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Letter

Microstructure and growth mechanism of SiC nanowires with periodically fluctuating hexagonal prisms by CVD

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ABSTRACT

SiC nanowires with periodically fluctuating hexagonal prisms were synthesized on graphite substrates by a simple and economical technique of chemical vapor deposition in an Ar atmosphere without catalyst assistant. The morphology and structure of SiC nanowires were characterized by X-ray diffraction, Raman scattering spectrum, scanning electron microscopy and transmission electron microscopy. The results showed that the as-synthesized SiC nanowires possessed well crystalled β-SiC, and were composed of periodically fluctuating hexagonal prisms along their whole length with the [1 1 1] growth direction. The growth of SiC nanowires with periodically fluctuating hexagonal prisms was governed by vapor–solid mechanism.

1. Introduction

SiC nanowires have been attracting considerable attention due to their excellent properties, such as high thermal stability, high strength, high thermal conductivity and large band gap [1–3]. Consequently, they are widely used in nanocomposites, nanoelectronics and field-emission devices [4,5]. In recent years, SiC nanowires with special shape and morphology have been successfully fabricated, such as bamboo-shaped [6,7], screw-like [8,9] and beaded [10–12]. The promise that special-morphology nanostructures may dramatically improve the desired properties for many applications even stimulates more interest. Shen et al. [6] have testified that bamboo-shaped SiC nanowires are good candidates for low-cost, large-area electron emitters due to their excellent field-emission properties. Compared with the common SiC nanowires, beaded SiC nanowires as reinforcing agents in composites could increase the tensile strength of the composites from 14% to 32% [12]. However, the reported preparation methods for special-morphology SiC nanowires have some shortcomings, such as low purity and the need of catalyst assistant. The as-received nanowires need to be purified or extra operation to remove the resident catalyst after the synthetic process, which is a complicated and expensive process. Therefore, an easy-operation and low-cost method for synthesizing the special-morphology SiC nanowires without catalyst assistant is of vital importance for the application of SiC nanowires.

In the present work, SiC nanowires with periodically fluctuating hexagonal prisms were synthesized on graphite substrates by a simple and economical chemical vapor deposition (CVD) without catalyst assistant. The microstructure and growth mechanism of the as-grown SiC nanowires were investigated.

2. Experimental

Small graphite specimens (10 mm × 10 mm × 10 mm) used as substrates were hand-abraded using 300 grit SiC paper, cleaned ultrasonically with ethanol and dried at 373 K for 2 h. The high-purity mixtures were composed of SiO_2, Si and C powders. The starting powder compositions were given as follows: 60–70 wt% SiO_2 (300 mesh), 15–25 wt% Si (300 mesh) and 5–15 wt% graphite (500 mesh). The above powders were weighed up and then mixed by tumbling in a ball mill for more than 2 h, where the mixtures of high-purity powder were put into a graphite crucible. Then the graphite substrates were placed above the mixture powder in the graphite crucible with graphite lid. The graphite crucible was placed in an electrical furnace, and then was heated to 1773–1873 K and held for 0.5–2 h with Ar flow rate at 300 ml/min to form SiC nanowires. Finally, the furnace was cooled down to room temperature naturally.

The morphology and microstructure of SiC nanowires were analyzed by a scanning electron microscopy (SEM, JEOL JSM-6460), a transmission electron microscopy (TEM, JEOL JEM3010), X-ray diffraction (XRD, X'Pert PRO) and Raman scattering spectrum (RENISHAW invia).

3. Results and discussion

XRD pattern of the product shows a typical β-SiC crystal with a low-intensity peak marked with SF (Fig. 1(a)), which was formed due to the stacking faults [13]. Three characteristic peaks can be found at 35.70°, 60.08°, and 71.83°, corresponding to the diffrac-

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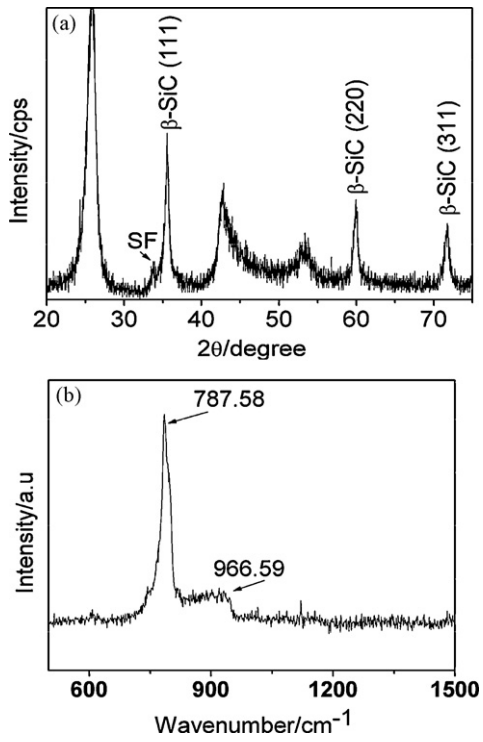

Fig. 1. XRD pattern (a) and Raman scattering spectrum (b) of the production on graphite substrate.

tions of the (1 1 1), (2 2 0) and (3 1 1) crystalline planes of a cubic lattice, respectively, which is in good agreement with the known results for β-SiC [5]. Moreover, the refined lattice parameters of the product calculated from the XRD pattern were 0.4358 nm. Further evidence for the formation of β-SiC phase can be obtained through Raman scattering spectroscopy. Fig. 1(b) shows two characteristic peaks at 787.58 cm^{-1} and 966.59 cm^{-1}, corresponding to the transversal optic mode and longitudinal optic mode of β-SiC, respectively, and the narrow transversal optic feature indicates that the as-grown SiC nanowires are well crystalled [14].

Fig. 2(a) reveals that SiC nanowires are randomly oriented with length ranging from tens to over 100 μm and a diameter of 50–300 nm. Fig. 2(b) shows that there are many decorated periodically fluctuating prisms along the whole nanowires. Moreover, the cross-section of the nanowires is hexagonal rather than circular, as shown in Fig. 2(c). SiC nanowires exhibit a contoured surface on the nanoscale and a hexagonal cross-section, consisting of stacking oblique hexagonal prisms. The corresponding EDS pattern of the nanowires indicates that the nanowires are composed of Si, C and O elements (Fig. 2(d)). An amorphous phase is found on the surface of the nanowires from Fig. 2(c), which corresponds to amorphous SiO_2 according to the EDS pattern (Fig. 2(d)) [15].

Fig. 3(a) shows TEM image of a typical SiC nanowire with periodically fluctuating prisms, from which a furrow can be found. SAED pattern from the prism (area A) shows that the prism is a single crystalline phase, and the nanowire grows along the [1 1 1] direction. While SAED pattern of the knot (area B) indicates that some defects exist in this area. Fig. 3(b) is the corresponding HRTEM image of the square region marked as "b" in Fig. 3(a), which corresponds to the joint part between the prism and the knot of SiC nanowires. The crystal at the part of prism is perfect without any stacking fault. The crystal lattice fringe spacing was measured to be 0.25 nm, which is consistent with the (1 1 1) plane space of β-SiC. At the same time, the lattice parameters of the product were also calculated to be 0.4330 nm, almost consistent with the result of XRD (0.4358 nm), indicating that the as-grown SiC nanowires were well crystalled. Moreover, some stacking faults can be observed at the joint part, consistent with the XRD pattern (Fig. 1(a)). These stacking faults

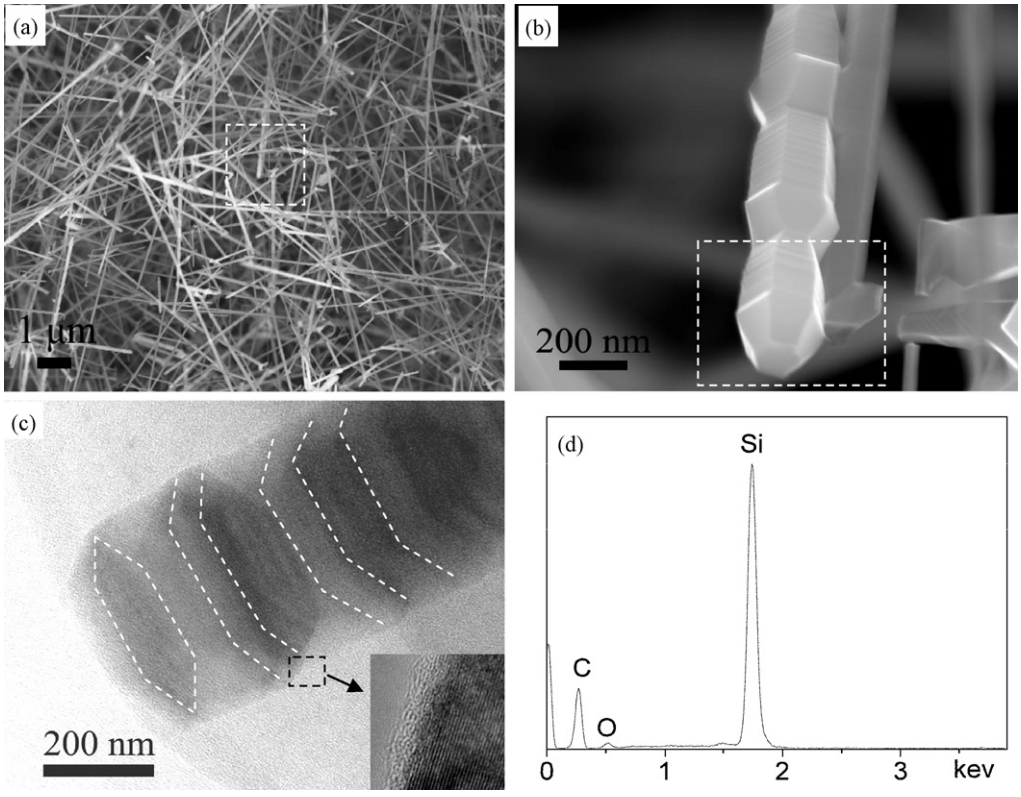

Fig. 2. General morphology of SiC nanowires. (a) SEM image of SiC nanowires at low-magnification view, (b) SEM image of SiC nanowires at high-magnification view, (c) TEM image of SiC nanowires, and (d) EDS pattern of SiC nanowires.

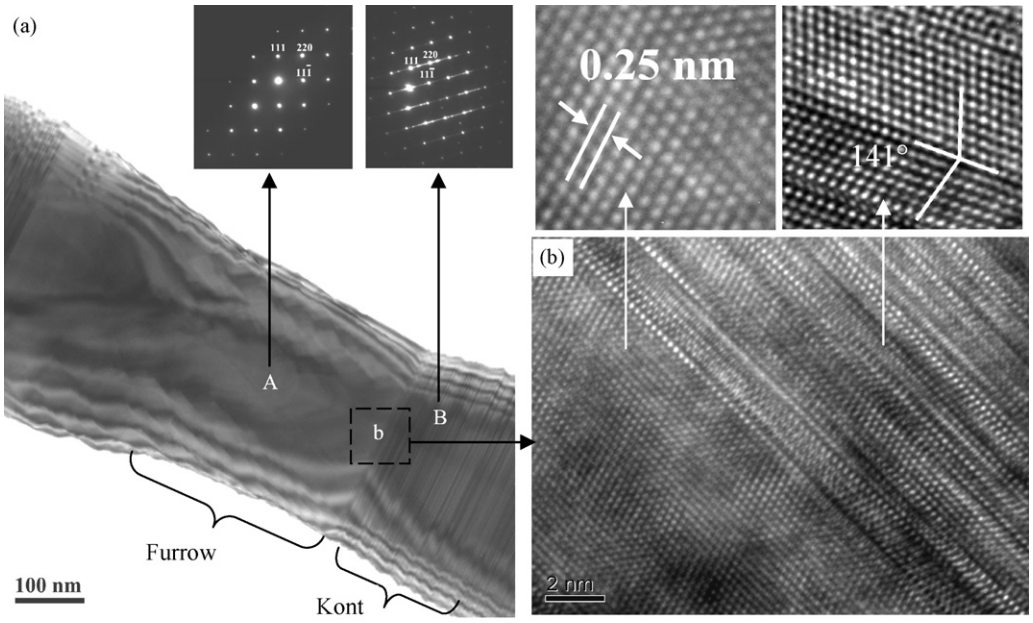

Fig. 3. (a) TEM image with SAED patterns taken from the areas marked as "A" and "B" of a furrow on SiC nanowire; (b) HRTEM images of the square areas marked as "b".

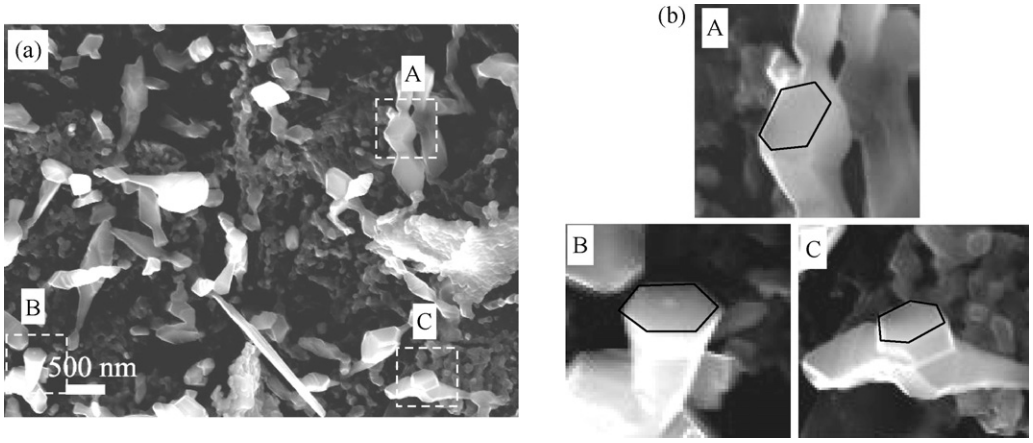

Fig. 4. (a) SEM image of the surface of graphite substrate heated to 1773 K in an Ar atmosphere for 0.5 h, (b) high-magnification SEM images of the square areas marked as "A" "B" and "C", respectively.

are generally produced from thermal stresses during the growth process [16]. From a high-magnification image of TEM (top-right corner in Fig. 3(b)), the atoms in this region are distributed in a mirror symmetry way. The symmetry angle is 141°, which is twice the interplanar angle of 70.5° between {1 1 1} planes in an FCC structure [17]. The formation of twins may be attributed to minimize the total energy [18], so that some twinning structures in SiC nanowires are advantageous to the growth of SiC nanowires with periodically fluctuating hexagonal prisms.

No metallic droplets can be found at the tips of SiC nanowires in Fig. 2(b), so the present SiC nanowires growth is probably governed by vapor–solid (VS) mechanism [19,20]. The formation of as-grown SiC nanowires is believed to involve three main reactions [21–23]:

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

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

$$3SiO(g) + CO(g) \rightarrow SiC(s) + 2SiO_2(s) \quad (3)$$

At a certain experimental condition, the reaction (1) will generate SiO and CO gas. Gaseous reactants SiO and CO will fill up the remaining space in the crucible, and gradually spread to the surface of graphite substrates. Then, SiC nanonucleus are formed on graphite substrates via the reactions (2) and (3). SiC nanonucleus will grow up with the continuous deposition. From Fig. 4(a), it can be observed that a large number of nanoparticles exist on graphite substrate. Some nanoparticles exhibit hexagonal surface in the high-magnification image (Fig. 4(b)). It is well known that all six side surfaces of the hexagonal prism are low-energy (1 1 1) planes [8]. Thus the hexagonal surface of the hexagonal prism possesses higher surface energy than its side surface, which could easily adsorbs active species and make it grow up quickly. With the prolonging of the deposition time, hexagonal-prism nanowires start to form. Their following growth is a complicated process that strongly depends on their preparation conditions such as SiO generation, transport and temperature variation [13,24]. The turbulence of these preparation conditions will cause the formation of some stacking faults in the SiC nanowires.

4. Conclusions

SiC nanowires were synthesized on graphite substrates by a simple and economical CVD technique without catalyst assistant.

They were composed of many periodically fluctuating hexagonal prisms along their whole length with the [1 1 1] growth direction. The hexagonal prisms were defect-free, while some stacking faults existed in the knot part and induced the periodical growth of the fluctuating hexagonal prisms. The growth of SiC nanowires with this structure was governed by VS mechanism.

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