Chemical surface transformation of SiC-based nanocables

M. BECHELANY[*], D. CORNU, F. CHASSAGNEUX, S. BERNARD, P. MIELE[§]

Laboratoire des Multimatériaux et Interfaces, UMR 5615 CNRS – University Claude Bernard Lyon 1, 43 bd du 11 novembre 1918, F-69622 Villeurbanne Cedex, France
[§] *Member of the IUF (Institut Universitaire de France)*

A black cotton-like solid made of pure interlaced SiC≅C nanocables was prepared and fully characterized. These SiC≅C NCs are made of SiC nanowires sheathed by a turbostratic carbon coating. Chemical surface modifications of these NCs have been performed. They can be transformed into SiC≅SiO$_2$ nanocables by a simple dry-air thermal treatment up to 550 °C. The nanofibrous shape is retained during the pyrolysis but the diameter of the ensuing NCs is smaller than that of the starting materials, due to a partial oxidation of the SiC core. The resulting amorphous silica coating can be removed by a concentrated HF treatment during 48H yielding pure SiC nanowires. These preliminary results demonstrate that chemical surface modifications of SiC-based fibrous nanostructures are possible. Applications are expected in the field of catalytic supports and composite materials.

1. Introduction

Since their first observation by S. Iijima in 1991 [1], an increasing number of works were devoted to the synthesis, characterization and utilization of single-wall then multi-walls carbon nanotubes, CNTs. In the same way, numerous studies are now exploring the preparation of nanowires (NWs) of various chemical compositions (SiC, Si$_3$N$_4$, ZnO, GaN, etc.). Indeed, nanowires can be more efficient than CNTs for some selected optical, electronic, mechanical or biological applications [2]. Among these materials, cubic silicon carbide (β-SiC) has attracted much interest due to its unique combination of valuable chemical and physical properties. Indeed, β-SiC is a wide band gap semi-conducting material which exhibits interesting properties, such as high thermal and chemical stability, high hardness and high mechanical strength. Due to these intrinsic properties, β-SiC is a good candidate for optoelectronic devices designed for high temperature, high power and high frequency applications, and even in harsh environments [3-7]. In addition, the possible uses of SiC nanostructures as catalyst supports [8-10] or as reinforcement materials in ceramic matrix composites [11] are also under investigation.

The large works started 30 years ago for the fabrication of SiC whiskers [12] was used in the past few years as a basis for developing a wide range of experimental techniques for the synthesis of SiC nanostructures. SiC nanowires have been prepared from CNTs and Si-rich vapor phase [5,13,14] or from Si NWs and carbon-rich vapor phase [15]. Similar carbothermal routes allow the synthesis of SiC NWs from carbon nanoparticles [16]. In a similar way, Li *et al.* have used a technique based on mechanical activation, with the ball-milling of a mixture of Si and SiO$_2$ powders, and a subsequent pyrolysis under a C$_3$H$_8$ flow [17]. In our group, we have synthesized SiC NWs from the reaction of commercial micrometric Si particles with gaseous "CN"-based reactants, generated in situ from solid carbon and nitrogen [18-20]. Lu *et al.* have also fabricated SiC NWs at low temperature, under high pressure, by using CCl$_4$, SiCl$_4$ and Na as raw materials [21]. More recently, Oya *et al.* prepared SiC NWs by melt-spinning of a polymer blend [22]. Finally, SiC NWs can also be prepared by using catalytic chemical vapor deposition (CCVD) process, and the vapor-liquid-solid (VLS) growth mechanism [23]. The same growth mechanism is used for the synthesis of SiC NWs by laser ablation [24], and by arc discharge [25]. All these techniques allow the production of SiC NWs at the lab-scale but the need for a simple route to produce large amount of SiC NWs has been clearly emphasized.

Recently, a breakthrough in the mass production of SiC-based nanostructures was performed in our group with the discovery of a simple and cheap method, based on a Vapor-Solid (VS) growth mechanism, allowing the fabrication of large amounts of SiC-based nanowires and nanocables [26]. The NCs can be seen as coaxial nanostructures made of SiC NWs sheathed by one or several coatings, and forming coaxial nanocomposites. Since it is now possible to produce amounts of SiC-based nanostructures compatible with industrial applications, we are now exploring the possible applications of these nanoobjects. For both catalytic and composite applications, one key point is to control the chemical nature of their surface. Indeed, this should open the way to

surface fonctionnalization of the NWs by catalytic active groups. Moreover, for composite applications, it is necessary to control the presence of a selected coating on the surface of the NWs, since this coating can act as an interphase between the NWs and the matrix. In this context, we describe in the present paper the first results concerning the chemical surface tuning of SiC-based nanostructures.

2. Experimental

All the nanostructures depicted in this paper were analyzed by the means of scanning electron microscopy (SEM, Model S800, Hitachi), high-resolution transmission electron microscopy (HRTEM, TOPCON 002B), energy dispersive X-ray spectroscopy (EDX, KEVEX SIGMA, NORAN Instruments), and XRD analysis using a Philipps PW 3040/60 X'Pert PRO X-ray diffraction system (Cukα radiation; $\lambda = 1.5406$ Å at 40 kV and 30 mA).

Samples of pure SiC≅C NCs were prepared as starting materials by the vapour-solid (VS) growth mechanism [26].

In a first experiment, an alumina boat filled with the black cotton-like solid made of pure SiC≅C NCs was placed into an alumina tube in a horizontal tube furnace. The tube was heated under a dry-air flow (5 mL min^{-1}) up to 550 °C (heating rate 200 °C h^{-1}). The temperature was maintained at 550 °C during 2 hours then allowed to cool down to room temperature. Finally, a white cotton-like solid was scraped from the alumina boat and then fully characterized.

In a second experiment, the ensuing white-cotton like solid was treated by concentrated hydrofluoric (HF) acid (50%) during 48 hours. After filtration, the product was washed by distilled water, absolute ethanol, and then acetone. After a drying step at 100 °C during 4 hours, the final product was obtained and subsequently analyzed.

3. Results and discussion

1. From SiC≅C NCs to SiC≅SiO$_2$ NCs

A sample of SiC≅C NCs was prepared by the catalytic decomposition of polypropylene onto a catalytic graphite surface, and in presence of SiO (g) [26]. The sample had an aspect of a black cotton-like solid and was analyzed by SEM and TEM. As illustrated by the image depicted in Fig. 1, SEM analysis of the sample indicates that it is wholly made of interlaced fibrous nanostructures. The latter are highly long and their length can be estimate up to 500 μm. The structure and chemical composition of the fibrous nanostructures were determined during TEM analysis.
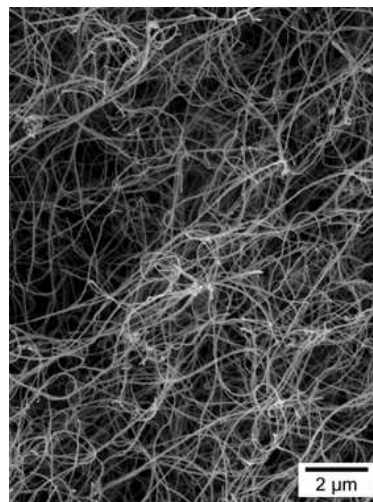

Fig. 1. SEM images of the black cotton-like solid made of SiC@C NCs.

Fig. 2 shows TEM images of the sample. In accordance with SEM observations, TEM investigations showed that the NWs prepared by this method were highly pure with no residual particles, and exhibited diameters falling in the range 50 to 100 nm. As evidenced by Fig. 2, the NWs exhibit a bumpy surface, which should be related to the presence of a heterogeneous coating onto their surface.
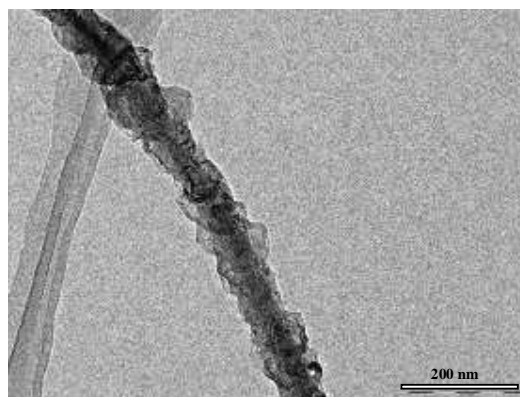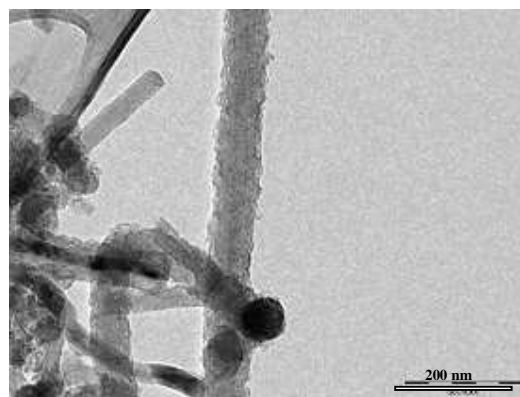

Fig. 2. TEM images of the black cotton-like solid.

HRTEM analyses were performed on these fibrous nanostructures and Fig. 3 shows an HRTEM image of a representative NW. The presence of a heterogeneous layer onto the surface of the NW can be clearly seen. The chemical compositions of the core and of the coating were determined by EDX analysis. The core of the fibrous nanostructure is composed of carbon and silicon. Selected area electron diffraction indicated that the core is made of the cubic polymorph of silicon carbide (β-SiC). The diameter of this central SiC nanowire was between 30 to 50 nm. As identified by HRTEM and electron diffraction, the preferential growth direction of the NWs is generally parallel to the [111] direction (see white arrow, Fig. 3), in agreement with previously reported studies [18]. EDX analysis revealed that the coating is made of pure carbon. As illustrated by the image on Fig. 3, HRTEM and electron diffraction revealed that that the coating is composed of turbostratic carbon, with an imperfect organization of the graphitic layers along the fibre axis. Therefore, the starting fibrous nanostructures were made of a β-SiC core sheathed by a turbostratic carbon layer, namely SiC≅C nanocables.
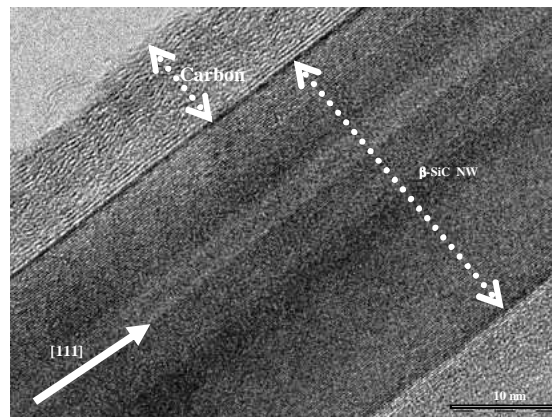

Fig. 3. HRTEM image of a β-SiC≅C nanocable.

In a first experiment, a sample of β-SiC≅C nanocables were heated up to 550 °C under a dry air flow. After 2 hours at this temperature, a white cotton-like solid was scrapped from the alumina boat and analyzed by SEM, TEM and DRX. Fig. 4 shows the diffractograms of the sample before and after the thermal treatment.
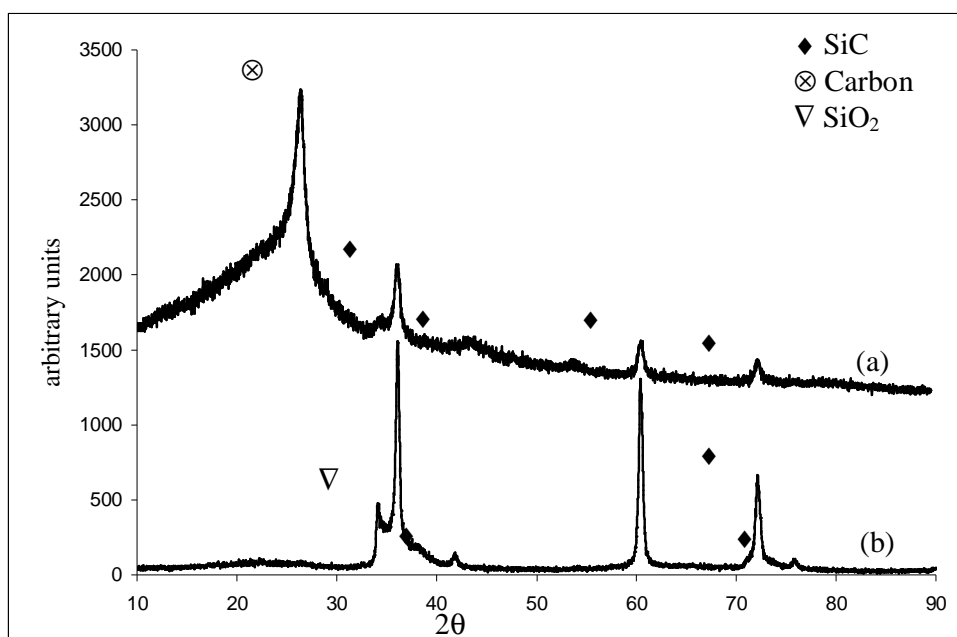

Fig. 4. Diffractograms of the sample of β-SiC≅C nanocables (a) before and (b) after the thermal treatment under dry-air up to 550 °C.

After the thermal treatment under dry-air, we observed that the diffraction peaks corresponding to turbostratic carbon are missing and that a broad wide peak at $2\theta = 34°$ appeared. This peak was attributed to SiO_2. These results evidence that the carbon coating was consumed during the dry-air pyrolysis and that silica has been generated from SiC. Next step is to determine if the nanofibrous shape has been retained during pyrolysis.

SEM analysis revealed that the sample is still made of interlaced fibrous nanostructures, and the recorded images were very similar to the ones corresponding to SiC≅C NCs. In contrast, a representative TEM image of the sample is given in Fig. 5.
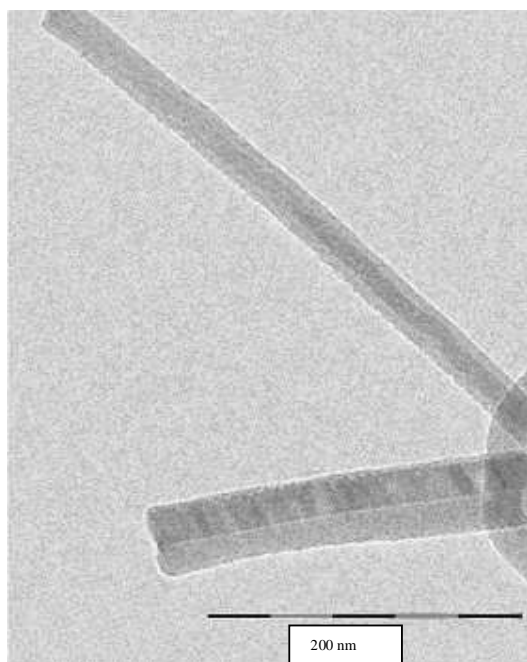
Fig. 5. TEM image of the β-SiC≅SiO$_2$ nanocables.

EDX and electron diffraction analyses indicated that the core is still made of cubic silicon carbide. The SiC nanowires exhibited diameters between 10 to 30 nm, which is smaller than before the thermal treatment. These SiC NWs are sheathed by an amorphous layer of silica, forming SiC≅SiO$_2$ NCs. The surface of the NCs was smooth compared to SiC≅C NCs. The layer thickness runs from 10 to 40 nm. Therefore, we can deduce from these observations that, during the thermal treatment under dry-air, the carbon layer was first removed by oxidation. In a second step, the SiC NWs were also oxidized yielding SiC≅SiO$_2$ NCs. Consistently with this assumption, the diameter of these NCs are in the same range than the initial SiC core of the SiC≅C NCs.

It is also interesting to notice than the SiC cores of the SiC≅SiO$_2$ NCs are generally not located at the geometric middle of the NCs. This could be due to the position of the starting carbon-coated NCs compared to the air flow during pyrolysis, which yield to an anisotropic oxidation of the SiC NWs.

Therefore, we have demonstrated that SiC≅C NCs can be transformed by air-oxidation into SiC≅SiO$_2$ NCs. The next step is now to determine if this silica coating can be removed to yield pure SiC NWs with low diameters.

2. From SiC≅SiO$_2$ NCs to SiC NWs

In order to eliminate the outer layer of amorphous SiO$_2$, the SiC≅SiO$_2$ NCs were treated by concentrated hydrofluoric acid (50%) during 48 hours. After filtration, the product was washed by distilled water, absolute ethanol, and then acetone. A drying step at 100 °C for 4 hours yielded a light-blue cotton-like solid. The SEM investigations reveals that the nanofibrous shape of the

samples was not affected by the HF treatment. The TEM analysis was carried out and a low magnification image is presented in Fig. 6. This image indicated that the sample was made of interlaced nanowires. They exhibit heterogeneous diameter going from 5 to 30 nm and lengths which can reach several hundreds of micrometers.
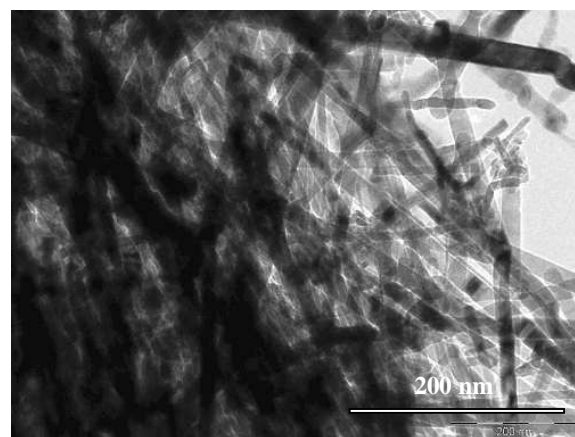

Fig. 6. TEM image of the blue-white cotton-like solid.

A great number of nanowires was studied and analyzed by TEM. As an illustration, Fig. 7a shows the TEM image of a typical nanowire. Its chemical analyses by EDX confirmed that it was made of pure silicon carbide without any coating layer. The SAED analysis (Fig. 7b) permitted to verify that we had obtained the cubic polymorph of SiC, β-SiC. Therefore, we have determined a two-spot route for the mass fabrication of SiC NWs from SiC≅C NCs via SiC≅SiO$_2$ NCs.
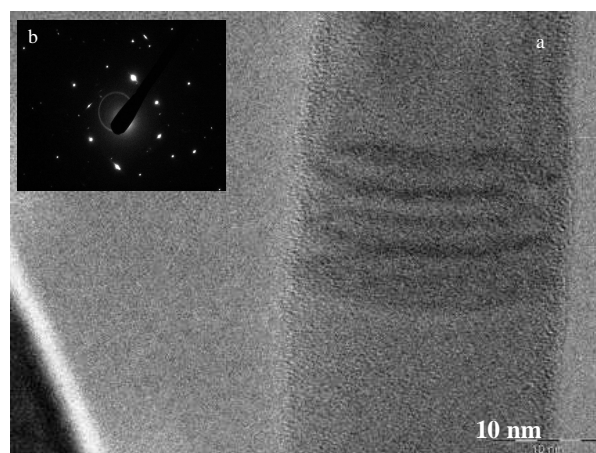

Fig. 7. (a) TEM image and the corresponding SAED of a SiC nanowire.

4. Conclusions

As we found, SiC≅C nanocables, which consist of SiC nanowires sheathed by a layer of turbostratic carbon, can

be transformed into SiC≅SiO$_2$ nanocables by a simple dry-air thermal treatment up to 550 °C. The nanofibrous shape is retained during the pyrolysis but the diameters of the ensuing NCs are smaller than those of the starting materials due to a partial oxidation of the SiC core of the SiC≅C NCs. The resulting amorphous silica coating can be removed by a concentrated HF treatment during 48H yielding SiC nanowires. These results open the way to a large range of possible surface modifications of SiC-based fibrous nanostructures and applications are expected in the field of catalytic supports and composite materials. Further works are now devoted to the control of the thickness of the different coating and of the diameter of the resulting SiC nanowires.

Acknowledgment

References

[1] S. Iijima, Nature **354**, 56 (1991).

[2] P. Yang, MRS Bulletin **30**, 85 (2005).

[3] J. A. Cooper, JR., Phys. Stat. Sol. (a) **162**, 305 (1997).

[4] W. Han, S. Fan, Q. Li, W. Liang, B. Gu, D. Yu, Chem. Phys. Lett. **265**, 374 (1997).

[5] X. T. Zhou, R. Q. Zhang, H. Y. Peng, N. G. Shang, N. Wang, I. Bello, C. S. Lee, S. T. Lee, Chem. Phys. Lett. **332**, 215 (2000).

[6] K. W. Wong, X. T. Zhou, F. C. K. Au, H. L. Lai, C. S. Lee, S. T. Lee, Appl. Phys. Lett. **75**, 2918 (1999).

[7] S. T. Lee, C. S. Lee, N. Wang, I. Bello, C. H. L. Lai, X. T. Zhou, F. C. K. Au, US patent No. 6,221,154 B1 (2001).

[8] J. M. Nhut, R. Vieira, L. Pesant, J. P. Tessonnier, N. Keller, G. Ehret, C. Pham-Huu, M. J. Ledoux, Catalysis Today **76**, 11 (2002).

[9] C. Pham-Huu, C. Bouchy, T. Dintzer, G. Ehret, C. Estournes, M. J. Ledoux, Appl. Catalysis A **180**, 385 (1999).

[10] Q.-M. Cheng, L. V. Interrante, M. Lienhard, Q. Shen, Z. Wu, J. Europ. Ceram. Soc. **25**, 233 (2005).

[11] W. Wang, H. Araki, A. Kohyama, Y. Katoh, Q. Hu, H. Suzuki, T. Noda, J. Nuclear Mater. **329-333**, 539 (2004).

[12] K. Sujirote, P. Leangsuwan, J. Mater. Sci. **38**, 4739 (1993) and ref. therein.

[13] H. Dai, E. W. Wang, Y. Z. Lu, S. Fan, C. M. Lieber, Nature **375**, 769 (1995).

[14] D. Zhou, S. Seraphin, Chem. Phys. Lett. **222**, 233 (1994).

[15] Y. F. Zhang, Y. H. Tang, Y. Zhang, C. S. Lee, I. Bello, S. T. Lee, Chem. Phys. Lett. **330**, 48 (2000).

[16] G. W. Meng, Z. Cui, L. D. Zhang, F. Philipp, J. Crystal Growth **209**, 801 (2000).

[17] Z. J. Li, H. J. Li, X. L. Chen, A. L. Meng, A. L. Meng, K. Z. Li, Y. P. Xu, L. Dai, Appl. Phys. A **76**, 637 (2003).

[18] K. Saulig-Wenger, D. Cornu, F. Chassagneux, G. Ferro, T. Epicier, P. Miele, Solid State Comm. **124**, 156 (2002).

[19] K. Saulig-Wenger, D. Cornu, F. Chassagneux, G. Ferro, P. Miele, T. Epicier, Ceram. Trans. **137**, 93 (2003).

[20] K. Saulig-Wenger, D. Cornu, F. Chassagneux, S. Parola, P. Miele, T. Epicier, Ceram. Trans. **148**, 131 (2004).

[21] Q. Lu, J. Hu, K. Tang, Y. Qian, G. Zhou, X. Liu, J. Zhu, Appl. Phys. Lett. **75,** 507 (1999).

[22] N. Patel, R. Kawai, A. Oya, J. Mater. Science **39**, 691 (2004).

[23] H. F. Zhang, C. M. Wang, L. S. Wang, Nanoletters **2**, 941 (2002).

[24] Y. Zhang, K. Suenaga, C. Colliex, S. Iijima, Science **281**, 973 (1998).

[25] P. Singjai, A. Womgjamras, L. D. Lu, T. Tunkasiri, Chem. Phys. Lett. **366**, 51 (2002).

[26] M. Bechelany, D. Cornu, P. Miele, French Pat. Appl. n° 04 13613 (21/12/2004).

---

* Corresponding authors: Mikhael.Bechelany@univ-lyon1.fr