W. M. Zhou, F. Fang, Z. Y. Hou, L. J. Yan and Y. F. Zhang, *IEEE Electron Device Lett.*, **27**, 463–465 (2006).
- 7) E. W. Wong, P. E. Sheeham and C. M. Lieber, *Science*, **277**, 1971–1975 (1977).
- 8) W. Han, S. Fan, Q. Li, W. Liang, B. Gu and D. Yu, *Chem. Phys. Lett.*, **265**, 374–378 (1997).
- 9) X. T. Zhou, N. Wang, F. C. K. Au, H. L. Lai, H. Y. Peng, I. Bello, C. S. Lee and S. T. Lee, *Mater. Sci. Eng. A*, **286**, 119–124, (2000).
- 10) W. M. Zhou, B. Yang, Z. X. Yang, F. Zhu, L. J. Yan and Y. F. Zhang, *Appl. Surf. Sci.*, **252**, 5143–5148 (2006).
- 11) T. Taguchi, N. Igawa, H. Yamamoto, S. Shamoto and S. Jitsukawa, *Physica E*, **28**, 431–438 (2005).
- 12) H. W. Shim and H. Huang, *Nanotechnology*, **18**, 335607 (5pp.) (2007).
- 13) D. Zhang, A. Alkhateeb, H. Han, H. Mahmood, D. N. McIlroy and M. G. Norton, *Nano Lett.*, **3**, 983–987 (2003).
- 14) Y. Zhang, K. Suenaga, C. Colliex and S. Iijima, *Science*, **281**, 973–975 (1998).
- 15) A. Meng, Z. Li, J. Zhang, L. Gao and H. Li, *J. Cryst. Growth*, **308**, 263–268 (2007).
- 16) D. H. Feng, T. Q. Jia, X. X. Li, Z. Z. Xu, J. Chen, S. Z. Deng, Z. S. Wu and N. S. Xu, *Solid State Commun.*, **128**, 295–297 (2003).
- 17) X. M. Liu and K. F. Yao, *Nanotechnology*, **16**, 2932–2935 (2005).
- 18) B. Li, R. Wu, Y. Pan, L. Wu, G. Yang, J. Chen and Q. Zhu, *J. Alloys Compd.*, **462**, 446–451 (2008).
- 19) Z. X. Yang, Y. J. Wu, F. Zhu and Y. F. Zhang, *Physica E*, **25**, 395–398 (2005).
- 20) W. M. Zhou, Z. X. Yang, F. Zhu and Y. F. Zhang, *Physica E*, **31**, 9–12 (2006).
- 21) W. Khongwong, M. Imai, K. Yoshida and T. Yano, *J. Ceram. Soc. Japan*, **117**, 194–197 (2009).
- 22) Z. L. Wang, Ed., “Nanowires and Nanobelts: Materials, Properties and Devices. Volume 1: Metal and Semiconductor Nanowires” Kluwer Academic Publishers, Massachusetts, USA (2003) pp. 415–428.
- 23) H. J. Choi and J. G. Lee, *J. Mater. Sci.*, **30**, 1982–1986 (1995).
- 24) L. Wang, H. Wada and L. F. Allard, *J. Mater. Res.*, **7**, 148–163 (1992).
- 25) W. Shi, Y. Zheng, H. Peng, N. Wang, C. S. Lee and S. T. Lee, *J. Am. Ceram. Soc.*, **83**, 3228–3230 (2000).
- 26) Z. W. Pan, H. L. Lai, F. C. K. Au, X. Duan, W. Zhou, W. Shi, N. Wang, C. S. Lee, N. B. Wong, S. T. Lee and S. S. Xie, *Adv. Mater.*, **12**, 1186–1190 (2000).
- 27) Y. Yao, S. T. Lee and F. H. Li, *Chem. Phys. Lett.*, **381**, 628–633 (2003).
- 28) B. C. Kang, S. B. Lee and J. H. Boo, *Thin Solid Films*, **464–465**, 215–219 (2004).
- 29) Q. G. Fu, H. J. Li, X. H. Shi, K. Z. Li, J. Wei and Z. B. Hu, *Mater. Chem. Phys.*, **100**, 108–111 (2006).
- 30) K. F. Cai, A. X. Zhang, J. L. Yin, H. F. Wang and X. H. Yung, *Appl. Phys. A*, **91**, 579–584 (2008).