

Large-Scale Synthesis of α - Si_3N_4 Nanofibers and Nanobelts from Mesoporous Silica-Carbon Nanocomposites

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received December 23, 2016; received in revised form February 14, 2017; accepted March 31, 2017

Abstract

This work presents a low-cost and large-scale synthesis technique for silicon nitride nanofibers and nanobelts based on the use of mesoporous silica-carbon nanocomposites as precursors via a carbothermal reduction and nitridation reaction. The growth mechanisms have been investigated by carrying out heat-treatment of precursors with different C/SiO₂ ratios in a flowing nitrogen gas with different flow rates. Highly crystalline silicon nitride nanofibers and nanobelts were obtained after easy separation from the unreacted powder underneath. A higher C/SiO₂ ratio gives a better yield of nitride products. The thickness of the ribbons can be maintained as constant while the width of the ribbons can be controlled by tailoring the flow rate of nitrogen gas. The growth direction of Si_3N_4 nanobelts is parallel to the [100] crystallographic orientation of α - Si_3N_4 .

Keywords: Silicon nitride, nanofibers, nanobelts, mesoporous, nanocomposites, carbothermal reduction and nitridation

I. Introduction

Silicon nitride (Si_3N_4) nanofibers and nanobelts have attracted much attention because of their unique one-dimensional (1D) nanostructures and excellent properties such as high strength retention at elevated temperature, low thermal expansion coefficient, good thermal shock resistance, high corrosion resistance and unique optical properties^{1–6}. This material is a promising candidate for matrix enhancement of composites in aerospace applications, the metallurgy industry, and aviation and military hardware. It is also a wide-band gap semiconductor and can be introduced by doping to tailor electronic/optical properties in building nanodevices. A variety of synthesis techniques are currently being used and investigated, including direct nitridation^{7,8}, imide process^{9,10}, vapor¹, laser and plasma synthesis^{11,12}, and carbothermal reduction^{13–16}. Among those, one of the most popular methods to form a large amount of silicon nitride nanowires or nanofibers is with catalyst-assisted pyrolysis of polysilazane^{17,18}, which is very expensive. It is also very difficult to separate the nanofibers from the remaining powder in both the pyrolysis process and vapor-solid reactions. The carbothermal reduction process promises to produce high-quality Si_3N_4 crystal at low cost, thanks to the wide availability of inexpensive, high-quality SiO₂ and C raw materials. However, it is still hard to control the formation of 1D nanostructures.

In our reported work^{19,20}, mesoporous silica-carbon has been proven to be an excellent candidate to synthesize silicon carbide with tailored nanostructures because

of two key factors: carbon and SiO₂ are mixed homogeneously at nanometer scale, and the mesopores provide nanochannels for releasing the gaseous by-products during carbothermal reduction. In this paper, mesoporous silica-carbon nanocomposites were used as precursors to synthesize silicon nitride nanofibers and nanobelts via a carbothermal reduction and nitridation reaction. The nitridation of mesoporous C-SiO₂ nanocomposites with nitrogen gas would be different from that with ammonia (the traditional way) because the oxygen in SiO₂ can be directly replaced by N under ammonia until silicon nitride (Si_3N_4) is formed while the nitridation goes through a SiO gas phase stage under nitrogen gas^{21,22}. Therefore, the growth mechanisms of this reaction process have been investigated by carrying out heat treatment of mesoporous SiO₂ nanocomposites with different C/SiO₂ ratios in a flowing nitrogen gas with different flow rates. The C/SiO₂ ratio and nitrogen gas flow rate were two major factors controlling the final microstructure of silicon nitride nanofibers or nanobelts.

II. Experimental

Mesoporous silica/carbon nanocomposites were prepared by using a reported sol-gel route^{19,20}. First, 5 g of deionized H₂O, 3.3 g of ethanol (anhydrous, Aldrich) and 0.5 g of 1 M HCl (Merck) were mixed in a capped polypropylene bottle with a magnetic stirrer. To this solution, 4.1 g of P123 (EO₂₀PO₇₀EO₂₀, MW5800, Sigma-Aldrich) was added under continuous agitation to obtain a P123 solution. Then 10 g of tetraethoxysilane (TEOS) (99 %, Sigma-Aldrich) and a given amount (7.06 g, and

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14.12 g) of furfuryl alcohol (FA, 99 %, Aldrich) were added into the P123 solution. The resulting mixtures were rigorously stirred at room temperature for 3 h, followed by aging at room temperature for 3 days, and drying at 80 °C for 3 days. The black monoliths obtained were carbonized at 550 °C for 5 h with flowing nitrogen, leading to mesoporous C-SiO₂ composites. To determine the C/SiO₂ ratios of the C-SiO₂ composites, thermogravimetric analysis (TGA) (Perkin-Elmer SPTG/DTA 6300, Pyris thermogravimetric analyzer) was conducted at a heating rate of 10 K/min to record the mass loss of the samples under flowing air. By 700 °C, all carbon was burned off. The C/SiO₂ ratio was then calculated by taking the total mass loss as the mass of carbon and the residual mass as the mass of SiO₂. In this paper, the mesoporous C-SiO₂ composites had C/SiO₂ molar ratios of 4.66/1 and 10.15/1 (TGA results are shown in Fig. 1 (a)), hence, the samples were denoted samples 4.66-CS and 10.15-CS, respectively.

The C-SiO₂ composites were transferred into a sealed tube furnace equipped with a vacuum pump. Before heating, the furnace was vacuumed to evacuate air for 30 min. The C-SiO₂ composites were heated under nitrogen atmosphere with different flowing rates at a heating rate of 2 K/min up to a setting temperature. The samples were kept at the setting temperature for different times and then cooled to room temperature at a cooling rate of 2 K/min.

X-ray diffraction (XRD) patterns were recorded on a Philips PW 1140/90 diffractometer with Cu K α radiation at a scan rate of 2°/min and a step size of 0.02°.

Scanning electron microscopy (SEM) images with electron diffraction X-ray (EDX) analysis were taken with a JEOL JSM 6300F microscope and a JEOL JSM 7100F microscope. Transmission electron microscopy (TEM) images were taken with a Philips CM20 TEM microscope. High-resolution TEM images were taken with a JEOL JEM 2100F FEGTEM microscope. Nitrogen adsorption-desorption experiments were performed at 77 K with a Micromeritics Tri-Star 3020 instrument (PsS Pty. Ltd.). The samples were degassed with a VacPrep063 instrument (PsS Pty. Ltd.) at 250 °C for 2 h prior to examination.

III. Results and Discussion

Mesoporous silica/carbon nanocomposites were synthesized successfully with this sol-gel route as reported^{19, 20}. TEM images of 4.66-CS in Fig. 1 (b) show a typical worm-hole pore structure of the precursor. Nitrogen adsorption-desorption results of as-received C-SiO₂ nanocomposites with different C/SiO₂ ratio revealed that both samples show a good mesoporosity with a pore size of 4–5 nm (as shown in Fig. 1 (d)), and a similar adsorption-desorption isotherm curve (as shown in Fig. 1 (c)). Sample 4.66-CS has a BET surface area of 379.94 m²/g and an average pore size of 4.25 nm, while sample 10.15-CS has a BET surface area of 367.54 m²/g and an average pore size of 5.37 nm. Although the effect of various factors on adsorption hysteresis is not fully understood, the hysteresis loops shapes of adsorption-desorption isotherm curves have often been used to identify specific pore structures.

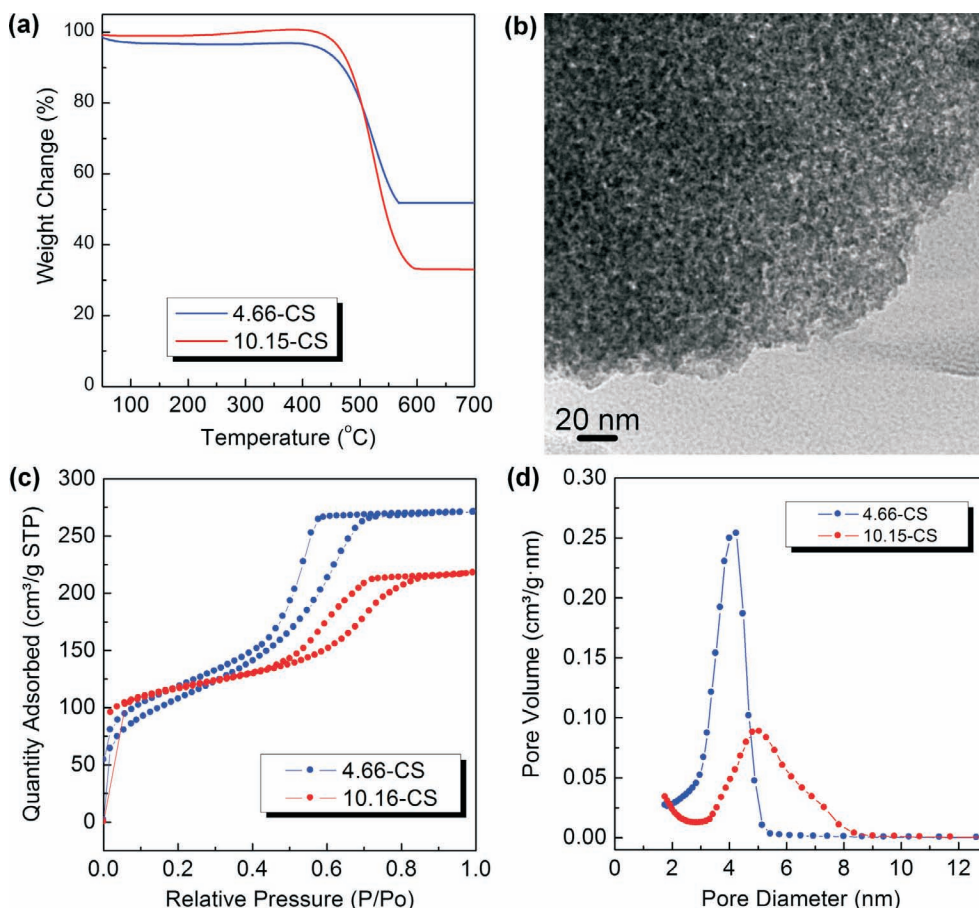


Fig. 1: (a) TGA results of the precursors; (b) TEM image of 4.66-CS; (c) nitrogen adsorption-desorption isotherm curves and (d) pore size distribution of the precursors.

Samples 4.66-CS and 10.15-CS, which have the same weight, were then heated at 1400 °C for 10 h under nitrogen atmosphere with a flow rate of 50 ml/min. Most of the nanofibers were grown on the top surface of the precursor particles. It could be concluded that the N_2 gas must play an important role in the product growth. The N element in the Si_3N_4 must come from the flowing N_2 gas during the carbothermal reduction and nitridation. But the N_2 gas was not able to reach the powders underneath, therefore the reaction occurred from the surface toward inside. Comparing the two samples, the yield of sample 10.15-CS-1400 °C/10 h is higher than that of sample 4.66-CS-1400 °C/10 h, suggesting that a higher C/SiO₂ ratio facilitates the growth of silicon nitride (the latter has more unreacted particles sitting in the crucible).

XRD patterns of sample 10.15-CS-1400 °C/10 h were plotted in Fig. 2 for comparison with the XRD patterns of sample 4.66-CS-1400 °C/10 h. Both samples showed XRD patterns corresponding to the standard values of α - Si_3N_4 (Joint Committee on Powder Diffraction Standards <JCPDS> card number 73–1210). The amorphous hump at about 20 degrees was a result of the residual amorphous carbon and silica. The increase in intensity of Si_3N_4 peaks in sample 10.15-CS-1400 °C/10 h suggests better crystallinity in the sample with a higher C/SiO₂ ratio.

SEM images of the as-received fibers in these two samples are presented in Fig. 3. The diameters of Si_3N_4 nanofibers obtained from the precursors with different C/SiO₂ ratios are similar at about 1–2 μm , indicating that the C/SiO₂ ratio has little effect on controlling the diameter of the fiber, which has been significantly influenced by the flow rate of N_2 gas (see following section). This phenomenon suggests that a higher C/SiO₂ ratio only facilitates the carbothermal reduction nitridation under N_2 gas by providing more SiO and CO during the heat treatments.

Besides the C/SiO₂ ratio, gas penetration is another important variable governing the effectiveness of the carbothermal reduction-nitridation reactions. In our work, it depends on the flow rate of N_2 gas through the furnace during the heat treatment. To examine the effects

of N_2 flow rate in this system, the N_2 flow rates of 25, 120 and 150 ml/min were used for carbothermal reduction-nitridation of 10.15-CS at 1400 °C for 10 h. SEM images of 10.15-CS heated at 1400 °C for 10 h under N_2 gas with different flow rates are presented in Fig. 4. With increasing the N_2 gas flow rate, the width of the Si_3N_4 nanofibers became larger while the thickness remained unchanged, indicating that the morphology of Si_3N_4 changes from nanofibers to nanobelts. The dimension of the Si_3N_4 nanofibers is 200 nm thick $\times$ 600 nm wide when the flow rate of N_2 gas is 25 ml/L, whereas that of the Si_3N_4 nanobelts is 200 nm $\times$ 6000 nm when the flow rate of N_2 gas is 150 ml/L. The lengths of the nanofibers and nanobelts are around several hundred micrometers; some of them even have lengths in the order of millimeters. Most of the nanofibers and nanobelts have uniform width throughout their entire length, and a small portion of the nanofibers and nanobelts has a broken or rippled edge. It is worth noting that the Si_3N_4 nanofibers and nanobelts are so thin that they are almost transparent to the electron beam.

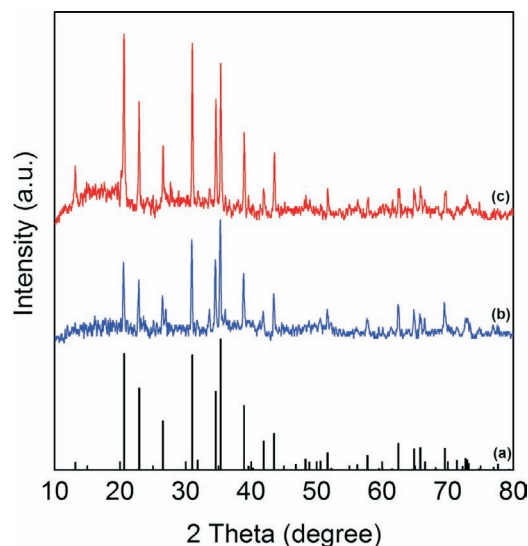


Fig. 2: XRD patterns of (a) standard α - Si_3N_4 patterns (JCPDS 73–1210); (b) 4.66-CS-1400 °C/10 h and (c) 10.15-CS-1400 °C/10 h.

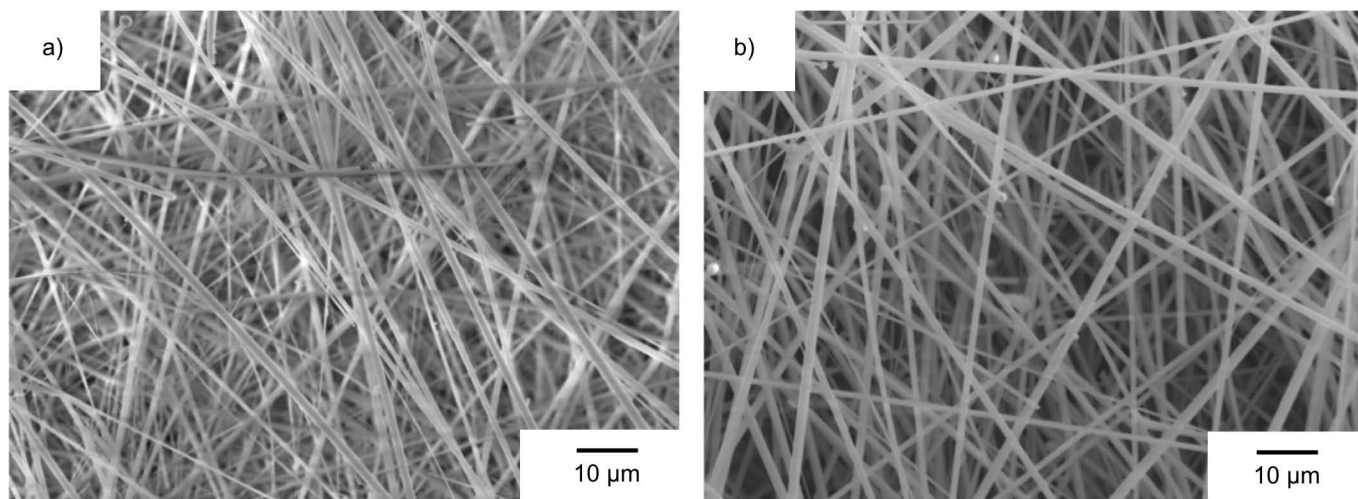


Fig. 3: SEM images of (a) 4.66-CS and (b) 10.15-CS heated at 1400 °C/10 h under N_2 gas with a flow rate of 50 ml/min.

TEM images of sample 10.15-CS heated at 1400 °C for 10 h under N₂ gas with different flow rates are presented in Fig. 5. Ripple-type contrast within the ribbon indicates the presence of strain that originates from the lattice distortion in these TEM samples. It also indicates the Si₃N₄ nanofibers and nanobelts are highly transparent to electrons, and the copper grid with carbon film can even be seen through the Si₃N₄ nanofibers and nanobelts, confirming that the Si₃N₄ nanofibers and nanobelts are very thin.

A high-resolution TEM (HR-TEM) study would provide further insights into the microstructures of the Si₃N₄ nanofibers and nanobelts. Sample 10.15-CS heated at 1400 °C for 10 h under N₂ with a flow rate of 150 ml/min was characterized by means of HR-TEM to investigate the growth of Si₃N₄ ribbons from carbothermal reduction nitridation of mesoporous silica-carbon. Fig. 6 (a) shows an

HR-TEM image of the end of a Si₃N₄ ribbon, in which the lattice fringes of {100} and {002} with *d* spacings of 0.67 and 0.28 nm, respectively, arise from the hexagonal α -Si₃N₄ structure (JCPDS card number 73–1210). Fig. 6 (b) is an HR-TEM image of the end of another type of Si₃N₄ ribbon, in which the lattice fringes of {100} and {001} with *d* spacings of 0.67 and 0.56 nm, respectively, arise from the hexagonal α -Si₃N₄ (JCPDS card number 73–1210). The insert SEAD patterns in Fig. 6 (b) show that the Si₃N₄ ribbon grows along the [100] direction. Both images indicate that the long axis direction of the Si₃N₄ ribbon is parallel to the [100] crystallographic orientation of α -Si₃N₄. In our experiment, several tens of as-grown Si₃N₄ ribbons have been examined with HR-TEM, and the results suggest that they are structurally uniform and single crystalline with only one growth direction of [100].

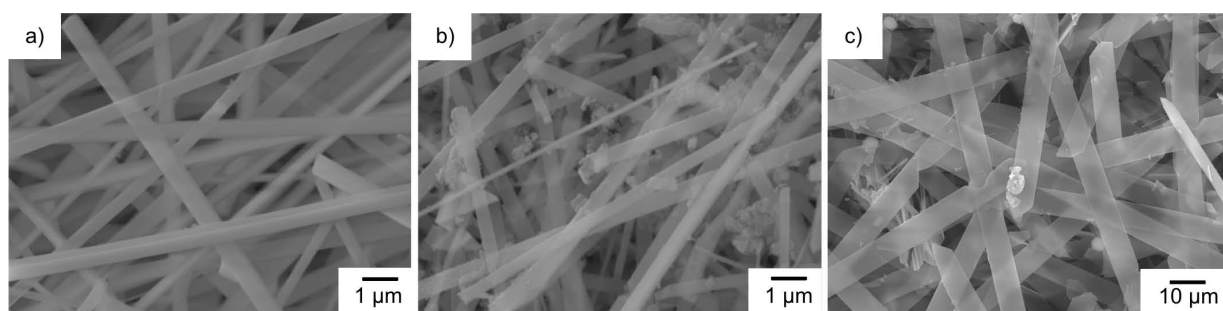


Fig. 4: SEM images of 10.15-CS heated at 1400 °C/10 h under N₂ gas with a flow rate of (a) 25 ml/min; (b) 120 ml/min and (c) 150 ml/min.

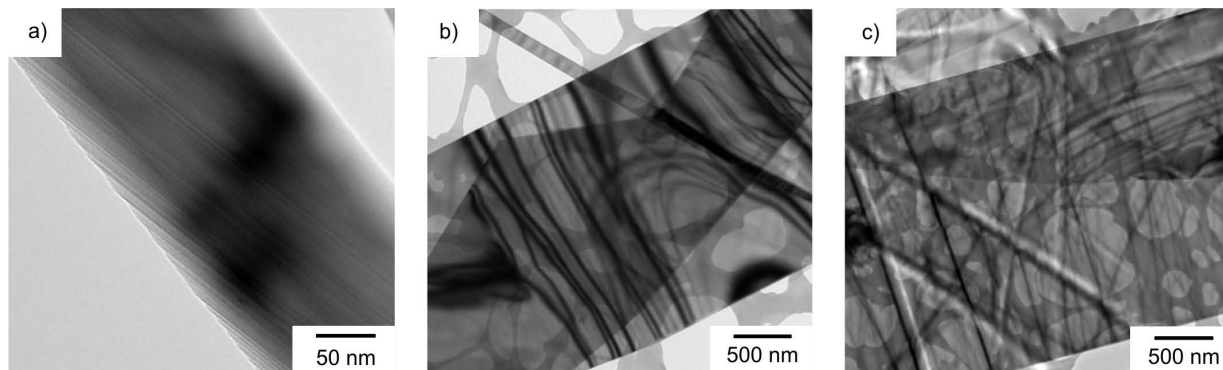


Fig. 5: TEM images of 10.15-CS heated at 1400 °C/10 h under N₂ gas with a flow rate of (a) 25 ml/min; (b) 120 ml/min and (c) 150 ml/min.

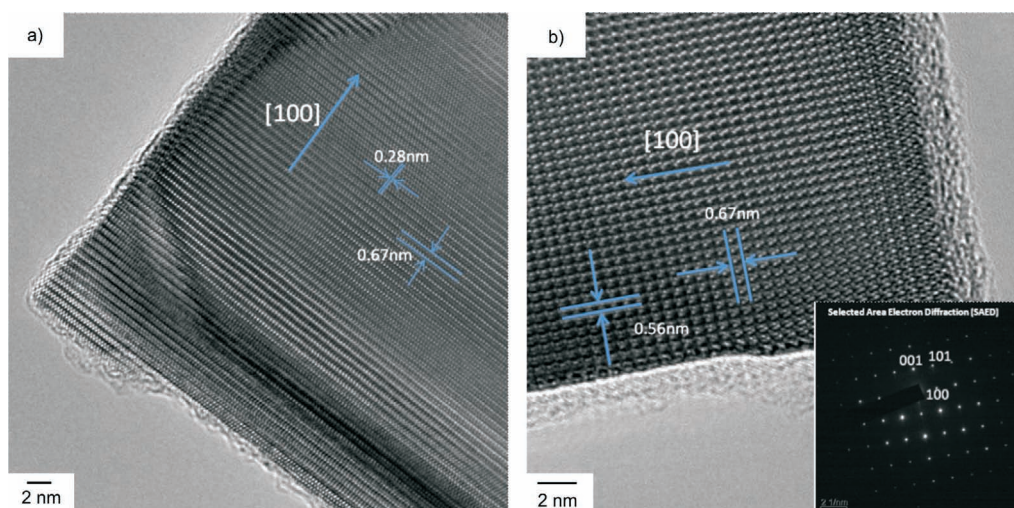
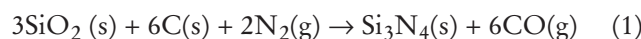


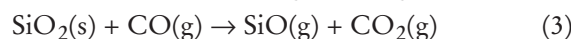
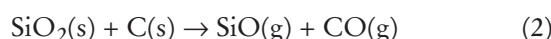
Fig. 6: a, b: HR-TEM images of Si₃N₄ micro-ribbons. The insert of (b) shows the corresponding indexed SAED patterns.

It has been widely accepted that the carbothermal reduction nitridation of silica and carbon under N₂ gas is via the following reaction^{21, 22}:

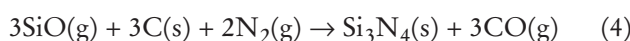


During the high-temperature heat treatment, SiO₂ reacts with C to form SiO and CO gases first, and then the SiO gas reacts with N₂ together with C, to nucleate Si₃N₄ crystallites according to the following reactions^{15, 22}:

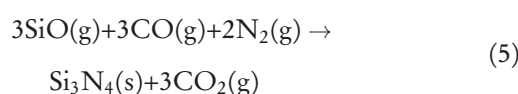
(i) Reduction of SiO₂ and generation of SiO:



(ii) Nitridation and nucleation of Si₃N₄:



(iii) Growth of Si₃N₄:



Upon the gradual release of SiO gas, the Si₃N₄ nanofibers or nanobelts would grow along a low direction, [100] direction in this work, to grow longer. However, the SiO and CO gases would also react with each other to form SiC crystals. But the Si₃N₄ is thermodynamically more stable in the present system than SiC phases under nitrogen gas, so the SiC crystals are quite small in size and quantity.

IV. Conclusions

Highly crystalline silicon nitride nanofibers and nanobelts were produced by means of carbothermal reduction and nitridation of mesoporous carbon-silica nanocomposites under nitrogen gas. The thickness of the ribbons was maintained as constant while the width of the ribbons can be controlled by tailoring the flow rate of nitrogen gas. At high temperature, C in the matrix starts to react with SiO₂ to release SiO and CO gases. SiO then reacts with the flowing nitrogen gas and residual carbon to form silicon nitride. Therefore, a higher C/SiO₂ ratio gives a better yield of nitride products. The growth direction of the Si₃N₄ nanobelts is parallel to the [100] crystallographic orientation of α -Si₃N₄. Since the carbothermal reduction and nitridation reaction occurred from the surface toward inside of precursor powder sitting in the crucible, it is very easy to separate Si₃N₄ nanofibers and nanobelts from the unreacted powder underneath. This study provides a low-cost and large-scale synthesis technique for Si₃N₄ nanofibers and nanobelts.

Acknowledgments

K.W. should like to express gratitude for the financial support of this work from the "Fundamental Research Funds for the Central Universities" (WUT: 2017IVA088). This work is also supported by State Key Laboratory of Advanced Technology for Materials Synthesis and Processing (Wuhan University of Technology). The authors acknowledge the use of facilities within the Monash Centre for Electron Microscopy for TEM and SEM.

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