A simple approach to controllably grow network-like branched single-crystalline Si$_3$N$_4$ nanostructures

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**A B S T R A C T**

We reported a simple, large-scale, and controllable growth method for network-like branched single-crystalline Si$_3$N$_4$ nanostructures by catalyst-assisted pyrolysis of a polysilazane. The templates were a silicon wafer deposited with a 5 nm Fe film. The processes simply involved in thermal cross-linking of the polymer precursor, crushing of the solidified preceramic polymer chunks into fine powder, and thermal pyrolysis of the powder under the protection of ultra-high purity nitrogen. The collected white network-like branched nanostructures were formed through “metal-absorption on the surface of nanostructures” model by vapor-liquid-solid mechanism. Microstructure characterizations indicate that the nanostructures are single-crystalline hexagonal $\alpha$-Si$_3$N$_4$. The reaction mechanism of Si$_3$N$_4$ nanonetworks was also proposed.

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1. Introduction

Along with the development of modern technology, the miniaturization of components for the construction of electronic and optoelectronic devices becomes an essential requirement. The formation of nanosstructures with controlled size and morphology promises the further miniaturization of components for the construction of electronic and optoelectronic devices [1–3].

Si$_3$N$_4$ is an important engineering ceramic and high-temperature semiconductor due to its superior properties, and previous studies reveal that Si$_3$N$_4$ nanowires exhibit novel electric and optical properties and possess higher bending strength than bulk Si$_3$N$_4$ [4]. So, Si$_3$N$_4$ nanostructures have been extensively investigated due to their potential applications as interconnects in optoelectronic nanodevices, and reinforcing element in ceramic-, metal- and polymer-matrix nanocomposites.

In recent years, many different chemical and physical routes [5–9] have been proposed to prepare various Si$_3$N$_4$ nanostructures [10–14]. Although Refs [15–18] have reported the synthesis of SiC nanowire networks, three dimensional WO$_3$–B nanowire networks, polyaniline nanofiber networks and carbon nanowire networks, up to now, the growth of network-like branched Si$_3$N$_4$ nanostructures has not been reported.

In this work, we reported a simple approach for the large-scale preparation of single-crystalline $\alpha$-Si$_3$N$_4$ network-like branched nanostructures by pyrolysis of a polysilazane on silicon wafers deposited with a Fe film as catalyst. The growth model and reaction mechanism of the as-received Si$_3$N$_4$ nanonetworks were proposed.

2. Experimental procedure

The applied polymer precursor is a polysilazane, which consisted of Si (~15 at%), N (~20 at%), C (~62 at%), and tricky O (less than 3 at%), and had an average molecular weight ($M_w$) in the range of 900–1200. The precursor was a yellowish liquid at room temperature. So, before pyrolysis, the precursor was first solidified by thermal cross-linking at 300 °C for 2 h under the protection of high-purity nitrogen (99.99 vol%). Then, the resultant chunk was crushed into fine powder in an agate mortar for use.

The pyrolysis process was conducted in a conventional horizontal tube furnace schematically shown in Fig. 1. In an optimum experiment, 0.8 g polymer preceramic powder was loaded in the high-purity alumina crucible (Φ45 × 40). And the Si wafer, deposited with a 5 nm Fe film by a magnetron sputtering system, was set over the preceramic powder by a ZrO$_2$ supporter with
a height of 10 mm. And the whole pyrolysis process was carried under high-purity nitrogen gas stream with a rate of 60 mL/min. During the pyrolysis process, the precursor powder was de-watered at 110 °C for half an hour, and then pyrolyzed at 1250 °C for 2 h with heating rate of 10 °C/min and natural furnace-cooling, respectively. After reaction, white products were collected on the surface of the Si wafer.

The as-prepared products were characterized by a FEI Quanta 200 FEG field emission scanning electron microscope (SEM, Holland), X-ray diffraction (XRD, Dmax-2500, Rigaku) with Cu Kα radiation (λ = 1.54178 Å), and a JEOL JEM 2011 high-resolution transmission electron microscope (HRTEM, Japan). Both SEM and TEM applied in this work were equipped with energy dispersive x-ray spectroscopy (EDX).

3. Results and discussion

3.1. Characterization of nanostructures

Fig. 2 shows two typical SEM images of the as-prepared network-like branched nanostructure. The low-magnification SEM image in Fig. 2a reveals that the nanonetworks can be prepared in mass production, which is essential in industrial application for such materials. The high-magnification SEM image in Fig. 2b clearly displays that the nanostructures are interconnected with each other to form nanonetworks, and these networks can construct more complicated nanostructures by multi-layer stack. The diameters of each linear part of the network-like nanostructure varied in the range of 150–400 nm, and most of the junctions are connected through three branches or more. From Fig. 2b, one can also see some nanoparticles on the surfaces of the nanostructures (see the circled spots), which were confirmed to be Fe-rich nanoparticles by SEM-EDX and TEM-EDX, indicating that the growth of the nanostructures was controlled by vapor-liquid-solid (VLS) mechanism [19], and it will be discussed detailedly later.

The XRD pattern of the product is shown in Fig. 4. Apart from one diffraction peak of the silicon substrate at 2θ = 69.14°, all the other sharp diffraction peaks are assigned to hexagonal α-Si3N4.
3.2. Growth mechanism of nanostructures

Although the detailed reaction mechanism of Si₃N₄ nanostructures by the proposed method has not been fully understood, we infer that the synthesis process is as follows. The polymer precursor was first decomposed at 1000–1100 °C into amorphous SiCN [20] which would then react with oxygen from the precursor or survival in air to produce SiO₂ via reaction (1) [21]. The CO₂ further reacted with the solid C resulted from the decomposition of the polymer precursor to form CO by reaction (2). And the SiO₂ further reacted with Si by reaction (3) to produce high partial pressures of metastable and highly reactive SiO, which would react with N from reaction (1)–(4) to form Si₃N₄. The Gibbs free energies at 1523 K, ΔrG(1523K), of the reactions of (2)–(4) were calculated to be −111.04 KJ/mol, −52.75 KJ/mol, −1466.93 KJ/mol, respectively, indicating that the reactions are spontaneous.

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\begin{align*}
2\text{SiCN(s)} + 8\text{O}(g) & \rightarrow 2\text{SiO}_2(g) + 2\text{N(g)} + 2\text{CO}_2(g) \quad (1) \\
\text{CO}_2(g) + \text{C}(s) & \rightarrow 2\text{CO}(g) \quad (2) \\
\text{Si}(s) + \text{SiO}_2(s) & \rightarrow 2\text{SiO}(g) \quad (3) \\
3\text{SiO}(g) + 4\text{N(g)} + 3\text{CO}_2(g) & \rightarrow \alpha - \text{Si}_3\text{N}_4(s) + 3\text{CO}_2(g) \quad (4)
\end{align*}
\]

On the basis of the reaction mechanism mentioned above and the observation of Fe-rich droplets on the tips of nanostructures, it was proposed that the growth of the as-prepared Si₃N₄ nanostructures was controlled by the classic VLS mechanism [19], and their growth model is illustrated in Fig. 6. At high temperature, the catalyst, Fe thin film would melt to form droplets of different sizes, and this process is a gradual one and time-consuming with the increase in temperature. The gaseous SiO, N and CO are solved in the Fe droplets to form Fe-rich eutectic liquid droplets, and with the increase of Si₃N₄ concentration in the eutectic droplets, solid Si₃N₄ aggregates to form nanowires and grow along its axial direction, with the minimization of its systemic energy [22]. When the nanowires grow out from the Fe droplets or liquid thin films, due to the high surface reactivity and absorptivity, Fe atoms in the vicinity around the nanowires are absorbed onto their surfaces, playing the role of new nucleation centers to develop new nanowires (branches) on the side of the original one. The newly-developed branches can also grow up with the same process, developing newer branches, leading to the formation of nanonetworks finally. And the diameters of each linear part of the nanostructures varied due to the different sizes of Fe droplets formed onto the silicon wafer and/or the surface of the primary nanowires during high-temperature thermal treatment.
4. Conclusion

Network-like branched Si$_3$N$_4$ nanostructures have been synthesized with high yield via pyrolysis of a polysilazane on Si wafers coated with a Fe film as catalyst. The nanomaterials have a perfect single-crystalline structure. The diameters of each linear part of the nanostructures ranged from 150 to 400 nm. The growth of the nanonetworks was controlled by VLS mechanism on the basis of “metal-absorption on the surface of nanostructure” model.

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