Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 37 (2011) 3759–3764
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Growth of SiC nanowhiskers from wooden precursors, separation, and characterization

Rajnish Dhiman [a], Erik Johnson [b], Per Morgen [a,*]

[a] Department of Physics and Chemistry, University of Southern Denmark, Campusvej 55, Odense 5230, Denmark
[b] Nano Science Center, Niels Bohr Institute, University of Copenhagen, Universitetsparken 5, Copenhagen 2100, Denmark

Received 3 May 2011; received in revised form 31 May 2011; accepted 1 June 2011
Available online 12 June 2011

Abstract

We have achieved a catalyst free, low cost, easy synthesis of straight and uniform, high-aspect ratio β-SiC nanowhiskers (of 25–100 nm diameters), and a suitable separation technique to produce large quantities of individual whiskers. We conclude that these nanowhiskers nucleate on initially formed SiC clusters by a sequential gas–gas-surface reaction. The SiC clusters are formed initially as the primary product of the contact reaction between carbon obtained from wood powder (saw dust) and SiO_2 from tetraethyl orthosilicate (TEOS).

Keywords: B. Electron microscopy; B. X-ray methods; SiC nanowhiskers; Gas–gas-surface reaction; Raman microscopy

1. Introduction

Nanowhiskers of SiC are among the most interesting nanostructured material elements today due to their versatile properties such as chemical inertness, electronic structure with a large band gap, high hardness, high thermal stability [1–3], and even ferromagnetic properties [4]. Individual SiC nanowhiskers have potential applications in highly integrated semiconductor and field emission devices [5], and bunches of whiskers are proposed as reinforcement of ceramic and metal matrix composites [6–7]. Silicon carbide whiskers have earlier been synthesized by thermal processing of natural carbon- and silica-containing materials like rice hulls [7–11], and from bleached and unbleached wood pulp [12]. Along other routes, SiC nanowhiskers were synthesized by electrospinning [13], vapor–liquid–solid (VLS) Fe-catalyzed growth [14], high temperature evaporation of solid reactants [15], shape memory synthesis over (expensive) CNT's [16,17] or activated carbon [18], by the process of carbothermal reduction of silica. The synthesis of SiC whiskers from natural materials like rice hulls [7–11] and *unbleached* wood pulp [12] involves the formation of composites of clusters and whiskers. The only exception was the case of *bleached* wood pulp [12] where the authors claim to directly produce camelback type (nonuniform) nanorods. The fact that SiC whiskers in all other cases appear along with SiC cluster material [7–12,19–20] when synthesized by carbothermal reduction of silica, without additional reagents, suggests that SiC materials (SiC particulates) and SiC whiskers must have grown by two sequentially connected reaction mechanisms, where planar areas or facets on the clusters act as nucleation sites.

Keeping in view the above mentioned properties and potential applications of β-SiC nanowhiskers, the present work shows how to grow individual straight and uniform, high-aspect ratio β-SiC nanowhiskers by a catalyst free process. β-SiC nanowhiskers are here formed during the carbothermal reduction of silica with carbon obtained from wood powder (saw dust) along with SiC clusters. An important challenge after this procedure was to separate the whiskers from the clusters. We have successfully achieved this by exploiting the difference in the hydrophilic nature of clean silicon carbide nanowhiskers and the opposite, hydrophobic nature of carbon. Thus carbon containing SiC clusters are hydrophobic. This difference in properties has earlier been utilized to separate whiskers from clusters during the synthesis of SiC whiskers from rice hulls, by a liquid–liquid separation [9], by froth flotation [10], or by selective flocculation liquid extraction [11]. We use the liquid–liquid separation method including ultra

* Corresponding author. Tel.: +45 6550 3529; fax: +45 6615 8760.
E-mail address: per@ifk.sdu.dk (P. Morgen).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.06.001

sonication. The success of this separation process depends upon the C:SiC ratio of the clusters, where the optimal ratio in our case is 1:0.8, and is achieved simply by controlling the total process time. When the converted SiC fraction is larger than the carbon fraction in the clusters, it becomes impossible to separate the clusters from the nanowhiskers.

The two methods of obtaining SiC whiskers from (1) rice hulls [7–11] or (2) from the Fe catalyzed VLS procedure [14] mentioned above, both form much thicker whiskers than our method, which also forms very long, straight whiskers, of a very high aspect ratio. Our method eliminates any oxidation of the nanowhiskers. Oxidation had to be employed as part of the synthesis of camelback type SiC nanorods from bleached wood pulp [12] for removal of excess carbon.

2. Experimental procedure

Wooden powder (saw dust) is here used as the carbon source; the wooden powder is obtained from Danish beech wood by using a hammer mill shredder. An acidic precursor solution is prepared from tetraethyl orthosilicate (TEOS), hydrochloric acid and ethanol by mixing these in the molar ratio 1:4:17. The wooden powder is left soaking in the precursor solution for 6 h and then dried for around 20 h to leave SiO_2 uniformly distributed inside the wood. After this, the dried composite is transferred into an alumina crucible and heated to 1450 °C in a tubular furnace for 6 h in an argon flow of 250–300 ml/min. The furnace is heated and cooled at the rate of 5 °C/min.

The separation process is started right after removing the sample from the furnace. The sample is shredded carefully and is mixed in a ten times water by weight and oil mixture (petroleum:benzene). Then it is ultra sonicated for 10 min in this mixture and finally left to settle down for some time. At this stage the carbonaceous-coated silicon carbide clusters (which are almost black in color) surface in the oil layer at the top of the beaker, while the pure SiC nanowhiskers settle in the lower layer of water with a light grey color. The top layer of oil with the carbonaceous-coated silicon carbide clusters is then carefully removed and the nanowhiskers are cleaned with ethanol and water and are dried for further handling.

The SiC samples were characterized by X-ray diffraction (XRD), using a Siemens Diffractometer D5000, and imaged in a LEO 435 VP scanning electron microscope (SEM). The morphology, structure, defects, and crystal phases of individual SiC nanowhiskers was examined by transmission electron microscopy (TEM) using a Philips CM20 instrument operated at 200 kV. The confirmation of the silicon carbide character of the nanowhiskers was also done with a Raman microscope from Dilor, using the 456 nm Ar-ion laser line. The laser was focused over bunches and over individual nanowhiskers with an optical microscope coupled to the Raman microscope.

3. Results and discussion

3.1. Characterization

Fig. 1a shows the XRD patterns of nanowhisker samples after separation, confirming the β phase of the SiC, which is also confirmed by Raman and TEM studies. The major peaks of SiC are observed at $2\theta = 35.6°$, 41.4°, 60°, and 71.7° corresponding to diffraction from SiC (1 1 1), SiC (2 0 0), SiC (2 2 0), and SiC (3 1 1) planes while the peak at 21.8° corresponds to silica. There is an additional peak observed at 33.6° which is the characteristic of stacking faults [21] and thus is used to measure and discuss the amount of stacking faults as mentioned later. The top layer of the sample (before separation) contains some white fibers, which have been confirmed as SiC fibers with a significant coverage by silica responsible for the silica peak at 21.8°. Fig. 1a also shows the XRD pattern of separated nanowhiskers after etching with conc. hydrofluoric acid (HF) for 1 h. The absence of a silica peak indicates that HF has etched away all the silica.

Fig. 1b shows the Raman spectra with light focused on the nanowhiskers, confirming the whiskers as β-SiC. The peak positions of these nanowhiskers are thus observed around 781–787 cm^{-1} and 950 cm^{-1} which are the locations of the known transverse optical (*TO*) and longitudinal optical (*LO*) modes of β-SiC. Bulk β-SiC has two optical modes at the Γ point of the Brillouin zone, a transverse optical (*TO*) mode at 796 cm^{-1} and a longitudinal optical (*LO*) mode at 972 cm^{-1} [22]. The full

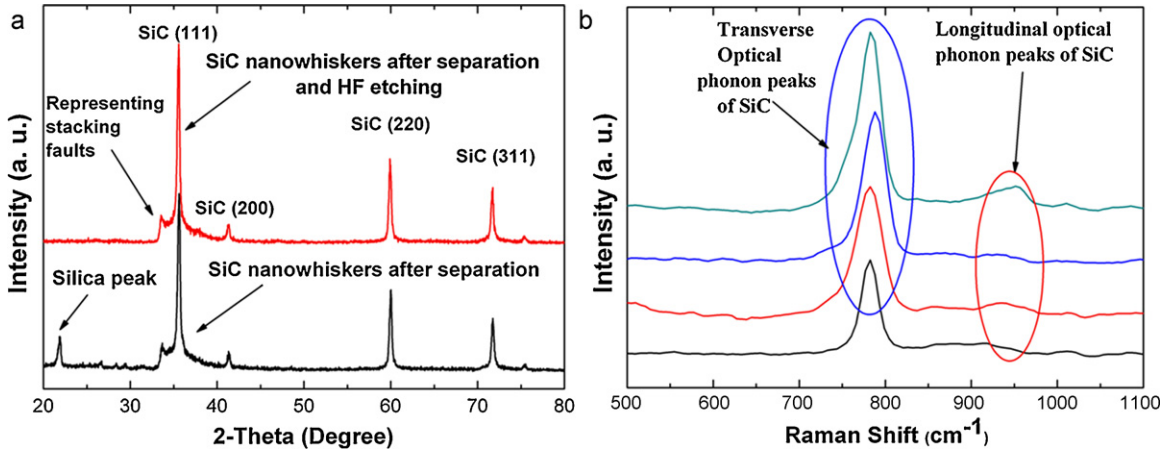

Fig. 1. (a) XRD pattern of the SiC nanowhiskers after separation and etching with HF and (b) Raman spectra of a few nanowhiskers.

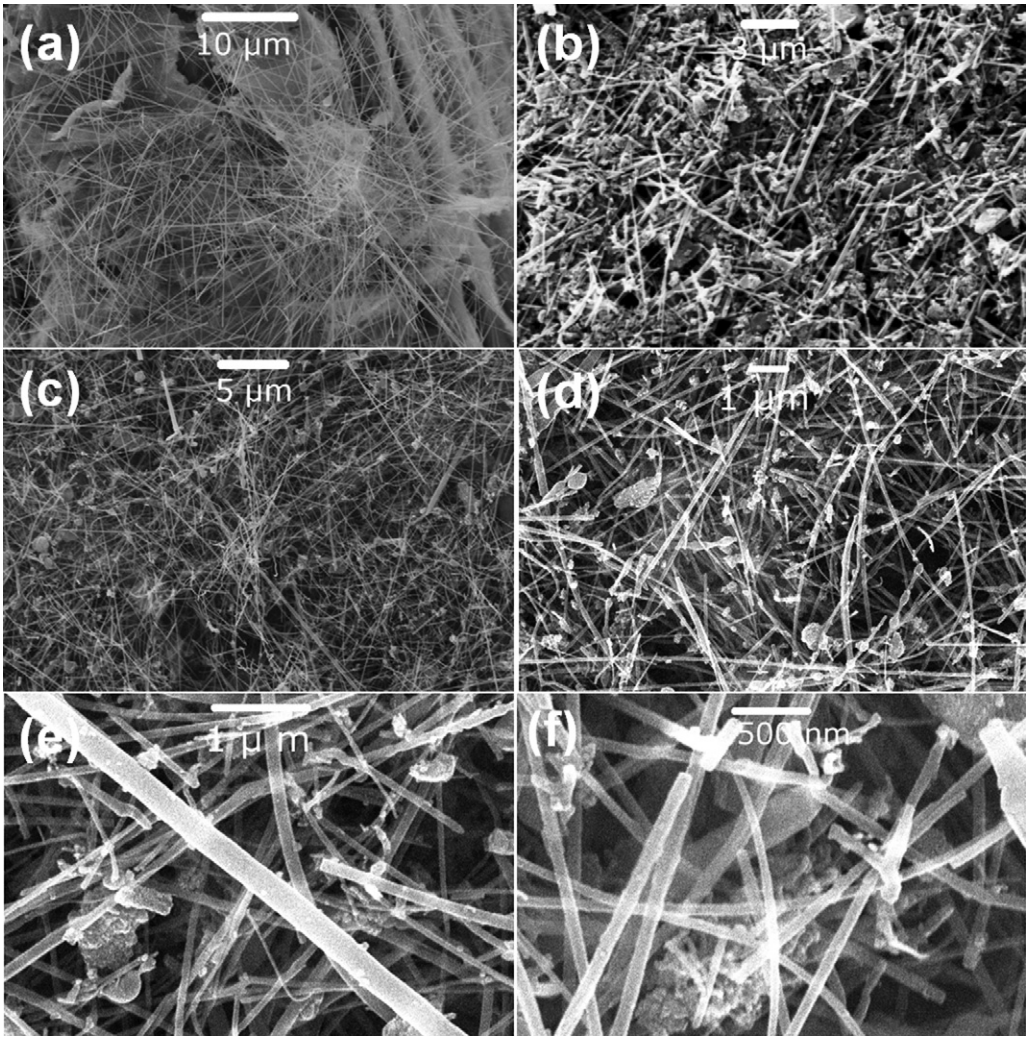

Fig. 2. SEM images of the nanowhiskers: (a) as grown, (b) mechanically separated, and (c–f) after separation at different magnifications.

width at half maximum (FWHM) of the observed peaks are in the range of 22–31 cm^{-1}, suggesting that the nanowhiskers contain defects and stacking faults, which are also responsible for the small variation of the peak positions of the TO and LO modes seen in Fig. 1b.

Fig. 2 shows SEM images of the nanowhiskers before and after separation. Fig. 2a shows the samples *as made* before separation. This figure shows the carbonaceous SiC clusters in the background and the needle-like nanowhiskers directed outward. Fig. 2b shows the SiC nanowhiskers separated using mechanical separation methods. In this case, the ultra sonication and centrifugation procedures broke the nanowhiskers to shorter lengths and only the top layer of the deposit contained whiskers. Fig. 2c–f shows the nanowhiskers after separation at different magnifications. The nanowhiskers have lengths in the range of 20–50 μm and they can sometimes be longer than 100 μm, as grown. After the separation process their average lengths are in the range of 15–40 μm. The average diameters are in the range of 60–80 nm but some diameters are as low as 25 nm and some as high as 300 nm. These dimensions after checking many SEM and TEM images. Small amounts of tiny SiC clusters are observed along with the separated nanowhiskers in the SEM images in Fig. 2c–f and they are below 2 μm in size.

Fig. 3 shows TEM images of the nanowhiskers with dimensions in complete agreement with those obtained from the SEM images. Fig. 3a and c show two straight nanowhiskers with diameters of 30 and 52 nm respectively. Fig. 3b shows two crossed nanowhiskers, one lying on the other with the diameters of 92 and 70 nm respectively. The nanowhiskers have non-uniform surfaces (as with all the other techniques). Fig. 3d shows the selected area electron diffraction (SAED) pattern of a straight nanowhisker. The diffraction pattern contains two equivalent ⟨1 1 0⟩ zone axis patterns from the β-SiC cubic zinc blende structure originating from two twin variants. The two patterns indicated in Fig. 3d are equivalent and rotated relative to each other to give two common (1 1 1) reflections and four separate (1 1 1) reflections and both twin variants are oriented with their interfaces perpendicular to the (1 1 1) whisker axis. The diffuse streaks in the diffraction pattern are believed to originate from planar defects such as stacking faults and/or twin-interfaces.

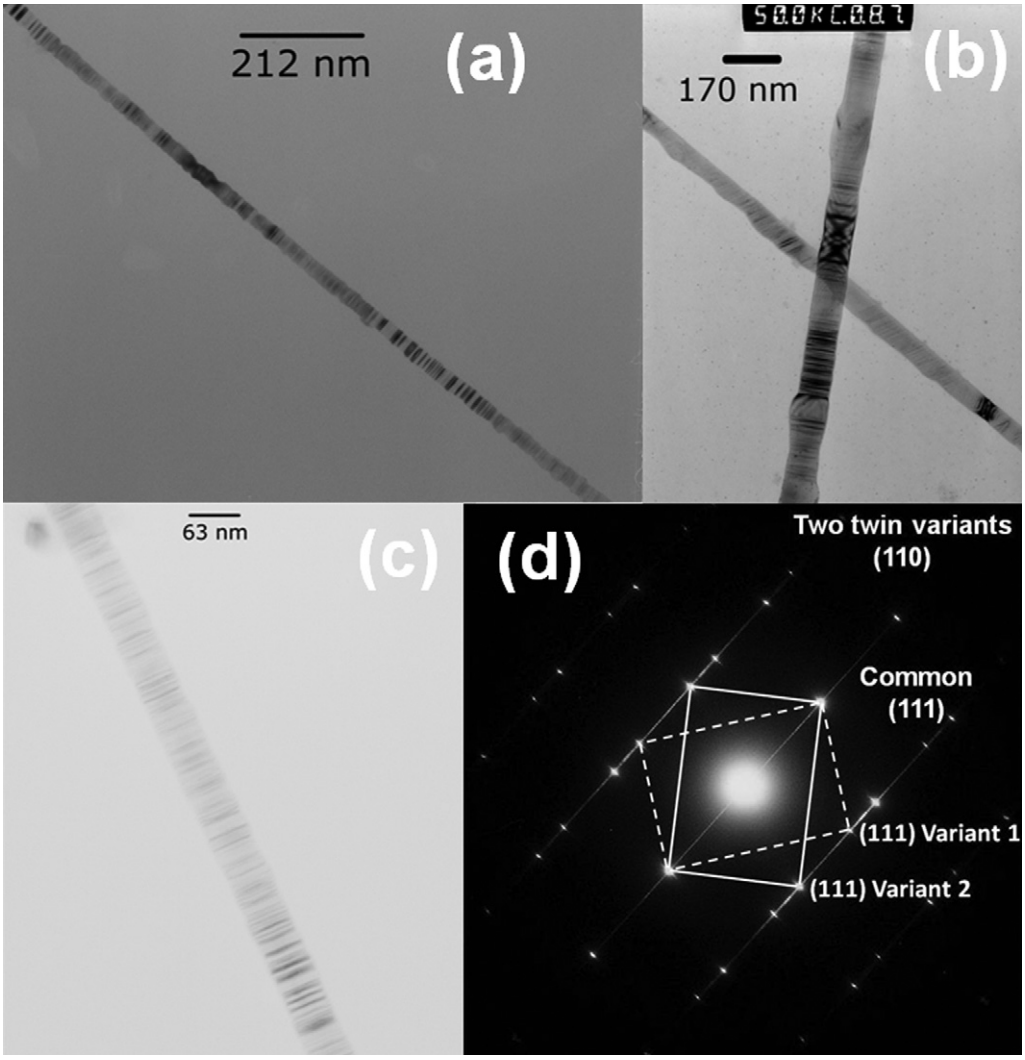

Fig. 3. (a–c) TEM images of few of the nanowhiskers with dense distributions of twins and stacking faults and (d) SAED pattern from the ⟨1 1 0⟩ zone axis of a nanowhisker containing two twin variants. The common (1 1 1) direction is parallel to the whisker axis. The diffuse streaks originate from planar defects such as stacking faults.

3.2. Growth mechanism

The SiC clusters are formed by the carbothermal reduction of silica, which liberates SiO and CO in the reaction cell by the following reaction:

$$SiO_2(s) + C(s) \rightarrow SiO(g) + CO(g) \quad (1)$$

$$SiO(g) + 2C(s) \rightarrow SiC(s) + CO(g) \quad (2)$$

The SiO and CO generated in reactions (1) and (2) react at nucleation sites on the SiC:C clusters formed earlier to form *outward growing, long, straight and uniform* SiC nanowhiskers which grow everywhere on all the clusters:

$$SiO(g) + 3CO(s) \rightarrow SiC(\text{nanowhiskers}) + 2CO_2(g) \quad (3)$$

The presence of these nanowhiskers, but in varying quantities, is always found for different synthesis routes with processing steps towards forming compact SiC structural elements by the contact reaction of SiO with a carbon preform, as also reported earlier [12,19,20]. The typically small quantity of whiskers in these cases is also an indirect evidence for a secondary nature of the reaction to grow the nanowhiskers because the primary reaction is the conversion of bulk carbon to bulk SiC, which consumes most of the SiO, and the secondary reaction is only taking place by residual SiO reacting with liberated CO. We are able to separate an amount up to 5–10% by weight of nanowhiskers from the total SiC (whiskers and clusters) grown. The ratio of whiskers to clusters was observed to increase (confirmed by optical microscope and SEM) when we increased the SiO and CO quantities inside the same reaction cell by placing solid carbon pieces over a 1:1 molar mixture of silicon and silica. The SiO vapors, produced by the reaction of silicon and silica, first react with carbon pieces placed overhead to produce SiC replicas of the carbon pieces and at the same time liberate CO. This residual gas of CO and SiO is carried away by the argon flow to carbon pieces impregnated with silica (TEOS) placed further downstream. But, the main drawback of enhancing whisker growth by such

in situ excess generation of SiO and CO is that it also increases the quantity of fully reacted SiC clusters, thus making the separation of whiskers difficult. Nanowhiskers have also been observed over the upper surfaces of carbon pieces placed directly over the silicon/silica mixture, which confirms the gas–gas-surface character of the reaction.

Thus, we conclude from all the above-mentioned observations and from the normally small ratio of whiskers to SiC clusters that the CO + SiO gas–gas-surface reaction is the growth mechanism for the nanowhiskers, and that it occurs sequentially to the formation of clusters. In a recent study of the conversion of SiC nanotubes to single crystal (β-) SiC whiskers (called fibers in that work), Cheng et al. [23] discussed three possible growth mechanisms: VLS, spiral growth, and vapor–solid (VS) growth, where VS growth in their work means the same as the mechanism adopted here. They found the VS mechanism to be consistent with their observations, and explained the participation of oxygen in the process, as well as the role of nucleation centers, as already discussed in a much earlier work [24]. In their discussion they speculate about the origin of the CO and possible nucleation sites.

Only a negligible amount of whiskers is observed when we use spherical Vulcan XC-72 carbon powder as the carbon source, under otherwise similar reaction conditions. This leads to the conclusion that the nanowhiskers must start nucleating at planar regions of defects, which are more likely to be created on the roughly textured SiC clusters formed from wooden powder during impregnation. Defects like grain boundaries, grain edges, dislocations, stacking faults etc. have already been proposed as nucleation sites for SiC filaments by Lotnyk et al. [25]. They stated that the proportion of the defect energy that is involved in the nucleation reduces the energy of formation of the whiskers. Other forms of pure carbon with rough surface structures obtained from wood have also shown growth of nanowhiskers. It has been reported [26,27] that most stacking faults were found in the relatively smaller diameter whiskers, which can be explained on the basis of lateral surface energy considerations. The small diameter whiskers have relatively higher lateral surface areas and the contribution of surface energy to the formation energy of nanowhiskers thus becomes important, but this effect may be reduced by the recurring creation of stacking faults, to lower the total formation energy and thus allowing continuous growth of the whiskers with uniform cross sections (cpr. camelback structures). The presence of nitrogen in the hot ambient residual atmosphere in the furnace may tend to favor the formation of β-SiC as previously discussed [25,28].

The intensity ratio of the XRD peaks at 33.6° and 41.4° ($I_{33.6^\circ}/I_{41.4^\circ}$) has been used [21] as indicator of the amount of stacking faults, and the value of 1.64 in our case indicates a high density of stacking faults, as also seen in the TEM images in Fig. 3.

4. Conclusions

We have successfully synthesized and separated β-SiC nanowhiskers starting from everyday wooden precursors, and have carefully observed and discussed the growth mechanism to involve totally or partly reacted SiC clusters. Separation of nanowhiskers from carbonaceous-coated-not-fully-reacted silicon carbide clusters has been accomplished with a liquid–liquid separation method. The SiC nanowhiskers grow by a *gas–gas surface defect nucleated reaction* unlike the SiC clusters, which grow in a solid–gas reaction process. The hydrophilic nature of pure SiC nanowhiskers and hydrophobic nature of non-fully reacted, carbonaceous-coated silicon carbide clusters is taken advantage of in the separation process of the nanowhiskers. This low cost and easy synthesis route can produce long and straight β-SiC nanowhiskers in large quantities.

Acknowledgements

The Danish Ministry for Research and Innovation, through its program for Sustainable Energy and The Environment, has funded this work with a grant to R. Dhiman, 2104-05-0073. The authors are grateful for advice and technical support from E. Skou, T. Warner, P.B. Hansen, D. Kyrping, and T. Sørensen at SDU, Odense, Denmark; and to R. Bala at HPU Shimla, India.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ceramint.2011.06.001.

References

[1] G.Z. Cambaz, G.N. Yushin, Y. Gogotsi, V.G. Lutsenko, Anisotropic etching of SiC whiskers, Nano Lett. 6 (2006) 548–551.
[2] B.Q. Wei, J.W. Ward, R. Vajtai, P.M. Ajayan, R. Ma, G. Ramanath, Simultaneous growth of silicon carbide nanorods and carbon nanotubes by chemical vapor deposition, Chem. Phys. Lett. 354 (2002) 264–268.
[3] A.M. Morales, C.M. Lieber, A laser ablation method for the synthesis of crystalline semiconductor nanowires, Science 279 (1998) 208–211.
[4] P. Lou, J.Y. Lee, Electrical control of magnetization in narrow zigzag silicon carbon nanoribbons, J. Phys. Chem. C 113 (2009) 21213–212217.
[5] K.W. Wong, X.T. Zhou, F.C.K. Au, H.L. Lai, C.S. Lee, S.T. Lee, Field-emission characteristics of SiC nanowires prepared by chemical-vapor deposition, Appl. Phys. Lett. 75 (1999) 2918–2920.
[6] K.W. Chen, Y.H. Yu, Y.M. Lei, L.L. Cheng, B. Sundaraval, E.Z. Luo, S.P. Wong, I.H. Wilson, L.Z. Chen, C.X. Ren, S.C. Zou, Non-Rutherford backscattering studies of SiC/SIMOX structures, Appl. Surf. Sci. 184 (2001) 178–182.
[7] R.V. Krishnarao, J. Subrahmanyam, Formation of SiC from rice husk silica-carbon black mixture: effect of rapid heating, Ceram. Int. 22 (1996) 489–492.
[8] R.V. Krishnarao, M.M. Godkhindi, M. Chakraborty, P.G. Mukunda, Formation of SiC whiskers from compacts of raw rice husks, J. Mater. Sci. 29 (1994) 2741–2744.
[9] B.K Parekh, W.M. Goldberger, Recovery of silicon carbide whiskers from coked, converted rice hulls by liquid–liquid separation, US Patent 4,249,700 (February 1981).
[10] B.K. Parekh, W.M. Goldberger, Recovery of silicon carbide whiskers from coked, converted rice hulls by froth flotation, US Patent 4,293,099 (October 1981).
[11] P. Somasundarn, K.P.A. Padmanabhan, Recovery of silicon carbide whiskers from coked, converted rice hulls by selective flocculation-liquid extraction, US Patent 4,256,571 (March 1981).

[12] Y. Shin, C. Wang, W.D. Samuels, G.J. Exarhos, Synthesis of SiC nanorods from bleached wood pulp, Mater. Lett. 61 (2007) 2814–2817.
[13] J. Li, Y. Zhang, X. Zhong, K. Yang, J. Meng, X. Cao, Single-crystalline nanowires of SiC synthesized by carbothermal reduction of electrospun PVP/TEOS composite fibres, Nanotechnology 18 (2007) 245606–245609.
[14] H.J. Choi, J.G. Lee, Continuous synthesis of silicon carbide whiskers, J. Mater. Sci. 30 (1995) 1982–1986.
[15] Y.J. Wu, J.S. Wu, W. Qin, D. Xu, Z.X. Yang, Y.F. Zhang, Synthesis of β-SiC nanowhiskers by high temperature evaporation of solid reactants, Mater. Lett. 58 (2004) 2295–2298.
[16] J.M. Nihut, R. Vieira, L. Pesant, J.P. Tessonnier, N. Keller, G. Ehret, C.P. Huu, M.J. Ledoux, Synthesis and catalytic uses of carbon and silicon carbide nanostructures, Catal. Today 76 (2002) 11–32.
[17] C.C. Tang, S.S. Fan, H.Y. Dang, J.H. Zhao, C. Zhang, P. Li, Q. Gu, Growth of SiC nanorods prepared by carbon nanotubes-confined reaction, J. Cryst. Growth 210 (2000) 595–599.
[18] S. Dhage, H.C. Lee, M.S. Hassan, M.S. Akhtar, C.Y. Kim, J.M. Sohn, K.J. Kim, H.S. Shin, O.B. Yang, Formation of SiC nanowhiskers by carbothermic reduction of silica with activated carbon, Mater. Lett. 63 (2009) 174–176.
[19] E. Vogli, J. Mukerji, C. Hoffman, R. Kladny, H. Sieber, P. Greil, Conversion of oak to cellular silicon carbide ceramic by gas-phase reaction with silicon monoxide, J. Am. Ceram. Soc. 84 (2001) 1236–1240.
[20] R. Dhiman, P. Morgen, Growth of SiC nano-whiskers on powdered SiC, nanotechnological basis for advanced sensors, NATO Science for Peace and Security Series B: Physics and Biophysics (Pt. 8) (2011) 281–285. , doi:10.1007/978-94-007-0903-4_31.
[21] W.S. Seo, K. Koumoto, Stacking faults in β-SiC formed during carbothermal reduction of SiO_2, J. Am. Ceram. Soc. 79 (1996) 1777–1782.
[22] M. Bechelany, A. Brioude, D. Cornu, G. Ferro, P. Miele, A Raman spectroscopy study of individual SiC nanowires, Adv. Funct. Mater. 17 (2007) 939–943.
[23] Q.M. Cheng, L.V. Interrante, M. Lienhard, Q. Shen, Z. Wu, Methylene-bridged carbosilanes and polycarbosilanes as precursors to silicon carbide—from ceramic composites to SiC nanomaterials, J. Eur. Ceram. Soc. 25 (2005) 233–241.
[24] W.Q. Han, S.S. Fan, Q.Q. Li, W.J. Liang, B.L. Gu, D.P. Yu, Continuous synthesis and characterization of silicon carbide nanorods, Chem. Phys. Lett. 265 (1997) 374–378.
[25] A. Lotnyk, J. Bauer, O. Breitenstein, H. Blumtritt, A TEM study of SiC particles and filaments precipitated in multicrystalline Si for solar cells, Sol. Energy. Mater. Sol. Cell 92 (2008) 1236–1240.
[26] H.J. Choi, J.G. Lee, Stacking faults in silicon carbide whiskers, Ceram. Int. 26 (2000) 7–12.
[27] L. Wang, H. Wada, L.F. Allard, Synthesis and characterization of SiC whiskers, J. Mater. Res. 7 (1992) 148–163.
[28] V. Heine, C. Cheng, R.J. Needs, The preference of silicon carbide for growth in the metastable cubic form, J. Am. Ceram. Soc. 74 (1991) 2630–2633.