PERGAMON

Solid State Communications 118 (2001) 595–598

solid state communications

www.elsevier.com/locate/ssc

Synthesis of SiC nanorods using floating catalyst

Yingjiu Zhang, NanLin Wang, Rongrui He, Xihua Chen, Jing Zhu*

Electron Microscopy Laboratory, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Received 25 October 2000; accepted 20 March 2001 by Z.Z. Gan

Abstract

The beta-silicon carbide (β-SiC) nanorods have been synthesized by a floating catalyst method. Iron particles, decomposed from ferrocene vapor while being carried into the reaction chamber by the flowing gases, are very tiny. These small Fe particles act as catalyst to promote the growth of SiC nanorods in the $SiCl_4$–C_6H_6–H_2–Ar system at 1100–1200°C. The diameters of the β-SiC in the products are less than 100 nm, and the SiC nanorods with uniform diameters are single crystals with the stacking faults on the {111} crystal planes. © 2001 Published by Elsevier Science Ltd.

PACS: 61.46.+w; 81.15.Gh; 81.16.Be; 81.16.Hc

Keywords: A. Nanostructures; B. Chemical synthesis; B. Crystal growth

1. Introduction

Since the discovery of carbon nanotubes by Iijima [1], one-dimensional nanoscale materials have received widespread interests due to their potential applications in both mesoscopic research and the development of nanodevices. Although carbon nanotubes are studied with most detail, other nanowires of Si [2–6], Ge [7,8], SiC [9,10] and Si_3N_4 [11,12] are also noticed for their special properties. For example, besides high strength and good flexibility [9], SiC nanorods are also found to have great potential in the area of electron field-emitting devices [10]. Thus, several methods to synthesize SiC nanorods have also been developed by now. Dai et al. [13] and Han et al. [14] firstly produced SiC nanorods by chemical vapor reaction of Si/SiO_2 with carbon nanotube templates. Recently, β-SiC nanorods of 5–20 nm diameter were grown on a porous silicon substrate by chemical vapor deposition (CVD) with iron catalysts [10], straight β-SiC nanowires of 20–70 nm diameter were produced by a hot filament assistant chemical vapor deposition [15] and β-SiC nanowires of 10 nm diameter were synthesized directly in an arc-discharge [16]. In these processes of synthesis, at least one of the reactants is solid.

The size of the metal catalysts usually affects the diameter of the nanotubes/nanorods. The larger the metal catalysts, the thicker the nanotubes/nanorods. Generally, the metal catalysts are fabricated (for example, deposited by CVD) before the nanotubes or nanaorods are grown. Nanoscale metal catalysts are difficult to synthesize and are easy to coarsen when they are heated to the desired reaction temperature. Thus, SiC whisker diameters less than 50 nm were not produced directly [10,16] until recently. In order to obtain nanoscale metal catalysts, H.M. Cheng et al. exploited a new method to synthesize single-wall carbon nanotubes by Fe powders pyrolyzed from ferrocene [17]. In this new method, the Fe metal particles were very small because Fe atoms were introduced from decomposed ferrocene vapor and collected as Fe catalysts through a very short time at high temperature. In the present work, we report an approach to the synthesis of the SiC nanorods by using the Fe catalysts pyrolyzed from ferrocene in the $SiCl_4$–C_6H_6–H_2–Ar system.

2. Experimental process

The schematic representation of the SiC nanorods growth apparatus is shown in Fig. 1. An Al_2O_3 boat about 10 cm in length, full of ferrocene in a quartz tube, was put about 5 cm away from the left end of the furnace. Then the horizontal quartz tube (reaction chamber) of 35 mm diameter was

* Corresponding author. Tel.: +86-10-62773998; fax: +86-10-62772507.

E-mail address: jzhu@mail.tsinghua.edu.cn (J. Zhu).

PII: S0038-1098(01)00181-8

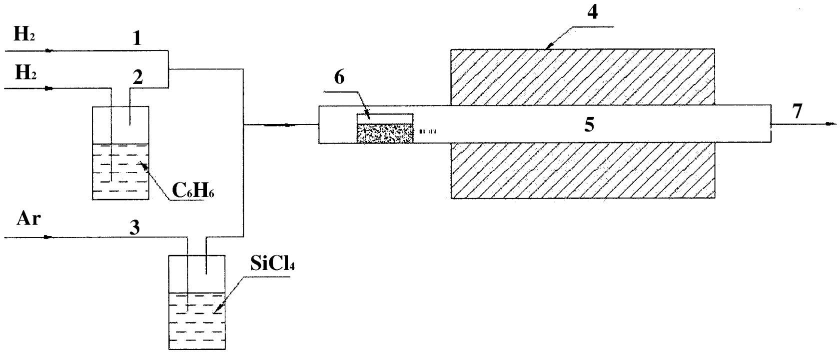

Fig. 1. Schematic representation of the SiC nanorods growth apparatus, (1)–(3) gas entrance; (4) furnace; (5) quartz tube; (6) Al_2O_3 boat full of ferrocene; (7) waste gases.

heated to 1100–1200°C in a flowing H_2 gas. A H_2 gas with 300 standard cm^3/min (sccm) flowed through C_6H_6 liquid (2–3 vol% thiophene) and an argon gas with 200 sccm passed through $SiCl_4$ liquid. Both these gases entered into the quartz tube together and in the meantime, the quartz tube was pulled from the right end until the left end of the Al_2O_3 boat reached the left end of the furnace at the rate of 0.5 mm/min so that the ferrocene could be gradually volatilized. The vapor of ferrocene was carried by the Ar and H_2 flow and turned into Fe clusters at the center of the furnace. Catalyzed by the Fe clusters, $SiCl_4$ and C_6H_6 reacted with each other. The reaction time was 30 min and a gray zone was deposited on the inner surface of the quartz tube after the reaction. The product was observed on a JEOL-2010F field emission gun transmission microscope (TEM) equipped with electron energy loss spectrum (EELS) system and energy dispersive spectrum (EDS).

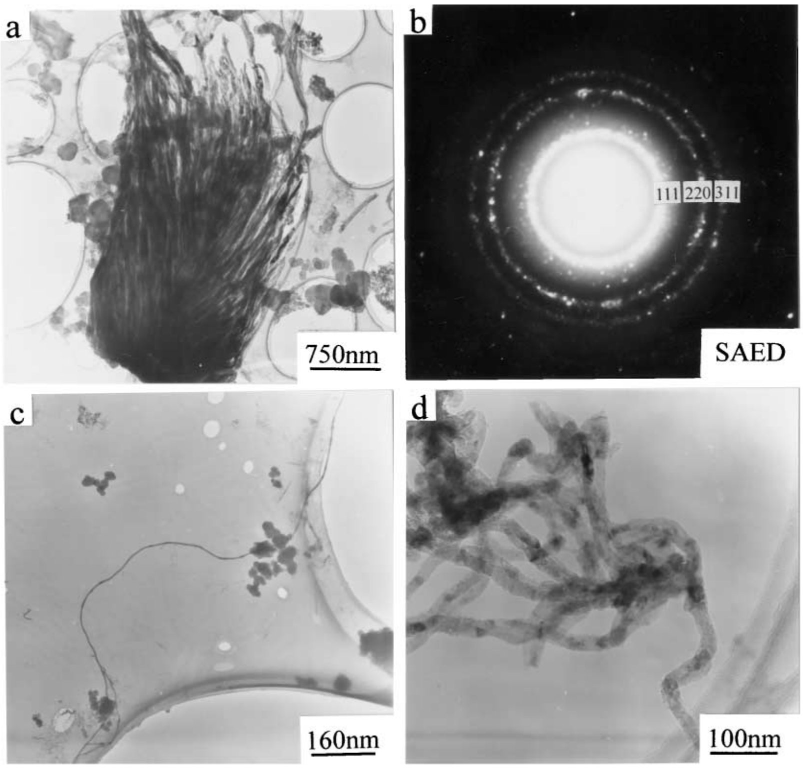

Fig. 2. The different morphologies and SAED of the products (a) SiC nanorods bundle; (b) SAED of the SiC nanorods bundle; (c) a long and thin SiC nanorod with uniform diameter; (d) SiC nanorods with slightly uneven diameters.

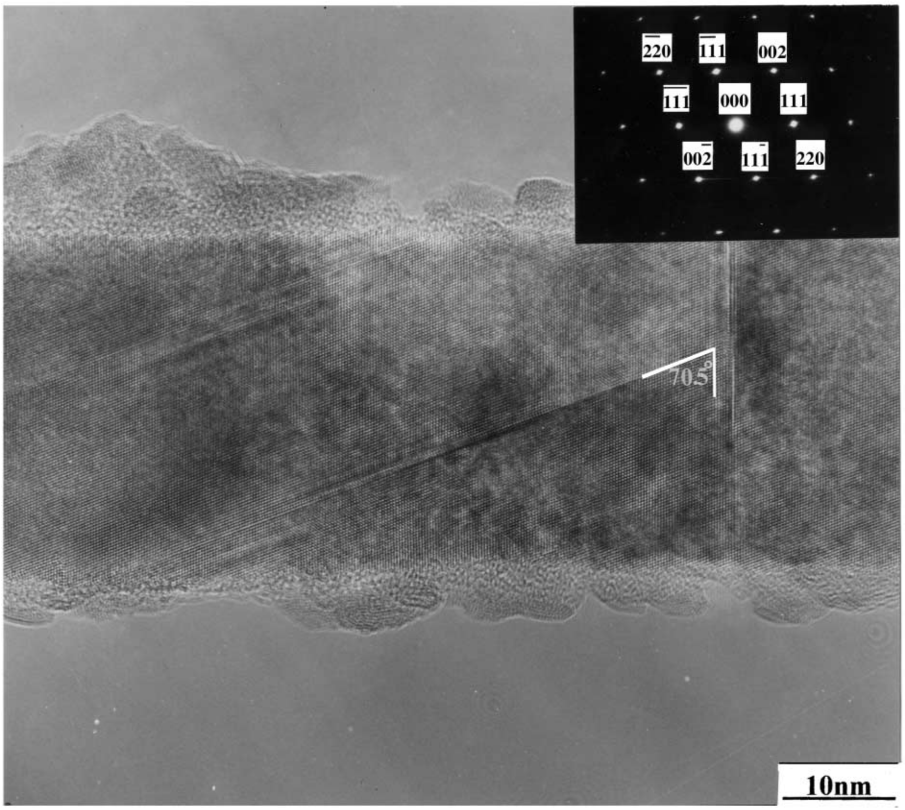

Fig. 3. The HREM photo of an individual SiC nanorod with stacking faults. Its growth direction is perpendicular to one of the {111} crystal planes.

3. Results and discussion

The morphologies of the products are shown in Fig. 2. The products can be classified into three types. The first is the particles and they appear in Fig. 2a and c. Their sizes are about several tens to several hundreds of nanometers, and their shapes are anomalous. Some of the particles are crystalline SiC while others are amorphous carbon identified by several techniques. It implies that some of the decomposed C_6H_6 does not react with Si. The second product is the bundle of the SiC nanorods (Fig. 2a). The SiC nanorods seem to grow from a big catalyst particle, and thus form a hairlike bundle. However, these nanorods with less than 70 nm in diameter are not very well shaped, their diameters are not uniform along their axes. The corresponding selected area electron diffraction (SAED) shown in Fig. 2b reveals that the nanorods are cubic β-SiC. The rings in the SAED correspond to the {111}, {220}, {311} crystal planes of cubic β-SiC.

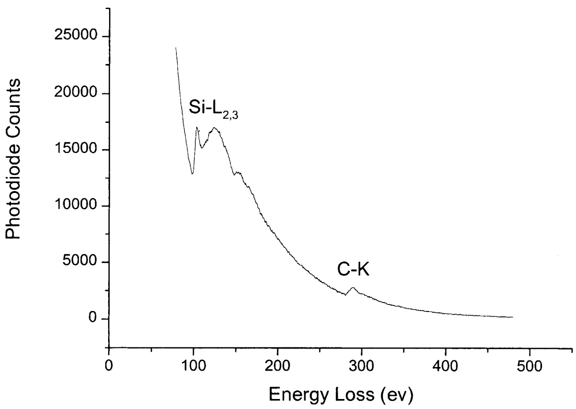

Fig. 4. EELS of an individual SiC nanorod.

The third product is the nanorods with high aspect ratio (length/diameter). Their lengths are usually several μm and their diameters are less than 100 nm, or even less than 10 nm. In Fig. 2c, a typical morphology of such a kind of SiC nanorod, which is more than 1200 nm in length and less than 15 nm in diameter, is shown. Most of these kind of nanorods have uniform diameters along their axes, although some nanorods have slightly uneven diameters (Fig. 2d). The nanorods with uniform diameters are usually single crystalline. A typical high-resolution electron microscopy (HREM) photo of the nanorod with single crystal is shown in Fig. 3. Its crystalline core is about 30 nm in diameter and is covered by an incoherent amorphous or a small crystalline layer. Its growth direction is normal to one of the {111} lattice planes. There are some stacking faults in this SiC nanorod. The stacking fault planes are parallel to the {111} crystal planes and the angle between the two groups of stacking fault planes is 70.5°. The number of the stacking faults is less than that in the SiC nanorods synthesized by carbon nanotube-confined reaction [18] but more than that in the SiC nanorods fabricated by arc-discharged [16]. The number of the stacking faults may be affected by the synthesis process.

EELS in Fig. 4 is taken from an individual nanorod. This spectrum is very similar to that of SiC nanorods produced by T. Seeger et al. [16], not only in the positions of the peaks, but also in the shape of the EELS. Two groups of the peaks in this spectrum can be identified as $Si-L_{2,3}$ and C–K edges. Thus, the EELS clearly shows that the nanorods in the present work mainly consists of SiC phase.

Similar to the growth of the single-wall carbon nanotubes by the floating catalyst ferrocene, the Fe catalyst clusters nucleate and grow during the ferrocene vapor being carried by the H_2 and Ar flow. Therefore, the sizes of most of the Fe catalyst particles are small enough to grow thin SiC nanorods (Fig. 2c). As the catalyst particles may have different size, the SiC nanorods with different diameters are fabricated in the present work. In some case, the catalyst particles may be as large as a few micrometers. However, these catalyst particles are anomalously shaped and may be full of sharp-angled surfaces. Thus, SiC nanorods have thin diameters and form a hairlike bundle (Fig. 2a) when they grow on this kind of surfaces.

Different from the recently developed methods [10,15, 16], the present work is similar to the conventional CVD method. In these methods, at least one of the reactants is solid. In the present work, like the traditional CVD, the gaseous reactants (and catalyst vapor) can be directly introduced into the reactant chamber continuously, thus the yield is large and the method is suitable for the modern industrial manufacture.

Compared with the system of synthesis of the single-wall carbon nanotubes by the floating catalyst, the system of $SiCl_4-C_6H_6-H_2-Ar$ in the present work is more complicated. One of the disadvantages is that the $SiCl_4$ is easy to react with or surround the Fe particles (or ferrocene). It reduces the catalyst effect of the Fe particles. Therefore, not all of the products in our work are pure and identical SiC nanorods (for example, the surplus carbon in this system grows into the amorphous carbon powders). However, the method provides a new way to produce one-dimensional carbide in nanoscale. Considering that the amount of ferrocene or other organometallic compound is much less than the reactants, the carbon in the ferrocene may not affect the compositions of the product, thus the method might also be used to fabricate other one-dimensional nanoscale materials without carbon.

4. Conclusion

The SiC nanorods have been synthesized in the $SiCl_4-C_6H_6-H_2-Ar$ system by using the floating catalyst. The Fe catalyst particles used are derived from the decomposition of ferrocene. Ferrocene is decomposed in the short time that it flows into the reaction chamber together with the carrier gases (H_2 and Argon), the Fe catalyst particles thus formed are small enough to grow thin nanorods. The SiC nanorods fabricated in the present work are smaller than 100 nm in diameter and can be identified as cubic β-SiC. The β-SiC nanorods with uniform diameter are single β-SiC crystal with stacking faults on the {111} crystal planes. The method may provide a new way to produce one-dimensional nanoscale materials.

Acknowledgements

This work was supported by Nature Science Foundation of China, National 973 Project, 985 Project of Tsinghua University.

References

[1] S. Iijima, Nature 354 (1991) 56.
[2] A.M. Morales, C.M. Lieber, Science 279 (1998) 208.
[3] D.P. Yu, C.S. Lee, I. Bello, X.S. Sun, Y.H. Tang, G.W. Zhou, Z.G. Bai, Z. Zhang, S.Q. Feng, Solid State Commun. 105 (1998) 403.
[4] N. Wang, Y.H. Tang, Y.F. Zhang, C.S. Lee, I. Bello, S.T. Lee, Chem. Phys. Lett. 299 (1999) 237.
[5] J.D. Holmes, K.P. Johnston, R. Christopher Doty, B.A. Korgel, Science 287 (2000) 1471.
[6] J. westwater, D.P. Gosain, S. Tomiya, S. Usui, H. Ruda, J. Vac. Sci. Technol. B15 (1997) 554.
[7] J.R. Heath, F.K. LeGoues, Chem. Phys. Lett. 208 (1993) 263.
[8] Y.Y. Wu, P.D. Yang, Chem. Mater. 12 (2000) 605.
[9] E.W. Wong, P.E. Sheehan, C.M. Lieber, Science 277 (1999) 1971.
[10] X.T. Zhou, H.L. Lai, H.Y. Peng, F.C.K. Au, L.S. Liao, N. Wang, I. Bello, C.S. Lee, S.T. Lee, Chem. Phys. Lett. 318 (2000) 58.
[11] W.Q. Han, S.S. Fan, Q.Q. Li, B.L. Gu, X.B. Zhang, D.P. Yu, Appl. Phys. Lett. 71 (1997) 2271.
[12] Y.J. Zhang, N.L. Wang, R.R. He, Q. Zhang, J. Zhu, Y.J. Yan, J. Mater. Res. 15 (2000) 1048.
[13] H. Dai, E.W. Wong, Y.Z. Lu, S.S. Fan, C.M. Lieber, Nature 375 (1995) 769.
[14] H.Q. Han, S.S. Fan, Q.Q. Li, W.J. Liang, B.L. Gu, D.P. Yu, Chem. Phys. Lett. 265 (1997) 374.
[15] H.L. Lai, N.B. Wong, X.T. Zhou, H.Z. Peng, F.C.K. Au, N. Wang, I. Bello, C.S. Lee, S.T. Lee, X.F. Duan, Appl. Phys. Lett. 76 (2000) 294.
[16] T. Seeger, P. Kohler-Redlich, M. Rühle, Adv. Mater. 12 (2000) 279.
[17] H.M. Cheng, F. Li, G. Su, H.Y. Pan, L.L. He, X. Sun, M.S. Dresselhaus, Appl. Phys. Lett. 72 (1998) 3282.
[18] J. Zhu, S.S. Fan, J. Mater. Res. 14 (1999) 1175.