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Synthesis and Photoluminescence Property of Silicon Carbide Nanowires Via Carbothermic Reduction of Silica

Xiaogang Luo · Wenhui Ma · Yang Zhou ·
Dachun Liu · Bin Yang · Yongnian Dai

Abstract Silicon carbide nanowires have been synthesized at 1400 °C by carbothermic reduction of silica with bamboo carbon under normal atmosphere pressure without metallic catalyst. X-ray diffraction, scanning electron microscopy, energy-dispersive spectroscopy, transmission electron microscopy and Fourier transformed infrared spectroscopy were used to characterize the silicon carbide nanowires. The results show that the silicon carbide nanowires have a core–shell structure and grow along <111> direction. The diameter of silicon carbide nanowires is about 50–200 nm and the length from tens to hundreds of micrometers. The vapor–solid mechanism is proposed to elucidate the growth process. The photoluminescence of the synthesized silicon carbide nanowires shows significant blueshifts, which is resulted from the existence of oxygen defects in amorphous layer and the special rough core–shell interface.

Keywords Silicon carbide nanowires ·
Carbothermic reduction · Bamboo carbon ·
Photoluminescence property · Growth mechanism

X. Luo · W. Ma · Y. Zhou · D. Liu · B. Yang · Y. Dai
Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, 650093 Kunming, People's Republic of China

X. Luo · W. Ma (✉) · Y. Zhou · D. Liu · B. Yang · Y. Dai
National Engineering Laboratory for Vacuum Metallurgy, Kunming University of Science and Technology, 650093 Kunming, People's Republic of China
e-mail: mwhsilicon@163.com

Introduction

Recently, the preparation of one-dimensional nanowires has received considerable attention due to their excellent properties and widely potential applications. The nanowires such as silicon (Si), zinc oxide (ZnO), gallium nitride (GaN), silicon carbide (SiC) and others [1] have been synthesized by various methods. Among these nanowires, silicon carbide nanowires (SiC NWs) have been attracting extensive interest due to their excellent electronic, physical and chemical properties and widely application in semiconductor, microelectronics and optoelectronics industry operating in harsh environment like high temperature, high power and high frequency [2, 3]. So far, SiC NWs have been successfully synthesized by various methods, such as carbon nanotubes-confined reaction [4, 5], laser ablation [6], high-frequency induction heating method [7], chemical vapor deposition (CVD) [8, 9] and thermal evaporation method [10]. Most of these methods, however, involved complicated equipments and processes, vacuum conditions and metallic catalyst, which limit their further application. Carbothermic reduction of silica is known to be a simple and economical process for the synthesis of SiC nanostructure. According to the previous reports [11, 12], carbon source is very important and has a substantial influence on the rate of reaction and the morphology or size of synthesized SiC. At present, carbon source such as active carbon, carbon nanoparticles and carbon nanotubes [13–15] were utilized to synthesize SiC NWs. These carbon sources, however, have some disadvantages which limited their further application in synthesis of SiC NWs. For example, active carbon and carbon nanoparticles produce SiC nanoparticles stick to the synthesized SiC NWs, and carbon nanotubes are too expensive to synthesize SiC NWs in large scale. Therefore, exploring a suitable carbon

source for the synthesis of SiC NWs in large-scale, large-quantity and low-cost production is still necessary.

Here, we reported that bamboo carbon was used as carbon source for the synthesis of SiC NWs via carbothermic reduction of silica under normal atmosphere pressure without catalyst. The structure and photoluminescence property of SiC NWs were investigated. Based on the results of experiment, we proposed a possible growth mechanism for the growth of synthesized SiC NWs.

Experimental

Synthesis of SiC NWs

Bamboo carbon (0.7 μm) and silica powder (analytical grade, 1–3 μm) were used as the raw materials in our experiment. The mixture of silica and bamboo carbon powders (molar ratio of $SiO_2/C = 1/3$) together with ethanol (3 ml) were grinded in ball mill for 24 h. The mixed powders were placed on a graphite crucible in a high-frequency induction heating furnace (Fig. 1). Before heating, high-purity argon gas (100sccm) was introduced to eliminate O_2 and maintain the inert atmosphere pressure through the whole experiment. Afterward, the furnace was heated from room temperature to 1400 °C within 10 min and maintained the temperature for 20 min. When the reaction was finished, a large quantity of gray–green products was obtained.

Characterization and Analysis

The morphology, structure and composition of the products were characterized by X-ray powder diffraction (XRD, Advance D8), scanning electron microscopy (SEM, XL30ESEM-TMP) equipped with energy disperse spectrum (EDS), f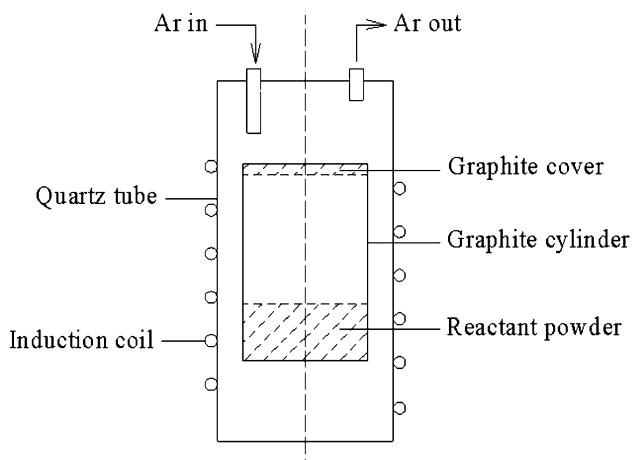ield emission scanning electron microscopy (FE-SEM, Hitachi S-4800), transmission electron microscopy (TEM, Hitachi JEM-2010), high-resolution transmission electron microscopy (HRTEM, Hitachi JEM-2010) and Fourier transformed infrared spectroscopy (FT-IR, EQUINOX55). Photoluminescence (PL) spectrum of the sample was measured in a Hitachi F-7000 fluorescence spectrophotometer with a Xe lamp at room temperature.

Results and Discussion

Characterization of SiC NWs

Figure 2 shows the XRD pattern of the obtained products. Five diffraction peaks at 35.8°, 41.5°, 60.0°, 72.0° and 75.7° can be indexed as the (111), (200), (220), (311) and (222) reflections of β-SiC, respectively. The lattice constant of β-SiC cell of the samples calculated from the XRD data is $a = 4.359$ Å, which is in good agreement with the known value ($a = 4.359$ Å, JCPDS Card No. 29-1129). The stronger intensities of β-SiC peaks indicate that the SiC nanowires are well crystalline with preferential orientation along the (111) plane. The low-intensity peak of α-SiC at 33.6° resulted from the stacking faults [16].

Figure 3 shows the FT-IR spectrum of the synthesized products. The absorption peak at 832 cm^{-1} is assigned to the Si–C stretching vibration, and the absorption peaks at 484 and 1089 cm^{-1} is due to the Si–O stretching vibration [17, 18]. Therefore, the products are mainly consisted of SiC with a small amount of SiO_2. Compared with the IR absorption of the bulk SiC (794 cm^{-1}), the blue shift at 832 cm^{-1} is attributed to the quantum size effects.

The previous report [19] indicated that porous carbon material could increase the formation rate of SiC NWs by favoring the SiO vapor diffusion. The SEM image of bamboo
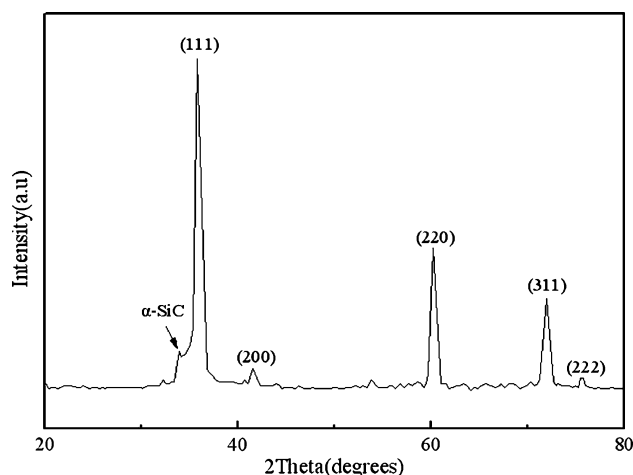

Fig. 1 Schematic diagram of experiment

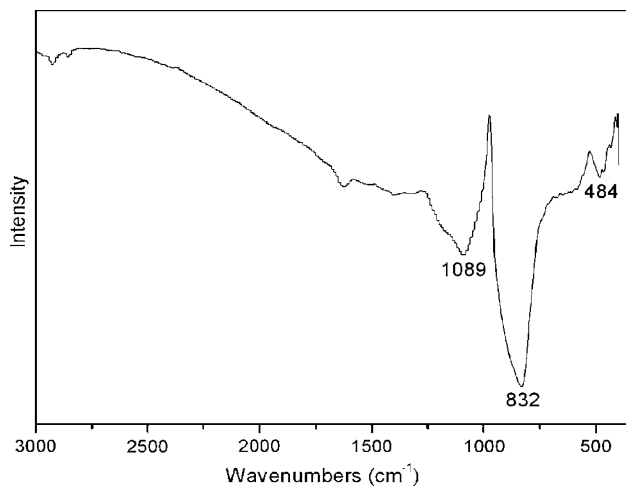**Fig. 2** XRD pattern of the obtained products

Fig. 3 FT-IR spectrum of the products

carbon (Fig. 4a) shows that it has highly porous and loose structure. Figure 4b shows a typical SEM image of the products. It can be seen that the products are composed of long straight and curved nanowires, which were found owing to different kinetic energy. The nanowires with diameter of 50–200 nm and length from tens to hundreds of micrometers have a rough surface morphology. Moreover, there is no metallic droplet found at the nanowires' tips confirmed by the FE-SEM and TEM image of the wires (Fig. 4c and the inset of Fig. 5a). The chemical composition of these SiC NWs were checked by EDS, and the result is shown in Fig. 4d. The nanowires are composed of silicon (38.91 at%), carbon (20.41 at%) and oxygen (40.68 at%).

The internal structure of SiC NWs was investigated by transmission electron microscopy. Figure 5 shows the TEM and HRTEM images of SiC NWs. Figure 5a showed that the nanowires had a core–shell structure. There also exist some structure faults such as stacking faults and planer faults in the nanowires. A high-resolution TEM image is shown in Fig. 5b. The distance between two fringes (indicated by parallel lines) is 0.253 nm corresponding to the {111} plane spacing indicating that the nanowires grow along <111> direction.

Growth Mechanism

During the experiment, no metallic catalyst was introduced and no metallic droplets were detected in the nanowires' tips. Thus, the growth of nanowires in our experiment was not following the conventional metal-catalyst VLS mechanism. Based on the previous reports [20, 21], we proposed the vapor–solid mechanism for the growth of synthesized SiC NWs.

The carbothermic reduction of SiO_2 according to the overall reaction as follows:

$$SiO_2(s) + 3C\ (s) \rightarrow SiC\ (s) + 2CO\ (g) \tag{1}$$
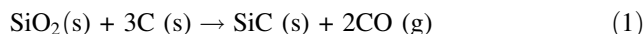
Reaction (1) is generally accepted to involve a multiple-step process [22, 23]. The first step begins with the reaction of SiO_2 and carbon to generate SiO gas and CO gas according to reaction (2).

$$SiO_2(s) + C\ (s) \rightarrow SiO\ (g) + CO\ (g) \tag{2}$$
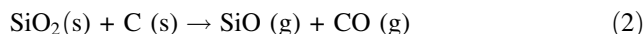
Then, the generated gaseous SiO reacts with C and CO to produce SiC according to reaction (3) and (4):

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

$$SiO\ (g) + 3CO\ (s) \rightarrow SiC\ (s) + 2CO_2\ (g) \tag{4}$$
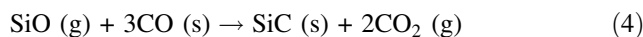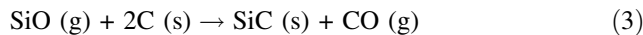
The generated CO_2 vapor can react with carbon to form CO gas by reaction (5):

$$CO_2(g) + C\ (s)\ \rightarrow 2CO\ (g) \tag{5}$$
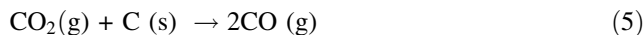
According to the reported thermodynamic data [24], the calculated standard Gibbs free energy change of reaction (3) and (4) at 1400 °C is -200.4 kJ/mol and 38.6 kJ/mol, respectively, which is similar to the result of W.M. Zhou et al. [25].

At 1400 °C, the standard Gibbs free energy change of reaction (4) is positive, so reaction (4) should not proceed. However, some authors have confirmed that the reaction could occur under a supersaturated condition of CO vapor [26, 27]. According to their reports, the supersaturated condition of CO vapor can be formed through reaction (4) and (5), and reaction (4) can carry out sufficiently, leading to the growth of SiC NWS along a fixed axis.

During the cooling stage, another reaction may occur:

$$3SiO\ (g) + CO\ (s) \rightarrow SiC\ (s) + 2SiO_2\ (g) \tag{6}$$
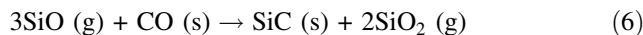
SiC nanoparticles can be formed by nucleation according to reaction (3) with gas–solid interaction but the growth of SiC NWs is believed to undergo a gas–gas interaction in reaction (4). As the reactions went on, more and more silicon and carbon atoms were adhere to the surface of the SiC nanoparticles, and then most of them moved to the lowest energy plane of SiC when supersaturated. The surface energy of {111} planes of SiC is much smaller than those of the other crystal planes; therefore, <111> oriented SiC NWs can be easily prepared. In the process of cooling down, SiC–SiO_2 nanowires with core–shell structure can be formed because of higher melting point and faster solidification speed of SiC than SiO_2, which is consistent with the previous reports [28, 29].

Photoluminescence Property of SiC NWs

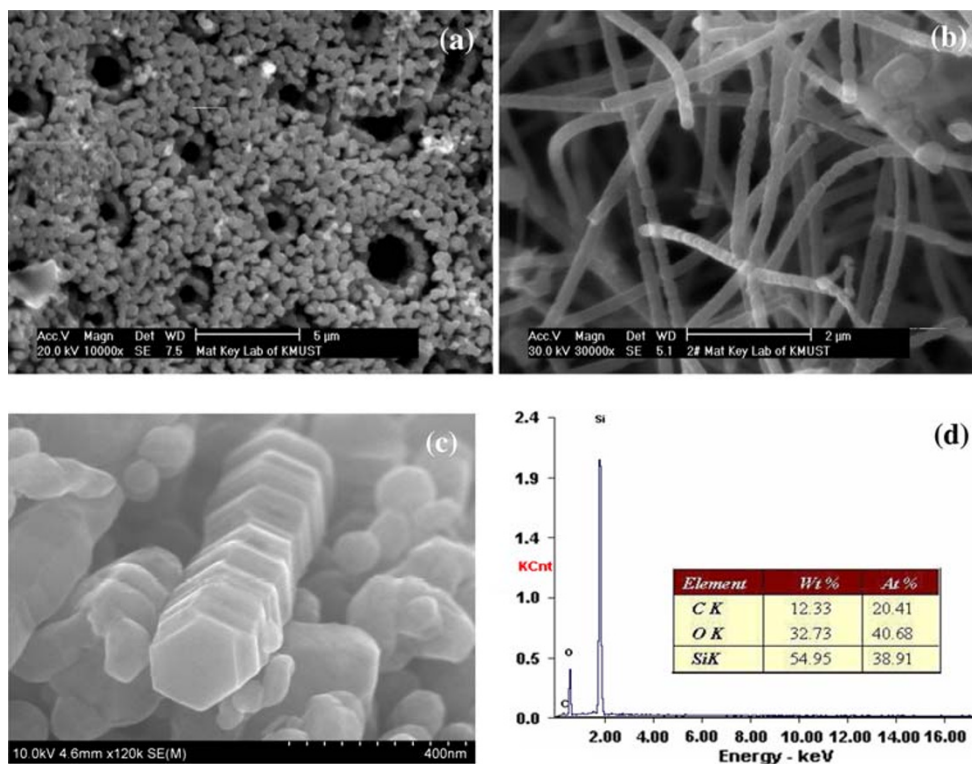Figure 6 shows the Photoluminescence (PL) spectrum of SiC NWs under 275 nm excitation at room temperature.

Fig. 4 **a** SEM image of bamboo carbon, **b** and **c** SEM and FE-SEM images of the synthesized β-SiC NWs, **d** EDS spectrum of β-SiC NWs
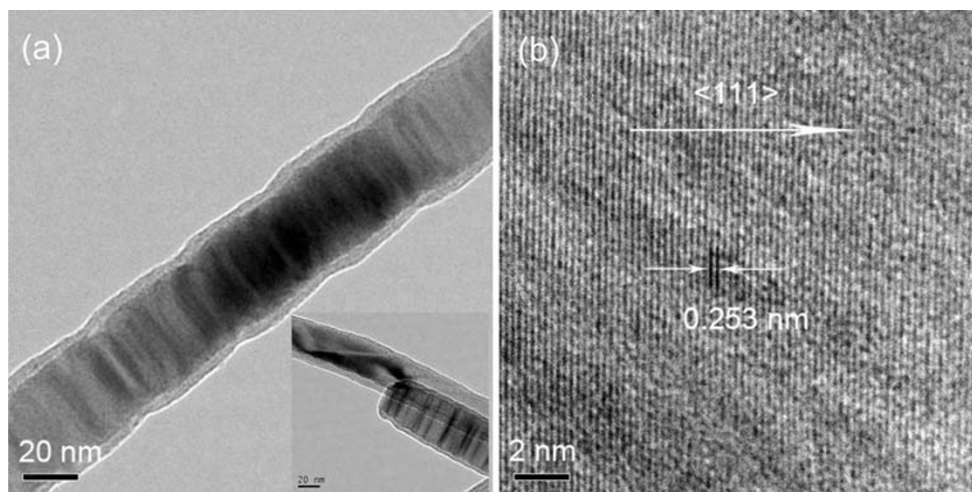

Fig. 5 TEM and HRTEM images of β-SiC NWs

The SiC NWs exhibit a strong ultraviolet emission peak at 300 nm, which is generally compatible to the value of 290 nm in the spectra of SiC NWs [30]. Previous reports have shown that the PL properties of SiC nanostructure strongly depend on the growth conditions, structure, morphology, excitation wavelength and irradiation spot. For example, Hierarchical SiC NWs showed a strong and sharp emission at 445.2 nm and a broad and weak cyan emission in the range of 475–500 nm with an excitation wavelength of 325 nm [31]. Feng et al. [32] reported that changing the irradiation spot of the SiC NWs lead to a slight shift of the PL peak wavelength from 440 nm to 460 nm. Stable violet–blue light emission peaks at about 315 nm and 360–400 nm were obtained from SiC/SiOx nanocables [33]. SiC nanocables were reported to have two broad emission peaks at 340 and 440 nm [34]. Compared with these previous reports, the emission peak for our SiC NWs is obviously blueshifted, which maybe due to the existence
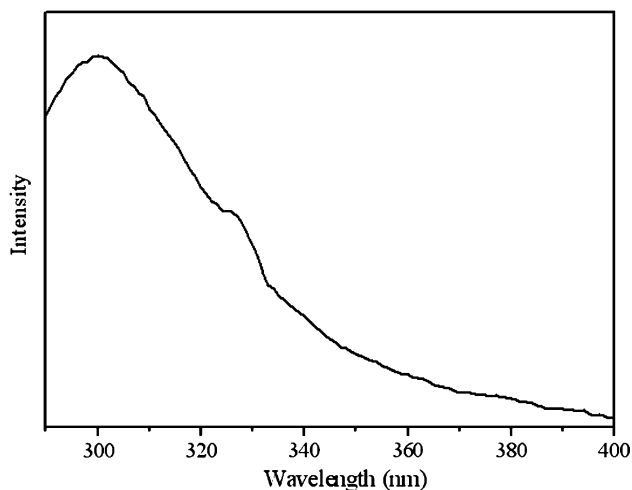
Fig. 6 Photoluminescence spectra of *β*-SiC NWs

of oxygen defects in amorphous layer and the special rough core–shell interface. However, the detailed emission mechanism of SiC nanostructures is still not fully understood and will be studied in the future.

Conclusions

In summary, we have successfully synthesized SiC NWs using bamboo carbon as carbon source via carbothermic reduction of silica under normal atmosphere pressure without metallic catalyst. The synthesized nanowires posses core–shell structure with diameter about 50–200 nm and grow along <111> direction with lengths from tens to hundreds of micrometers. The vapor–solid mechanism demonstrated the growth process of SiC NWs via carbothermic reduction of silica. The PL spectrum shows the nanowires have an ultraviolet emission peaks at 300 nm, which indicates that the nanowires are a promising material candidate for nanooptoelectronic and light emitting devices applications.

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