A novel method for synthesis of $\alpha$-$\text{Si}_3\text{N}_4$ nanowires by sol–gel route

Mahua Ghosh Chaudhuri, Rajib Dey, Manoj K Mitra, Gopes C Das and Siddhartha Mukherjee

Department of Metallurgical and Material Engineering, Jadavpur University, Kolkata, India
E-mail: smukherjee03@yahoo.co.in

Received 5 February 2007
Accepted for publication 9 October 2007
Published 13 March 2008
Online at stacks.iop.org/STAM/9/015002

Abstract
Silicon nitride ($\text{Si}_3\text{N}_4$) nanowires have been prepared by carbothermal reduction followed by the nitridation (CTRN) of silica gel containing ultrafine excess carbon obtained by the decomposition of dextrose over the temperature range of 1200–1350 $^\circ$C. This innovative process involves repeated evacuation followed by purging of nitrogen gas so that the interconnected nanopores of the gel are filled with nitrogen gas prior to heat treatment. During heat treatment at higher temperatures, the presence of nitrogen gas in the nanopores of the gel starts the CTRN reaction simultaneously throughout the bulk of the gel, leading to the formation of $\text{Si}_3\text{N}_4$ nanowires. The in situ generated ultrafine carbon obtained by the decomposition of dextrose decreases the partial pressure of oxygen in the system to stabilize the nanowires. The nanowires synthesized by this process are of $\sim$500 nm diameter and $\sim$0.2 mm length. The product was characterized by scanning electron microscope (SEM), energy dispersive x-ray analysis (EDX), x-ray diffraction (XRD) and infrared (IR) spectra.

Keywords: sol–gel, nanowires, $\alpha$-$\text{Si}_3\text{N}_4$

1. Introduction
$\text{Si}_3\text{N}_4$ has attracted considerable interest because of its excellent high-temperature mechanical properties, such as strength, hardness, wear resistance, thermal shock resistance and chemical inertness. This material is utilized for structural applications at high temperatures and its domains of application extend from vessels for chemical reactions to heat-exchanger bearings, engines and gas turbine components [1–3]. $\text{Si}_3\text{N}_4$ is also a wide-band-gap semiconductor used in the optical and electrical device industries [4]. However, $\text{Si}_3\text{N}_4$ nanotubes and nanowires have recently attracted much attention because of their enhanced hardness associated with their unique optical and other mechanical properties [5–7] as compared with coarse-grained $\text{Si}_3\text{N}_4$ ceramic materials. As a result, different physical and chemical routes have been proposed and developed for the synthesis of $\text{Si}_3\text{N}_4$ nanowires. Chemical vapor deposition [8, 9], the carbothermal reduction of silica and carbon in nitrogen-containing ambient [10, 11], the nitridation of silicon powder [12, 13] and the nitridation of a Fe–Si catalyst [14] are frequently used for nanowire synthesis. Wang and Wada synthesized $\text{Si}_3\text{N}_4$ nanowires by the carbothermal reduction of silica followed by 10 h nitridation at 1350 $^\circ$C in ultrapure nitrogen atmosphere [15]. The same route has been used by Ramesh and Rao [16] to synthesize $\alpha$-$\text{Si}_3\text{N}_4$. $\text{Si}_3\text{N}_4$ forms only after the carbothermal reduction of preoxidized $\text{SiO}_2$ for 10 h followed by nitridation in very high purity nitrogen (partial pressure of oxygen: $10^{-20}$ atmosphere) at 1350 $^\circ$C but long fibers of $\alpha$-$\text{Si}_3\text{N}_4$ are only formed after 24 h of the above treatment [16]. The carbothermal reduction of silica xerogels followed by 30 h of nitridation at 1300 $^\circ$C in ultrahigh-purity nitrogen atmosphere results in the generation of long and pure $\alpha$-$\text{Si}_3\text{N}_4$ nanowires [17]. All these synthesis methods of $\text{Si}_3\text{N}_4$ nanowires are kinetically slow and require very lengthy heat treatment. In all the above processes, the nitrogen gas has to first diffuse to the reaction sites and only then does the CTRN reaction occur for the synthesis of $\text{Si}_3\text{N}_4$ nanowires. It is therefore expected that if nitrogen gas was present beforehand at the reaction sites, the carbothermal reduction followed by the nitridation (CTRN) reaction kinetics would be much faster during heat treatment. In this paper, we report the effect of the
presence of nitrogen gas in the nanopores of the gel, obtained by repeated evacuation followed by purging of nitrogen gas to enhance the kinetics of the CTRN reaction for the synthesis of Si$_3$N$_4$ nanowires.

2. Thermodynamics of Si–N–O system

The thermodynamics of the carbon-saturated Si–N–O system can be used to determine the permissible oxygen content in nitrogen that ensures the stability of the Si$_3$N$_4$ phase at a given temperature. This is important because the nitrogen used is not completely free from oxygen. Figure 1 shows a stability diagram of the Si–N–O system at 1350 °C. The equilibrium isobar of $p_{SO} = 10^{-4}$ superimposed on the stability diagram will help us to determine the mechanism of the synthesis of Si$_3$N$_4$ nanowires, as explained later.

From the stability diagram, we can observe that Si$_3$N$_4$ exists as a stable phase at a maximum permissible partial pressure of oxygen of $10^{-17.7}$ atmosphere at 1623 K corresponding to a pressure of 1 atmosphere of nitrogen. Similar analysis also for 1300 and 1200 °C show that the maximum permissible partial pressure of oxygen ensuring the stability of Si$_3$N$_4$ gradually decreases to nearly $10^{-19}$ and $10^{-20}$ atmospheres, respectively. Excess carbon, over the theoretical amount required for the synthesis of Si$_3$N$_4$, is added to the system and is responsible for the generation of the extremely low partial pressure of oxygen required for the stability of Si$_3$N$_4$.

3. Experimental

Tetraethyl orthosilicate (TEOS) and dextrose (AR grade) are used as precursors of Si and C, respectively. A clear solution of TEOS and alcohol (99.9%) is obtained by constant stirring. A clear solution of dextrose, double-distilled water and ethyl alcohol was added dropwise to the previous solution under constant stirring. The resultant solution was left in a beaker at room temperature to form a gel. After about seven days a transparent gel was obtained. The molar composition of the gel thus prepared is TEOS : water : ethyl alcohol = 1 : 1 : 2, containing 200% excess of stoichiometric dextrose.

Dried gels were initially preheated at 300 °C for 30 min in an inert atmosphere to completely remove moisture and to generate extremely fine C in the nanopores of the gel by the decomposition of the dextrose. Each preheated sample was introduced into a vacuum furnace evacuated using a double-stage rotary pump, then purged with nitrogen gas at ambient temperature. Repeated evacuation and purging was carried out to ensure the maximum replacement of air with nitrogen. The temperature of the furnace was raised to 1200–1350 °C and was held isothermally for a period of 2 or 3 h under a constant flow of nitrogen. For comparison, another sample was heat-treated at 11350 °C for 3 h in a furnace under a constant flow of nitrogen gas but without prior evacuation followed by purging with nitrogen gas.

The heat-treated samples are ground in an agate mortar and passed through a 300-mesh sieve. X-ray diffraction (XRD) patterns of the powder samples were recorded using an x-ray diffractometer (Rigaku Miniflex) with CuKα radiation ($\lambda = 0.15418$ nm) in a continuous scan mode from 20° to 80° at a scan rate of 0.1 s.

A powder sample was placed on a conducting carbon tape, and a scanning electron microscope (SEM) (JEOL, JSM 6063) was used to observe the morphological details of phases present. The elemental analysis of the phases was carried out by energy dispersive x-ray analysis (EDX) (Oxford Instruments, INCA).

Infrared (IR) spectra were obtained using a PerkinElmer 833-IR spectrometer. A small amount of ground sample was mixed with KBr and a pellet was formed. The spectrum was obtained over 4000–450 cm$^{-1}$ at room temperature. The spectrum of KBr powder was used as the background.

4. Results and discussions

Figures 2(a)–(c) show SEM images and an EDX plot, respectively, of the samples heat treated in dynamic nitrogen atmosphere at 1350 °C for 3 h after repeated evacuation followed by purging of nitrogen gas. Figure 2(a) shows that Si$_3$N$_4$ nanowires were formed with a diameter of ~500 nm (later confirmed by XRD). Figure 2(b) shows an SEM image of the same sample at lower magnification and shows that the wires are sufficiently long. No accurate measurement of the length of the wires could be carried out, but the wires formed after 3 h of carbothermal reduction followed by nitridation were always more than ~0.2 mm long. The EDX plot of the same sample taken from the white wires is shown in figure 2(c) and it shows the presence of Si, N and O. The adjacent table contains the atomic percentages of the elements, and the atomic ratio of Si : N is ~ 3 : 4. This suggests that the nanowires are Si$_3$N$_4$.

White nanowires of $\alpha$-Si$_3$N$_4$ were obtained only after 3 h of heat treatment using ordinary nitrogen gas, in contrast with the 24 or 30 h of heat treatment using ultrahigh-purity nitrogen gas required to form similar nanowires by other methods [16, 17]. This experiment clearly indicates the beneficial role of the presence of nitrogen in the nanopores of the gel.

Table 1 contains EDX data for the sample heat-treated at 1350 °C for 2 h under constant flow of nitrogen with prior
Figure 2. (a) SEM image of sample with 200% excess dextrose gel heat treated at 1350 °C for 3 h under a constant flow of nitrogen with prior evacuation followed by purging with nitrogen gas. (b) SEM image of sample shown in (a) at lower magnification. (c) EDX plot of sample shown in (a).

Table 1. EDX data for the samples heat-treated as described.

| Sample                                      | 200% excess dextrose gel heat-treated at 1350 °C for 2 h under constant flow of nitrogen with prior evacuation of the furnace followed by purging with nitrogen gas | 200% excess dextrose gel heat-treated at 1350 °C for 3 h under constant flow of nitrogen but without prior evacuation of the furnace followed by purging with nitrogen gas |
|---------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------|
| Si (wt. %)                                  | 50.49                                                                                                                            | 37.84                                                                                                                              |
| O (wt. %)                                   | 34.22                                                                                                                            | 62.16                                                                                                                              |
| N (wt. %)                                   | 15.29                                                                                                                            | nil                                                                                                                                |
| Total                                       | 100                                                                                                                               | 100                                                                                                                                |

evacuation of the furnace followed by purging with nitrogen gas and the EDX data of the sample heat-treated at 1350 °C for 3 h under a constant flow of nitrogen gas but without prior evacuation followed by purging with nitrogen gas. Compared with figure 2(c) the table shows that less nitrogen is present in the sample reduced at 1350 °C for 2 h under constant flow of nitrogen with prior evacuation and purging with nitrogen, and this indicates that a lower percentage of the sample was converted to Si₃N₄. On the other hand, when reduction is carried out at 1350 °C in nitrogen atmosphere for 3 h without prior evacuation of the furnace and followed by purging with nitrogen is completely absent and thus it is concluded that hardly any Si₃N₄ is formed.

Figures 3(a)–(c) show XRD patterns of the samples obtained after heat treatment at 1200, 1300 and 1350 °C, respectively, in nitrogen atmosphere for 3 h with prior repeated evacuation followed by purging with nitrogen gas. Figures 3(a) and (b) confirm the presence of a broad amorphous silica peak between 15° and 30° [18] and diffraction peaks corresponding to α- and β-Si₃N₄ phases. It is further observed that with increasing heat treatment temperature, the amount of α-Si₃N₄ formed increases and that
Figure 3. For caption see following page.
of β-Si₃N₄ decreases. Figure 3(c) shows only diffraction peaks corresponding to the α-Si₃N₄ phase with a conspicuous absence of the amorphous silica peak. It is clear from the above discussion that the conversion from SiO₂ to α-Si₃N₄ increases with temperature. An almost complete conversion to α-Si₃N₄ is obtained at a temperature of 1350 °C within 3 h. Figure 3(d) depicts the XRD pattern of the sample heat treated at 1350 °C for 2 h under constant flow of nitrogen with prior evacuation of the furnace followed by purging with nitrogen gas. It consists of diffraction peaks corresponding to α- and β-Si₃N₄ and a small amorphous silica peak. This means that the conversion to α-Si₃N₄ is not completed within 2 h.

Figure 3(e) shows the XRD pattern of the sample heat-treated at 1350 °C for 3 h in nitrogen atmosphere without prior evacuation and purging with nitrogen gas. There is a major amorphous silica peak and hardly any diffraction peaks for Si₃N₄. This is consistent with the EDX data (see table 1), which reflects the absence of nitrogen, resulting in the formation of hardly any Si₃N₄. This clearly establishes the importance of the presence of nitrogen in the nanopores of the gel prior to the heat treatment.

Observations based on SEM-EDX and XRD analyses are further confirmed by FTIR spectroscopic analysis. Figure 4(a) shows the IR spectrum of the sample with 200% excess dextrose gel heat-treated at 1350 °C for 3 h under a constant flow of nitrogen with prior evacuation of the furnace followed by purging with nitrogen gas. The IR absorption bands at 847, 682, 597 and 492 cm⁻¹ correspond to the characteristic absorption bands of α-Si₃N₄ [19, 20], and this confirms the presence of α-Si₃N₄. Figure 4(b) shows the IR spectrum of the sample heat-treated at 1350 °C for 3 h under a constant flow of nitrogen gas without prior evacuation of the furnace followed by purging with nitrogen gas. This shows the presence of the characteristic absorption band at 1100 cm⁻¹ corresponding to the Si–O bond in silicon oxide [21]. However, the absorption bands of α-Si₃N₄ are absent indicating the absence of Si₃N₄.

5. Role of evacuation and proposed mechanism of synthesis

The results of different characterization techniques reveal that repeated evacuation followed by purging with nitrogen plays an important role in the synthesis of Si₃N₄ nanowires.

Figure 4. (a) IR spectrum of sample with 200% excess dextrose gel heat-treated at 1350 °C for 3 h under a constant flow of nitrogen with prior evacuation of the furnace followed by purging with nitrogen gas. (b) IR spectrum of the sample with 200% excess dextrose gel heat treated at 1350 °C for 3 h under a constant flow of nitrogen but without prior evacuation of the furnace followed by purging with nitrogen gas.

Hardly any nanowires were formed without prior evacuation and purging with nitrogen gas. This leads us to propose the following mechanism for the synthesis of silicon nitride nanowires.

Dry silica gel contains interconnected nanopores filled with air and dextrose. Carbon is generated in situ by the decomposition of dextrose in the nanopores of the gel at 300 °C. When the gel is heat treated directly at a high temperature in a dynamic nitrogen atmosphere, the nitrogen gas has to first reach the nanopores by a slow diffusion process before nitridation can start. Thus, the process is kinetically slow and is the most plausible reason for the absence of Si₃N₄ (see figure 3(e)). On the other hand, if nitrogen gas was present a priori throughout the nanopores of the bulk gel, the reaction is much faster. This is exactly what was achieved by repeated evacuation followed by purging with nitrogen gas. In each evacuation–purging cycle, the nanopores of the gel are evacuated and subsequently filled with nitrogen gas.
cycles ensure better filling of the nanopores with nitrogen. Then the temperature of the furnace is raised to the heat treatment temperature in a dynamic nitrogen atmosphere, and unlike the first case, the diffusion of nitrogen to the nanopores is no longer necessary; thus, the carbothermal reduction followed by nitridation starts simultaneously throughout the entire porous network of the gel, leading to the much faster synthesis of Si3N4. The following is the probable reaction mechanism. First the \textit{in situ} generated carbon uniformly distributed in the nanopores reacts with silica gel on the pore surface to form SiO (g) and CO (g) as given by the reaction (1) below \cite{16}. SiO maintains an equilibrium partial pressure of 10^{-4} atmosphere in 1 atmosphere of nitrogen at 1623 K (see figure 1). This gaseous SiO produced in the nanopores of the gel mixes homogeneously with the nitrogen and CO. This gas mixture undergoes a reaction to yield Si3N4 by reaction (2) as stated below. The other possibility is that Si3N4 is yielded by reaction (3) \cite{16}. The solid Si3N4 is deposited on the carbon particles, which act as nucleating sites. As Si3N4 is formed and deposited, the partial pressure of SiO decreases from its equilibrium value, which is restored by the reduction of SiO2 and drives equilibrium in the forward direction as in reaction (1). Since the reaction occurs within the porous network of the gel, the Si3N4 thus formed is expected to be in the form of nanowires. Thus, the most likely reactions, under the experimental conditions, for the synthesis of silicon nitride nanowires are given below:

\begin{equation}
\text{SiO}_2(\text{s}) + \text{C}(\text{s}) = \text{SiO}(\text{g}) + \text{CO}(\text{g}), \quad (1)
\end{equation}

\begin{equation}
3\text{SiO}(\text{g}) + 2\text{N}_2(\text{g}) + 3\text{CO}(\text{g}) = \text{Si}_3\text{N}_4(\text{s}) + 3\text{CO}_2(\text{g}). \quad (2)
\end{equation}

The other possible gas-phase reaction is

\begin{equation}
3\text{SiO}(\text{g}) + 2\text{N}_2(\text{g}) + 3\text{C}(\text{s}) = \text{Si}_3\text{N}_4(\text{s}) + 3\text{CO}(\text{g}). \quad (3)
\end{equation}

6. Conclusions

1. Si3N4 nanowires of diameter \~500 nm and length \~0.2 mm have been synthesized by the carbothermal reduction of silica followed by nitridation through the sol–gel route.

2. Repeated evacuation followed by purging with N2 fills the nanopores of the silica gel with N2 prior to heat treatment, and this greatly enhances the kinetics of the conversion from SiO2 to α-Si3N4.

3. The thermodynamic study of Si–N–O system shows that extremely low partial pressure of oxygen is required for the stability of Si3N4 phase, which is achieved by the addition of excess dextrose.

Acknowledgments

We gratefully acknowledge the Council of Scientific and Industrial Research, New Delhi, for sponsoring this research. The work was also partially supported by UGC Potential for Excellence, Nanoscience and Technology, Jadavpur University. We also acknowledge the instrumental assistance of Dr R Bhar and Mr P Das Gupta of the Department of Instrumentation Science, Jadavpur University.

References

\begin{itemize}
\item [1] Backhaus-Ricoult M, Guerin V, Huntz A-M and Urbanovich V S 2002 \textit{J. Am. Ceram. Soc.} \textbf{85} 385
\item [2] Riley F L 2000 \textit{J. Am. Ceram. Soc.} \textbf{83} 245
\item [3] Buljan S T and Baldoni J G 1989 \textit{Mater. Sci. Forum} \textbf{47} 249
\item [4] Oba F, Tatsumi K, Tanaka I and Adachi H 2002 \textit{J. Am. Ceram. Soc.} \textbf{85} 97
\item [5] Carduner K R, Blackwell C S, Hammond W B, Reindinger F and Hartfield G R 1990 \textit{J. Am. Chem. Soc.} \textbf{112} 4676
\item [6] Xu Y J, Cao C B, Chen Z, Li J, Wang F C and Cai H N 2006 \textit{J. Phys. Chem. B} \textbf{110} 3088
\item [7] Tang C C, Bando Y, Sato T and Kurashima K 2002 \textit{J. Mater. Chem.} \textbf{12} 1910
\item [8] Kijima K, Setaka N and Tanaka H 1974 \textit{J. Cryst. Growth} \textbf{24–25} 183
\item [9] Motojima S, Yamana T, Araki T and Iwanage H 1995 \textit{J. Electrochem. Soc.} \textbf{142} 3141
\item [10] Arik H 2003 \textit{J. Eur. Ceram. Soc.} \textbf{23} 2005
\item [11] Wu X C, Song W H, Zhao B, Huang W D, Pu M H, Sun Y P and Du J 2000 \textit{J. Solid State Commun.} \textbf{115} 683
\item [12] Gopalakrishnan P S and Laksmimarsimhan P S 1993 \textit{J. Mater. Sci. Lett.} \textbf{12} 1422
\item [13] Inomata Y and Yamane T 1974 \textit{J. Cryst. Growth} \textbf{21} 317
\item [14] Hao K F, Ma Y W, Hu Y M, Fu J J, Lu B, Lu Y N, Hu Z and Chen Y 2005 \textit{Nanotechnology} \textbf{16} 2282
\item [15] Wang M-J and Wada H 1990 \textit{J. Mater. Sci.} \textbf{25} 1690
\item [16] Ramesh P D and Rao K J 1994 \textit{J. Mater. Res.} \textbf{9} 2330
\item [17] Wang F, Jin G and Guo X-Y 2006 \textit{J. Phys. Chem. B} \textbf{110} 14546
\item [18] Liu Y Z, Zhou Y Q, Shi W Q, Jiao L L, Sun B Y and Ye T C 2004 \textit{Mater. Lett.} \textbf{58} 2397
\item [19] Theodossiou E, Bauman H, Matz W and Macklich A 2002 \textit{Phys. Status Solidi a} \textbf{194} 47
\item [20] Mazdiyasni K S and Cooke C M 2001 \textit{J. Am. Ceram. Soc.} \textbf{56} 628
\item [21] Luo Y M, Zheng Z M, Xie Z M and Zhang Z J 2004 \textit{J. Mater. Lett.} \textbf{58} 2114
\end{itemize}