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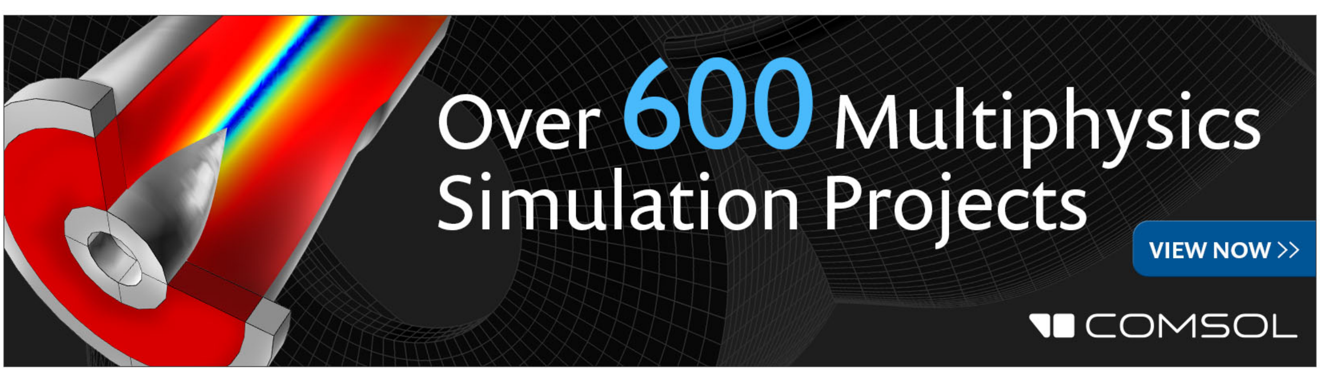

Synthesis of silicon nitride nanorods using carbon nanotube as a template

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A method to prepare silicon nitride nanoscale rods using carbon nanotube as a template has been presented in this letter. The products of the reaction of carbon nanotubes with a mixture of Si and SiO_2 powder in nitrogen atmosphere are β-Si_3N_4, α-Si_3N_4, and Si_2N_2O nanorods. The sizes of the nanorods are 4–40 nm in diameter and up to several microns in length. The formation mechanism of the nanorods has also been discussed.
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Synthesis of nanoscale one dimensional structures still remain a challenge. Since the discovery of carbon nanotube,[1] efforts have been made on synthesis of one dimensional nanoscale materials by using carbon nanotube as a template.[2–6] Recently, Dai *et al.* reported that carbide nanorods whose diameters were similar to or much smaller than the diameters of the carbon nanotubes could be produced via the reaction of the carbon nanotubes with volatile transition-metal and main-group halide or oxide species.[7] We also synthesized SiC nanorods in a two-step process involving the generation of SiO followed by reacting with carbon nanotubes and proposed a model for growth mechanism of SiC nanorods.[8] It could be suggested that in the formation of carbide nanorod the carbon nanotube might confine the reaction in a local space around the nanotube. In the experiment reported here, we found that the nanotube space confined reaction is more general than forming carbide nanorods. We successfully prepared nanometer Si_3N_4 rods of the diameters similar to the diameters of starting carbon nanotubes through a reaction of the carbon nanotubes with Si-SiO_2 powder mixture in nitrogen atmosphere. Although the final products do not contain carbon element, carbon nanotube might play an important role as a removable template during the reaction.

Carbon nanotubes used in this study were prepared by metal catalytic decomposition of ethylene and hydrogen in a chemical vapor deposition system.[8] The catalytic growth procedure yielded relatively pure multishell carbon nanotubes with typical diameters around 15 nm. The preparation apparatus for synthesis of nitride nanorods is a conventional furnace with a sintered alumina tube. An alumina crucible containing Si-SiO_2 powder mixture covered with carbon nanotubes was placed in the hot zone inside the alumina tube. Nitrogen gas was flowing during the overall reaction period. The reaction was carried out at 1673 K for 1 h. After the reaction, a white woollike layer formed at the original nanotube bed. This layer of products was identified by x-ray diffraction (XRD, D/max-RB), transmission electron microscopy (TEM, Philips-CM200), and high resolution transmission electron microscopy (HREM, Hitachi-9000NAR).

Figure 1 is an XRD pattern of the products, which is identified as a mixture of β-Si_3N_4, α-Si_3N_4 and Si_2N_2O. As can be seen from Fig. 1, the peaks assigned to β-Si_3N_4 are stronger than the others, indicating the products are dominantly β-Si_3N_4. There is no peak associated with crystalline SiC, graphite, or other crystalline forms connected with carbon in the XRD pattern. Figure 2(a) is a TEM micrograph of the products. The TEM image shows that the products are relatively straight nanorods with diameters ranging from 4 to 40 nm, which are close to the diameters of the starting carbon nanotubes [Fig. 2(b)]. The lengths of the nanorods are up to several microns. The diameters of the produced nitride nanorods are significantly smaller than the previous observations made on the Si_3N_4 whiskers prepared by other methods.[9,10] The Si_3N_4 nanorods are solid other than the hollow core structure of carbon nanotubes. Figures 3(a) and 3(b) show the selected area electron diffraction patterns of a nitride nanorod, which are consistent with single crystalline nature of the sample. The patterns can be indexed to the reflection of β-Si_3N_4[001] and β-Si_3N_4[100], respectively. Figure 4 shows a HREM image of a β-Si_3N_4 nanorod with a

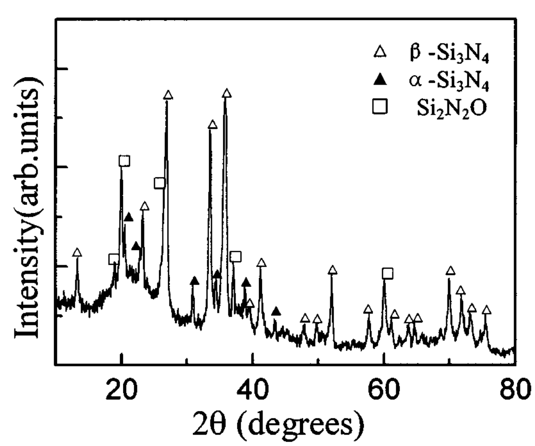

FIG. 1. An x-ray diffraction spectrum of the sample.

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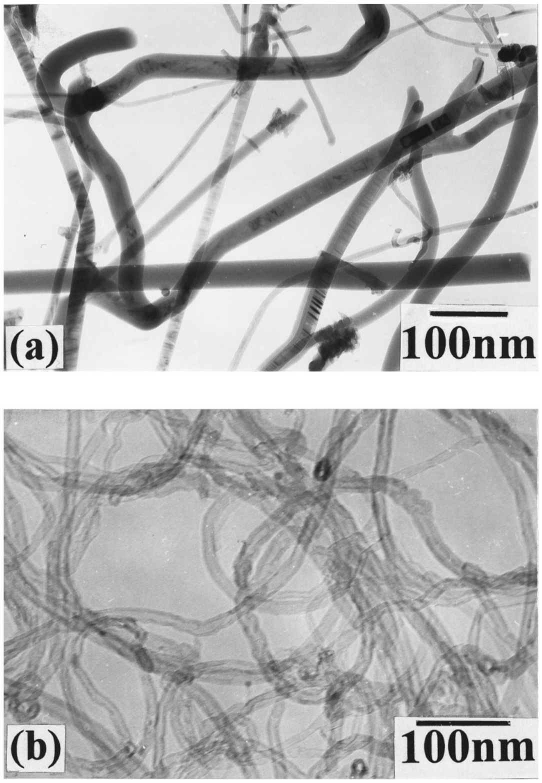

FIG. 2. TEM micrographs of (a) silicon nitride nanorods and (b) carbon nanotubes.

diam about 7.4 nm. The (100) fringes with a spacing of 0.66 nm are parallel to the edge of nanorod and the axis of nanorod is along β-Si_3N_4 crystallographic **c** direction ([001] direction). Figure 5 shows a HREM image taken from a Si_2N_2O nanorod, which is about 13 nm in diam and the axis of the nanorod is along its crystallographic **a** direction ([100] direction).

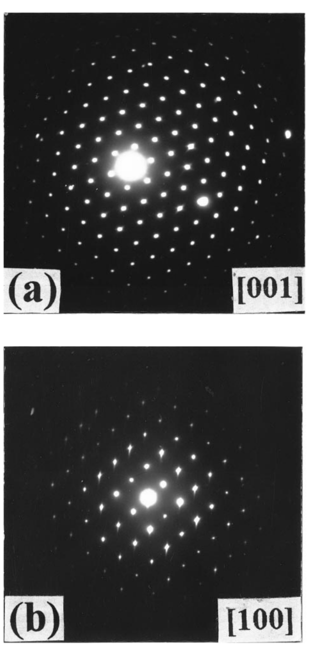

FIG. 3. Selected area electron diffraction patterns of a β-Si_3N_4 nanorod: (a) [001] diffraction pattern; (b) [100] diffraction pattern.

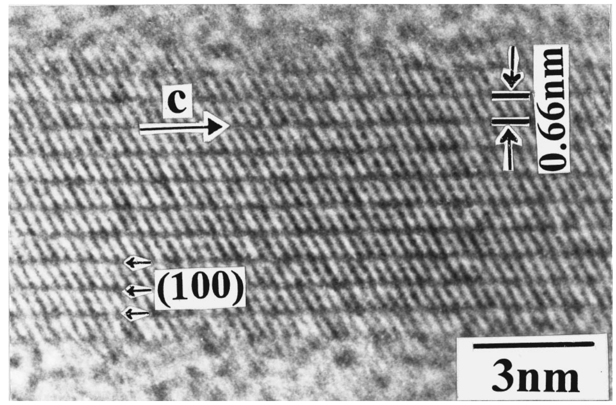

FIG. 4. A HREM image of a β-Si_3N_4 nanorod with a diameter about 7.4 nm. The (100) fringes with a spacing of 0.66 nm are parallel to the edge of the nanorod and the nanorod axis is along β-Si_3N_4 crystallographic **c** direction ([001] direction).

In the reaction process, the important SiO gas for formation of Si_3N_4 and Si_2N_2O nanorods was first generated via the silicon reduction of silica,

$$SiO_2(s)+Si(s)\rightarrow 2SiO(g). \tag{1}$$

The generated SiO gas and inlet N_2 gas flowed toward the region of carbon nanotubes from the lower and upper directions, respectively, then reacted with carbon nanotubes together. In a Si–C–N–O system, there are two reactions that could be responsible for the formation of Si_3N_4 and Si_2N_2O nanorod, which can be expressed as[9]

$$3SiO(g)+3C(s)+2N_2(g)\rightarrow Si_3N_4(s)+3CO(g), \tag{2}$$

$$2SiO(g)+C(s)+N_2(g)\rightarrow Si_2N_2O(s)+CO(g). \tag{3}$$

We believe that the carbon nanotube might act as a removable template in the reaction to confine the reaction in a local space around carbon nanotube. Therefore, the products almost hold the shape and the diameter size of nanotube skeletons, even if they do not contain carbon element.

In summary, silicon nitride nanorods have been successfully synthesized by carbon nanotube confined reaction. Al-

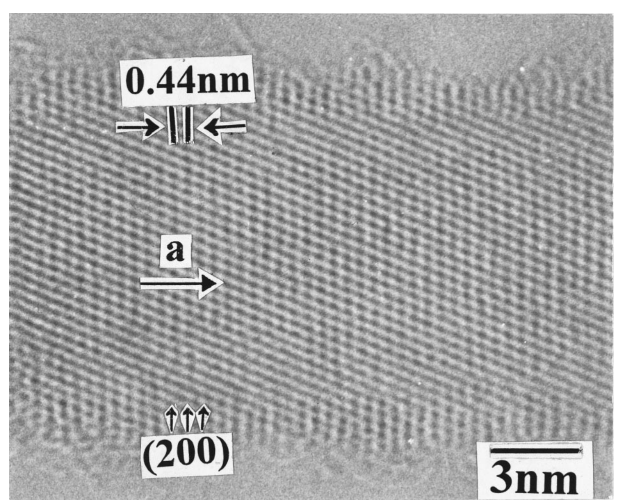

FIG. 5. A HREM image taken from a Si_2N_2O nanorod, which is about 13 nm and the nanorod axis is along its crystallographic **a** direction ([100] direction).

though a deeper understanding of growth mechanism of the silicon nitride nanorod is needed, our results suggest the carbon nanotube confined reaction could in principle be used to synthesize other nitride nanorods which might be of interest to both fundamental research and possible applications.

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[1] S. Iijima, Nature (London) **354**, 56 (1991).
[2] P. M. Ajayan and S. Iijima, Nature (London) **361**, 333 (1993).
[3] E. Dujardin, T. W. Ebbesen, H. Hiura, and K. Tanigaki, Science **265**, 1850 (1994).
[4] P. M. Ajayan, O. Stephan, P. Redlich, and C. Colliex, Nature (London) **375**, 564 (1995).
[5] D. Ugarte, A. Chelain, and W. A. Heer, Science **274**, 1897 (1996).
[6] A. A. Setlur, J. M. Lauerhaas, J. Y. Dai, R. P. H. Chang, Appl. Phys. Lett. **69**, 345 (1996).
[7] H. Dai, E. W. Wong, Y. Z. Lu, S. Fan, and C. Lieber, Nature (London) **375**, 769 (1995).
[8] W. Han, S. Fan, Q. Li, W. Liang, B. Gu, and D. Yu, Chem. Phys. Lett. **265**, 374 (1997).
[9] M. Wang and H. Wada, J. Mat. Science **25**, 1691 (1990).
[10] Y. Mizuhara, M. Noguchi, T. Ishihara, and Y. Takita, J. Am. Ceram. Soc. **78**, 109 (1995).