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Synthesis of silicon carbide nanorods without defects by direct heating method

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Abstract High quality silicon carbide single crystal nanorods were successfully synthesized through gas–solid reaction between silicon and multiwall carbon nanotubes (CNTS) by direct heating methods. The X-ray diffraction (XRD) analysis showed that the reaction product of Si vapor with CNTS is β-SiC. SEM and HRTEM images suggested that the SiC nanorods are 3C-SiC single crystals almost free of defects. Based on these results, it is presumed that the reaction first took place at an end of CNTS giving β-SiC nuclei, one of which with its [111] parallel to the tube direction could grow consecutively along this direction so that a straight and solid SiC single crystal rod was formed without defects.

Introduction

Since the discovery of carbon nanotubes (CNTS) in 1991 [1], one-dimensional nanostructure materials have stimulated great interests of research in expectation of their exotic optical, electrical and mechanical properties. In particular, many inorganic nanomaterials such as MoS_2, BN, MgO, GaN, ZnSe, CdS, Cu_2S and ZnO were synthesized aside from carbon nanotubes [2–9].

Silicon carbide as one of the most important wide-band gap semiconductors is suitable for the use in severe environments such as high temperature, high frequency and high power [10]. Recent study on the nanobeam mechanics showed that individual SiC nanorods exhibited highly superior elasticity and strength to bulk SiC [11]. Combined with high thermal and chemical stability, the outstanding mechanical properties of SiC nanorods or nanowires make them possibly be used as reinforcements in polymer, metal and ceramic matrix composites [12, 13]. In addition, field-emission properties of oriented SiC nanowires suggested promising applications in vacuum microelectronic devices [14].

Therefore, considerable efforts have been devoted to the preparation of SiC nanorods and nanowires. The first synthesis of silicon carbide nanorods was realized by the reaction between carbon nanotubes and SiO or SiI_2 [15]. Later, several methods to synthesize SiC nanostructure materials were developed. Meng et al. have fabricated β-SiC nanorods by carbothermal reduction of sol–gel-derived silica xerogels containing carbon nanoparticles [16]. Zhou and co-workers grew SiC nanorods on silicon substrate by hot filament chemical vapor deposition [17]. Lu et al. prepared the SiC nanorods through a one-step reaction that was carried out in an autoclave by using $SiCl_4$ and CCl_4 as reactants and metal Na as co-reductant at low temperature [18]. Park et al. reported that aligned silicon carbide nanowires were synthesized directly from the silicon substrates via a novel catalytic reaction with a methane–hydrogen mixture at 1,100 °C [19]. Recently, other nanostructure silicon carbide such as SiC nanosprings, three-dimensional crystalline nanowire flowers, and β-SiC nanobelts were also successfully synthesized [20–23]. However, the SiC nanorods or nanowires that prepared by the above mentioned

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methods had stacking faults, screw dislocation or other defects, which maybe limited applications in many fields.

In this paper, we report a novel method for SiC nanorods preparation. By this method high yield of long SiC nanorods was produced simply by Si vapor towards CNTS. The reaction is believed to adopt vapor (Si)—solid (CNTS) reaction mechanism without seriously reconstruction of the solid CNTS framework. To characterize the obtained SiC nanorods and as-received CNTS as well, several techniques including powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and high resolution transmission electron microscopy (HRTEM) were used. The quality of SiC nanorods is first proved high for their long and straight rod shape with clean and clear surfaces, and further illustrated by their perfect single crystal structures without defects.

Experimental details

CNTS provided by Shenzhen Nanotech Part Co., Ltd and high purity silicon fragments provided by Haina Semiconductor Company were used as raw materials. The experimental apparatus is schematically shown in Fig. 1. A thin alumina plate with regularly arrayed through-holes was placed on the top of a graphite crucible with a dimension of Φ80 × 50 mm, in which silicon fragments had been contained. CNTS were situated loosely on the surface of the holed alumina plate. Other graphite crucible (Φ80 × 30 mm) was put upside down to cover the CNTS. The configuration guaranteed no direct contact between silicon and CNTS. The whole set was moved in the center of the vertical graphite furnace (VSF-120/150, Institute of Vacuum Technologies, Shenyang, China), and then heated at a rate of 30 °C /min up to 1,450 °C and maintained at this temperature for 6 h. The fast cooling was then following by turning the power off and leaving the cooling water on. The whole experimental process was protected by argon flow so that any oxidation effect was avoided. After reaction, a grayish colored product was formed on the surface of the holed alumina plate.

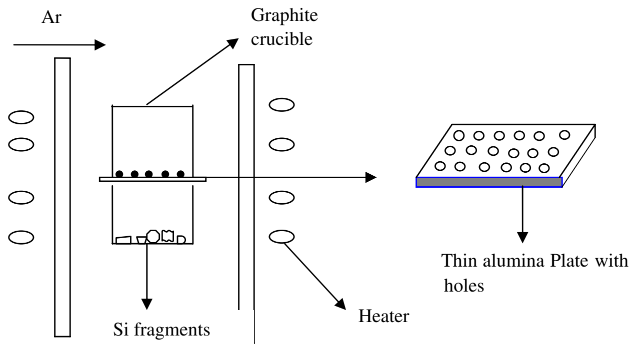


Fig. 1 Schematic illustration of the experimental setup for SiC nanorods preparation

The phase composition and polytype of the product was then determined by XRD in the diffractometer Rigaku, Geigerflex/D with Cu-Kα radiation. The morphologies and elemental composition were observed in the SEM (FESEM, FEI-SIRION100) with EDX attached. The crystal structure was further studied using HRTEM (JEM-2010, HR).

Results and discussion

The black CNTS over the holed alumina plate turned to be grayish after the experiment, indicating a chemical reaction took place. The reaction supposedly adopted solid (CNTS) and vapor (Si) mechanism since no direct contact between solid CNTS and liquid Si in the whole course of the experiment. The XRD pattern of the product shown in Fig. 2 suggests that the phase of the product is crystalline *β*-SiC. Peaks from Si and C, and low intensity peaks from stacking faults as reported by previous researchers [18, 19, 24, 25] could not be detected in the pattern. The lattice parameter of *β*-SiC cubic cell calculated from the XRD data is 4.361 Å, which is very close to the reported value for 3C-SiC (*a* = 4.359 Å, JCPDS29-1129).

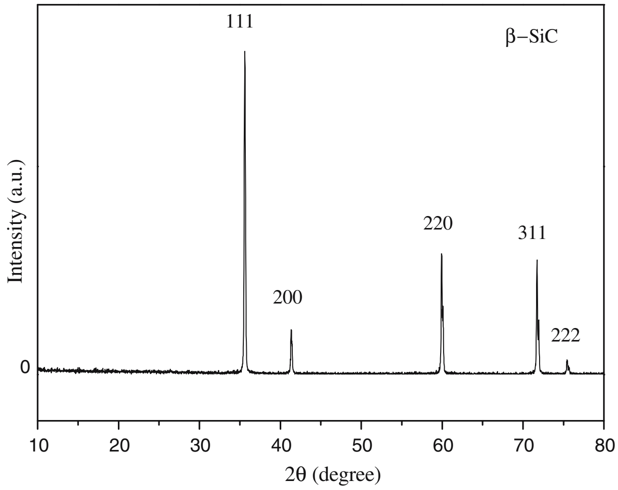


Fig. 2 Typical X-ray powder diffraction pattern of the products

The SEM and HRTEM studies were carried out not only for the product but also for as-received CNTS. The morphologies of the CNTS observed under SEM

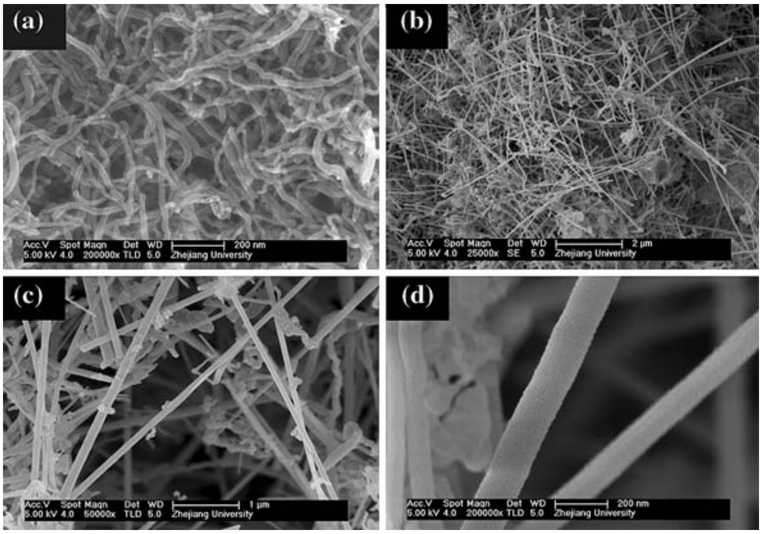


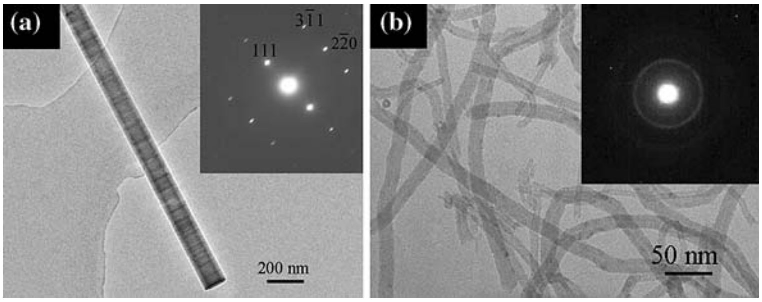
Fig. 3 Scanning electron microscopy (SEM) images: (**a**) multiwall carbon nanotubes. (**b**) Low-magnification SEM image of obtained β-SiC nanorods. (**c**) Low-magnification SEM image of obtained β-SiC nanorods, the average diameter of the nanorods is 80 nm. In addition clean and straight β-SiC nanorods with some spring like wires are also shown. (**d**) High-magnification SEM image of syntheses β-SiC nanorods showing that the nanorods is very clean and clear without any covering of amorphous materials and the surface is smooth relatively

and TEM are shown in Figs. 3a, 4b, respectively. The high magnification SEM image (Fig. 3a) shows the CNTS a random curve characteristic. The bright field TEM image of the CNTS (Fig. 4b) further shows that the CNTS are not straight in microscope scale and of multiwall tubes. The inset in Fig. 4b is the diffraction patterns of the CNTS, suggesting a poorly crystalline feature. The CNTS typically have diameters of 10–30 nm and lengths of 10–30 μm.

The morphologies of the β-SiC product were first studied in the SEM. Figure 3b–d were taken from different areas at different magnifications. After the reaction, originally randomly curved CNTS mainly tuned to be straight β-SiC rods with smooth and clean surfaces. A few of spring like wires and agglomerates distributing within the rod forests should also be β-SiC since no minor phase was found (Fig. 2). The diameter of the rods ranges from 50 to 100 nm, which is larger than the original CNTS, but the lengths did not change much except that some CNTS seemed sintered and then reacted becoming small irregular agglomerates. The morphology study strongly suggests that the reaction of CNTS with Si vapor did not change the atomic configuration of the CNTS very much but rather shifting carbon atoms a little during the intake of vaporous Si atoms to produce β-SiC nanorods. The β-SiC nanorods were basically formed along the framework of CNTS but became solid instead of hollow cores.

In order to characterize the structure in further details, TEM bright field image and a selected area electron diffraction (SAED) pattern of a β-SiC nanorod were taken and are displayed in Fig. 4a. It is confirmed by Fig. 4a that, instead of the multiwall tubular structure of CNTS (Fig. 4b), the obtained β-SiC nanorod is solid and free of any hollow core structure. The diffraction spots can be indexed on the basis of 3C-SiC single crystal, they are (111), $(3\bar{1}1)$and $(2\bar{2}0)$ etc., and the zone axis is consequently determined to be $[11\bar{2}]$. The length direction of the nanorod

Fig. 4 (**a**) TEM image of a β-SiC nanorod and its diffraction pattern; (**b**) TEM image of multiwall carbon nanotubes and diffraction pattern



is obviously [111] of 3C-SiC single crystal, and the cross-section of the rod exhibits hexagonal by a close look. The surface of the rod in Fig. 5 is clean and composed of many ridge traces, which are believed to be the traces of (111) plane of the 3C-SiC single crystal. A conclusion may be drawn that the reaction of poorly crystalline, curved and hollow CNTS shown (Fig. 4b) with vaporous Si atoms at 1,450 °C can produce perfectly crystallized, straight and solid 3C-SiC single crystal rods.

Figure 5a is a HRTEM image of another β-SiC nanorod prepared in this study. The central part of the rod is crystalline but the surface appears rough and maybe a little amorphous. Elemental analyses by EDX show that the central (part A) of the β-SiC nanorod in Fig. 5b. The results show that Si/C is close to 1:1. The Cu signal came from the TEM grids. Figure 5c is the same β-SiC nanorod but more highly magnified, in which the crystal lattice plane fringes the normal of which is along the rod length direction are more clearly seen, and the d-spacing of the plane can be determined to be 0.25 nm.

Considering SiC_4 tetrahedron as the basic unit of SiC crystal, the distance between one C at the corner and centered Si is 1.89 Å, and the distance between the Si and the plane with three C is 0.63 Å. The inter-spacing of two neighboring C planes is thus 0.25 nm, corresponding to the (111) lattice planes of crystalline β-SiC. It can also be seen in Fig. 5c that (111) plane fringes perfectly array throughout the rod, suggesting that the SiC rod is a perfect single crystal. The HRTEM images showing the single crystal free of any defects have been actually many, and Fig. 5c is just one of them illustrated here in.

To propose the growth mechanisms of nanostructure materials of different shapes, many models were proposed such as the effect of monomer concentration on the shape of the semiconductor quantum dots (QDS), vapor–liquid–solid growth for nanowires by CVD and PVD methods, and light-induced Shape change mechanism of metal nanorods [26]. This paper is also intended to give an explanation how the SiC rods were formed under the experimental conditions. Since the argon used was high purity, oxygen and water vapor were avoided so that SiO, which has been regarded in many cases as a gas reactant for the formation of nanostructure SiC, was not involved in this study. Furthermore the Si and C sources were supplied separately from the gas phase and the solid phase, so the reaction mechanism of SiC nanorods can be uniquely understood as a vapor–solid mechanism. HRTEM images show that the β-SiC nanorods are almost all perfect 3C-SiC single crystals Based on these facts, the formation mechanism may be proposed. Si

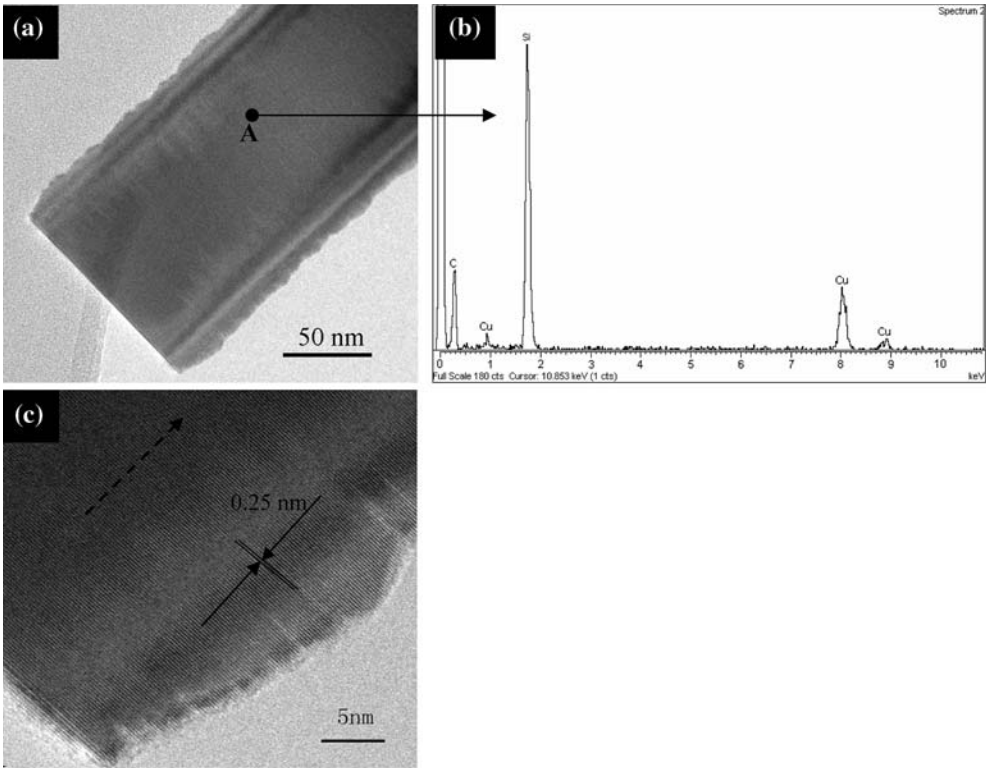


Fig. 5 (**a**) HRTEM image of a typical SiC nanorod, (**b**) EDX spectrum of part A: central section, (**c**) HRTEM image of SiC nanorod with higher magnification

vapor could diffuse rapidly into the nanotubes and react with carbon to form SiC nanoparticles via the reaction (1)

$$\text{Si (vapor)} + \text{C (solid)} \rightarrow \text{SiC (solid)} \tag{1}$$

and Si (vapor) came from

$$\text{Si (liquid)} = \text{Si (vapor)}. \tag{2}$$

According to the thermodynamic data concerned [27], the partial pressure of Si vapor at 1,450 °C can be estimated to be $10^{-6.2}$ atmospheres. Such a sparsely drifting Si atoms first react with C in the most active parts, the ends of CNTS, to form 3C-SiC nuclei. The orientation of the nuclei may be random, but only that whose growing direction is along the carbon nanotubes can grow until reaching other end of the nanotubes, or meeting that grown from other end. From crystallographic point of view, the growing direction is preferentially normal to the lowest energy plane, which is (111) plane for 3C-SiC [28]. This can explain why the curved CNTS transformed to be straight β-SiC nanorod and the β-SiC nanorod is a perfect single crystal with a stable orientation of its [111] direction parallel to the rod length direction.

Conclusion

High quality β-SiC nanorods without defects can be successfully synthesized using Si vapor onto CNTS at 1,450 °C for 6 h in graphite furnace by direct heating method. Originally curved CNTS (10–30 nm in diameter and 10–30 μm in length) transformed to straight β-SiC nanorods (50–100 nm in diameter and 10–30 μm in length) with smooth and clean surfaces through the reaction of two components. The synthesized β-SiC nanorods are all perfect 3C-SiC single crystals with [111] direction parallel to the rod direction. Based on the results, the reaction of Si vapor and C may presumably started at end position, the most active parts of CNTS to form randomly orientated 3C-SiC nuclei, and only that whose growing direction, i.e. [111] parallel to the rod direction grows by subsequently taking in Si atoms.

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