Direct synthesis of one-dimensional silicon carbide nanostructures on graphite by pyrolysis of rice husks

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One-dimensional (1D) β -SiC/SiO₂ nanochains, β -SiC nanowires and rod-like β -SiC were directly obtained from the vapor deposited products that formed on graphite by pyrolysis of rice husks (RHs) in argon atmosphere. 1D β -SiC/SiO₂ nanochains composed of β -SiC stems and amorphous SiO₂ beads were synthesized at 1500°C for 2 h. Pure 1D β -SiC nanowires having diameter of around 160 nm and tens of micrometers in length were obtained at 1500°C for 4 and 6 h. As pyrolysis temperature was increased to 1600 and 1700°C, β -SiC nanowires and rod-like β -SiC with larger diameters and shorter lengths were received, respectively. The possible growth processes based on vapor–solid (VS) mechanism were proposed to explain the formation of the 1D β -SiC nanostructures.

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1. Introduction

Recently, one-dimensional (1D) silicon carbide (SiC) nanostructures have drawn a great attention due to their versatile physical and chemical properties such as high thermal stability and hardness, chemical inertness, wide band gap and unique optical performance.^{1)–3)} These unique properties make 1D SiC nanostructures suitable for various applications such as nanocomposites,⁴⁾ microelectronics,⁵⁾ optoelectronics,⁶⁾ catalyst supports,⁷⁾ etc. A variety of techniques for fabricating 1D SiC nanostructures, particularly SiC nanowires, have been developed, including chemical vapor deposition (CVD),^{8),9)} carbon nanotube confined reaction,¹⁰⁾ arc-discharge,¹¹⁾ metal catalyst-assisted vapor–liquid–solid (VLS) growth^{12),13)} and carbothermal reduction.¹⁴⁾ However, most of these methods involved complex procedures, expensive precursors or usage of metal catalyst. Therefore, more simple and low-cost approaches are still needed for synthesis of 1D SiC nanostructures.

Rice husks (RHs), a prolific and low-cost agricultural by-product, is considered as a good candidate for fabricating SiC due to the high contents of SiO₂ and C. According to the formation mechanism of SiC by pyrolysis of RHs,^{15)–17)} it can be known that the producing of SiO and CO vapors is inevitable by reactions (1)–(3):

Thus, large amounts of these vapors will diffuse to the inner surface of crucible walls and form the vapor deposited products of SiC by via reaction (4) and (5):

In this study, several kinds of 1D SiC nanostructures were synthesized from the vapor deposited products by pyrolysis of RHs in argon atmosphere. The effects of pyrolysis temperature

and time on morphology and microstructure of 1D SiC nanostructures were investigated in details.

2. Experimental section

RHs were obtained from a local rice mill factory of Japan. The RHs are composed of about 75 mass % organic constituents (hemicelluloses, cellulose and lignin), 5 mass % water, 18 mass % SiO₂ and 2 mass % other impurities (0.88 mass % K₂O, 0.46 mass % SO₃, 0.31 mass % Al₂O₃, 0.23 mass % CaO, 0.07 mass % P₂O₅, 0.04 mass % MnO and 0.01 mass % Fe₂O₃). In a typical procedure, 6 g RHs were placed in a cubic graphite crucible (80 × 80 × 10 mm) and covered by a graphite plate. The graphite crucible was put into a vertical graphite furnace. After evacuating to ~5 Pa by a rotary pump, high-purity argon gas (>99.999%) was introduced to the furnace at a flow rate of 2 L/min and maintained at a positive pressure of ~50 kPa throughout the whole following experiment. The furnace was firstly heated to 1000°C at a rate of 15°C/min and then up to target temperature at a rate of 10°C/min. Pyrolysis of RHs were carried out at 1500°C for 2, 4, 6 h and at 1600, 1700°C for 2 h, respectively. After the pyrolysis process, the furnace was cooled to room temperature naturally. Finally, the film-like vapor deposited products formed on graphite were collected.

The as-received products were characterized by X-ray diffraction using an X-ray diffractometer (XRD, Rigaku, UltimaIV) with Cu K α (λ = 1.5406 Å) radiation, Fourier transform infrared spectra recorded on a FT-IR spectrophotometer (FT-IR, JASCO, FT/IR 6200), field emission scanning electron microscopy (FESEM, JEOL, JSM-7600F), transmission electron microscopy (TEM, JEOL, JEM2010) and selected area electron diffraction (SAED).

3. Results and discussion

Figure 1 shows the XRD patterns of the as-received products and reveals the formation of β -SiC. The diffraction peaks at 2θ = 35.6, 41.4, 60.0, 71.8, 75.5° can be indexed as (111), (200), (220), (311) and (222) reflections of β -SiC structure (JCPDS Card No. 29-1129). The stronger (111) diffraction peak indicates that [111] is the dominant growth direction of the β -SiC. The

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Fig. 1. XRD patterns of the as-received products.

Fig. 2. FT-IR spectra of the as-received products.

small peak at 33.6° marked with SF is attributed to the stacking faults of β -SiC.¹⁸⁾ The intensity ratio of the peaks at 33.6 and 41.4° ($R=I_{33.6^\circ}/I_{41.4^\circ}$) can be used as indicator of stacking faults density.¹⁹⁾ In our case, the products obtained at 1500°C for different duration have a same R value of 0.34 . As the pyrolysis temperature increase to 1600 and 1700°C , the R value decrease to 0.12 and 0.09 , respectively. It seems that lower density of stacking faults is formed at higher temperature, whereas the products obtained at 1500°C for different duration have a same density of stacking faults.

Figure 2 displays the FT-IR spectra of the as-received products. The absorption peak at around 798 cm^{-1} corresponds to Si–C stretching vibration of β -SiC. Whereas the characteristic peaks at 1127 and 483 cm^{-1} are ascribed to the Si–O stretching vibration of amorphous SiO_2 .²⁰⁾ Thus, it can be concluded that a composite of β -SiC and amorphous SiO_2 is received at 1500°C for 2 h , while other products are pure β -SiC.

As shown in **Figs. 3(a)** and **3(b)**, the product obtained at 1500°C for 2 h mainly consists of nanochains structure having one stem with diameters of 150 – 160 nm and tens of micrometers in length. The beads periodically disperse on the stem with a nearly equal distance of around 600 nm . **Figure 4(a)** presents the TEM image of a typical single β -SiC/ SiO_2 nanochain. It can be known that the stem is crystalline β -SiC, whereas the beads are amorphous SiO_2 . As shown in the high magnification TEM image of a β -SiC/ SiO_2 heterojunction structure [inset of **Fig. 4(a)**], there are lots of stacking faults on the β -SiC stems and the amorphous SiO_2 beads prefer to form on the surface where

Fig. 3. FESEM images of the as-received products obtained at: (a, b) 1500°C for 2 h ; (c, d) 1500°C for 4 h ; (e, f) 1500°C for 6 h ; (g, h) 1600°C for 2 h ; (i, j) 1700°C for 2 h .

more stacking faults exist. Bright spots as well as obvious streaks can be observed in the selected area electron diffraction (SAED) pattern of the β -SiC/ SiO_2 heterojunction structure [**Fig. 4(b)**], indicating that the β -SiC stem grows along $[111]$ in length direction and having lots of stacking faults.

Figures 3(c)–3(j) show the FESEM images of the products obtained at 1500°C for 4 , 6 h and at 1600 , 1700°C for 2 h , respectively. The products obtained at 1500°C for 4 and 6 h are β -SiC nanowires having tens of micrometers in length and uniform diameter of around 160 nm . As the pyrolysis temperature increase to 1600°C , however, the as-received β -SiC nanowires show shorter length and larger diameter. Moreover, the β -SiC obtained at 1700°C for 2 h exhibits rod-like shapes with enhanced lateral growth.

Raman scattering is a useful method for the characterization of nanostructured materials and a qualitative probe of lattice defects. According to previous research, bulk β -SiC has two strong characteristic peaks at 796 and 980 cm^{-1} , which correspond to the transverse optical (TO) phonon mode and longitudinal optical (LO) phonon mode at the Γ point of β -SiC, respectively.²¹⁾ As shown in the Raman spectra of the as-received products (**Fig. 5**),

Fig. 4. (a) TEM image of a typical single β -SiC/SiO₂ nanochain. The inset is the high magnification TEM image of a typical β -SiC/SiO₂ heterojunction structure. (b) SAED pattern of the β -SiC/SiO₂ heterojunction structure.

Fig. 5. Raman spectra of the as-received products.

however, no obvious LO phonon peak can be observed, which is similar to the results reported by Frchette et al.²²⁾ and Li et al.²³⁾ The products obtained at 1500C for different time have an intensive TO phonon peak with a same peak position at 785 cm⁻¹. Compared with bulk β -SiC, the obvious asymmetric broadening and down-shift are observed on the TO phonon peak, which can be ascribed to the size confinement effect and stacking faults of β -SiC nanostructures.²⁴⁾ As the pyrolysis temperature up to 1600 and 1700C, the TO phonon peak shifts to 794 and 796 cm⁻¹, respectively. Furthermore, weakened asymmetric broadening are observed, which is attributed to the larger diameter and lower density of stacking faults.

Because the 1D β -SiC nanostructures are synthesized without the aid of metal catalyst, vapor–solid (VS) growth mechanism

is more plausible in this case. On the basis of the above experimental results, the possible growth mechanism of the 1D β -SiC nanostructures are suggested as follows:

The SiO and CO vapors generated via reactions (1)–(3) diffuse to the inner surface of graphite crucible. The SiC nucleuses are formed on graphite via reaction (4) and (5), and then grow up with continuous deposition to the β -SiC nanowires by reaction (5). Furthermore, the β -SiC nanowires prefer to grow along [111] direction due to the lowest surface energy.²⁵⁾ However, reaction (5) can only occur under a supersaturated condition of CO at higher temperature. When pyrolysis was carried out at 1500C for 2 h, the reaction (5) cannot be finished completely. During the cooling stage, SiO vapor is prevail and reaction (6) will occur with generating SiC and SiO₂ simultaneously.

Furthermore, part of the SiO₂ is likely to react with the volatile of alkaline compound, which derives from the K₂O in RHs, with forming poly alkaline silicates. Because the temperature in furnace is still higher than the melting point of poly alkaline silicates, the poly alkaline silicates show liquid phase and prefer to aggregate on the high stacking faults surfaces of β -SiC stem due to their better wettability and lower growth energy.²⁶⁾ After continuous deposition of SiO₂, the SiO₂ beads are formed. When pyrolysis time is prolonged to 4 and 6 h, the nanowires grow up entirely by reaction (5), resulting in pure β -SiC nanowires. On the other hand, the reaction rate becomes higher and the lateral growth will be enhanced at higher temperature. Therefore, β -SiC nanowires and rod-like β -SiC having larger diameters and shorter lengths are obtained at 1600 and 1700C, respectively.

4. Conclusions

A simple way to fabricate 1D β -SiC nanostructures was developed in this study. 1D β -SiC/SiO₂ nanochains, β -SiC nanowires and rod-like β -SiC were synthesized on graphite by pyrolysis of rice husks in argon atmosphere. The pyrolysis temperature and time greatly influence the morphology and microstructure of β -SiC. Finally, the 1D β -SiC nanostructures were suggested to grow by VS mechanism.

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