JOURNAL OF
Materials
CHEMISTRY

Synthesis and characterization of silicon carbide, silicon oxynitride and silicon nitride nanowires

Gautam Gundiah, G. V. Madhav, A. Govindaraj, Md. Motin Seikh and C. N. R. Rao*

Chemistry and Physics of Materials Unit and CSIR Centre of Excellence in Chemistry, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India. E-mail: cnrrao@jncasr.ac.in

Received 4th January 2002, Accepted 27th February 2002
First published as an Advance Article on the web 3rd April 2002

Several methods have been employed to synthesize SiC nanowires. The methods include heating silica gel or fumed silica with activated carbon in a reducing atmosphere, the carbon particles being produced *in situ* in one of the methods. The simplest method to obtain β-SiC nanowires involves heating silica gel with activated carbon at 1360 °C in H_2 or NH_3. The same reaction, if carried out in the presence of catalytic iron particles, at 1200 °C gives α-Si_3N_4 nanowires and Si_2N_2O nanowires at 1100 °C. Another method to obtain Si_3N_4 nanowires is to heat multi-walled carbon nanotubes with silica gel at 1360 °C in an atmosphere of NH_3. In the presence of catalytic Fe particles, this method yields α-Si_3N_4 nanowires in pure form.

Introduction

The discovery of carbon nanotubes[1] has triggered exploration for various types of one-dimensional nanomaterials over the last few years. Several inorganic nanotubes and nanowires have been reported, those of the metal chalcogenides being noteworthy.[2] These nanomaterials are associated with interesting mechanical, electronic, optical and other properties. Thus, silicon carbide (SiC) nanowires possess high elasticity and strength and are good candidates for making various types of composites. Nanowires of silicon nitride (Si_3N_4) may have potential applications in nanodevices and in the fabrication of composites. There are several reports on the preparation of SiC nanowires in the literature, but fewer on the preparation of Si_3N_4 nanowires. The methods employed for the synthesis of SiC nanowires have been varied. SiC nanowires were prepared by Dai *et al.*[3] by the reaction between carbon nanotubes and SiO or SiI_2 in a sealed tube under vacuum at 1300–1400 °C and 1100–1200 °C, respectively. Han *et al.*[4] employed a two-step reaction in which SiO vapour was first generated *via* the reduction of silica and then reacted with carbon nanotubes at 1400 °C in an Ar atmosphere to form SiC nanowires. β-SiC nanowires with and without amorphous silica (SiO_2) wrapping layers have also been obtained by the carbothermal reduction of sol–gel-derived silica xerogels containing carbon nanoparticles, at 1800 °C and 1650 °C, respectively, in an Ar atmosphere.[5] SiC nanorods have also been prepared from solid sources of carbon and silicon by hot filament chemical vapour deposition.[6] Liang *et al.*[7] used the reaction between activated carbon and sol–gel derived silica embedded with Fe nanoparticles at 1400 °C in an H_2 atmosphere to produce β-SiC nanowires, while Hu *et al.*[8] prepared β-SiC nanowires by the reaction of silicon with carbon tetrachloride (CCl_4) and metallic sodium at 700 °C. Zhang *et al.*,[9] on the other hand, used a floating catalyst method wherein $SiCl_4$ was reacted with benzene and floating Fe catalyst particles derived from ferrocene in the presence of H_2 and Ar at around 1150 °C. In the various procedures listed above, the diameters of the nanowires varied between 10 and 100 nm, while the lengths were in the micrometer (μm) range. The reaction of aligned carbon nanotubes with SiO has however been considered to be advantageous, the diameter and the length of the nanowires depending on the nature of the starting carbon nanotubes.[10]

In spite of many of the studies mentioned above, there is a need for a simple procedure for the synthesis of SiC nanowires which uses common chemicals as starting materials and avoids extreme conditions. Since both SiC and Si_3N_4 are products of the carbothermal reduction of SiO_2, it should be possible to establish conditions wherein one set of specific conditions favours one over the other. We have carried out detailed investigations on the preparation of SiC nanowires starting with silica gel and activated carbon and by employing NH_3 or H_2 as the reducing agent, the former enabling us to obtain silicon nitride nanowires as well, under slightly modified conditions. The procedure employed by us for SiC nanowires has the advantage that it does not require carbon nanotubes or the use of SiO as the starting material. In addition to the synthesis of SiC nanowires, we have carried out studies to establish a procedure for the synthesis of pure silicon nitride nanowires as well. Han *et al.*[11] obtained nanorods of a mixture of α- and β-forms of silicon nitride along with Si_2N_2O, by heating a mixture of Si and SiO_2 powders with carbon nanotubes in a nitrogen atmosphere at 1400 °C. Silicon nitride whiskers have been prepared by the gas phase reaction between SiO, CO and N_2 at 1350 °C[12] while α-Si_3N_4 nanowires sheathed with Si and SiO_2 have been obtained by heating silicon oxide nanoparticles with carbon in a flowing N_2 atmosphere at 1450 °C.[13] We have found that the reaction of SiO_2 gel with carbon nanotubes or activated carbon with Fe catalyst in the presence of NH_3 yields pure α-Si_3N_4 nanowires.

Experimental

For the preparation of SiC nanowires, we have employed several methods. In procedure (i), silica gel prepared in admixture with activated carbon, was dried, and heated to 1360 °C (4–7 h) in an NH_3 or a H_2 atmosphere. Activated carbon was prepared by the thermal decomposition of polyethylene glycol (600 units) at 700 °C for 3 h in an Ar atmosphere. In a typical experiment, 2 ml of tetraethylorthosilicate (TEOS) was mixed with 10 ml of ethanol under stirring for 10–15 min. To this solution, 0.424 g of activated carbon was added (giving a C : Si molar ratio of 4 : 1), followed by 1 ml of aqueous HF (48% A.R.) and the stirring continued. After gelation of the above solution, the gel was dried at 125 °C for 12–15 h. The gel containing finely distributed activated carbon was powdered, taken in an alumina boat and placed in a

DOI: 10.1039/b200161f

tubular furnace, purged earlier with NH_3 gas for 15 min. The gel powder was heated at an appropriate temperature in the 1100–1360 °C range for several hours with the flow of NH_3 maintained at 10 ml min^{-1}. Instead of NH_3, H_2 was also used in this procedure. A grey, wool-like product was deposited on the walls of the alumina boat. This was collected and analyzed.

Procedure (ii) for the preparation of SiC nanowires involved a solid state synthesis in which fumed silica (Grade M-5, surface area 210 m^2 g^{-1}, Cabot Corporation) was finely ground with activated carbon, keeping the molar ratio of C : Si at 4 : 1. The mixture was reduced under conditions similar to those in procedure (i). In procedure (iii), a homogenous gel was prepared by the reaction of ethylene glycol with citric acid in the presence of TEOS at elevated temperatures, by the following procedure. In a typical synthesis, 1.5 ml of ethylene glycol was mixed with 3.5 g of citric acid followed by the addition of 2 ml of TEOS. The sample was heated at 80 °C for 12 h, at 120 °C for 6 h and finally at 180 °C for 12 h. The dried gel so obtained was reduced as in procedure (i).

In order to prepare Si_3N_4 nanowires, we have used multi-walled carbon nanotubes as the carbon source instead of activated carbon. The nanotubes have higher thermal stability than activated carbon. The multi-walled nanotubes were prepared by the arc discharge method as well as by the pyrolysis technique outlined in the literature.[14,15] The procedure was similar to procedure (i) used for the synthesis of SiC nanowires. NH_3 was used to provide a reducing atmosphere as well as to carry out nitridation. The reaction was also carried out in the presence of an Fe catalyst prepared *in situ* by taking ferric nitrate along with the other reactants. The proportion of Fe was varied between 0.1 and 0.5 mol%. Instead of using multi-walled carbon nanotubes prepared by the arc-discharge method, we have also used aligned multi-walled carbon nanotubes with or without catalytic Fe particles. Aligned multi-walled nanotubes were prepared by the pyrolysis of ferrocene along with acetylene in an Ar atmosphere.[16] Most of the reactions were carried out at 1360 °C and a few of them at 1100 °C. The grey coloured, wool-like product in each case was collected and analyzed.

In order to prepare Si_3N_4 nanowires, we have also used the reaction of silica gel and NH_3 in the presence of activated carbon (as in procedure (i) for SiC nanowires) and catalytic iron particles. The Fe particles were incorporated by taking ferric nitrate along with TEOS and activated carbon during the preparation of the silica gel.

Graphite powder was also used in place of the other carbon sources in procedure (i). The reaction of graphite powder at 1360 °C did not give us the carbide or the nitride due to the stability of graphite as compared with the other carbon sources.

Powder X-ray diffraction (XRD) patterns were recorded using Cu-Kα radiation on a Rich-Siefert, XRD–3000-TT diffractometer. Scanning electron microscopy (SEM) images were obtained on a LEICA S440i scanning electron microscope. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM 3010 operating with an accelerating voltage of 300 kV. Photoluminescence (PL) measurements were carried out at room temperature using 260 nm wavelength as the excitation wavelength with a PerkinElmer model LS50B luminescence spectrometer. Infrared spectra were recorded with a Bruker FT-IR spectrometer. The Raman experiments were performed in a quasi-backscattering geometry. The Raman spectra were measured at room temperature using a Nd-YAG laser at 532 nm, and an Ar-ion laser at 488 and 514.5 nm. The Raman spectra show no remarkable resonance enhancement. The scattered light was collected using an optical fiber through a Super Notch filter, dispersed by a single monochromator with $f = 0.55$ m (Spex 550) and detected by a cooled CCD.

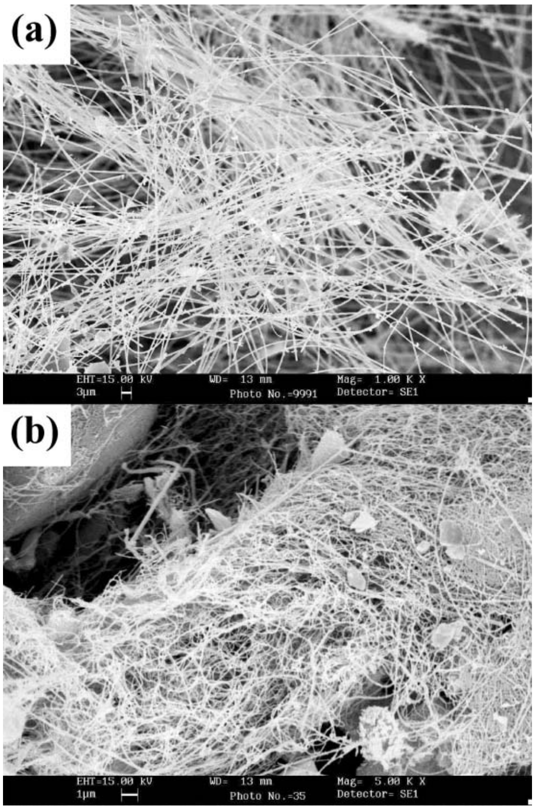

Fig. 1 SEM images of the β-SiC nanowires obtained by procedure (i) (heating the gel containing the activated carbon and silica at 1360 °C in NH_3) for (a) 4 h and (b) 7 h.

Results and discussion

SiC nanowires

The reaction of activated carbon with silica gel at 1360 °C by procedure (i) gave a good yield of SiC nanowires after a period of 4 h. In Fig. 1a we show the SEM image of the nanowires obtained by this procedure. The diameter of the nanowires is around 350 nm and the length extends to several tens of microns. The XRD pattern of this sample shown in Fig. 2a

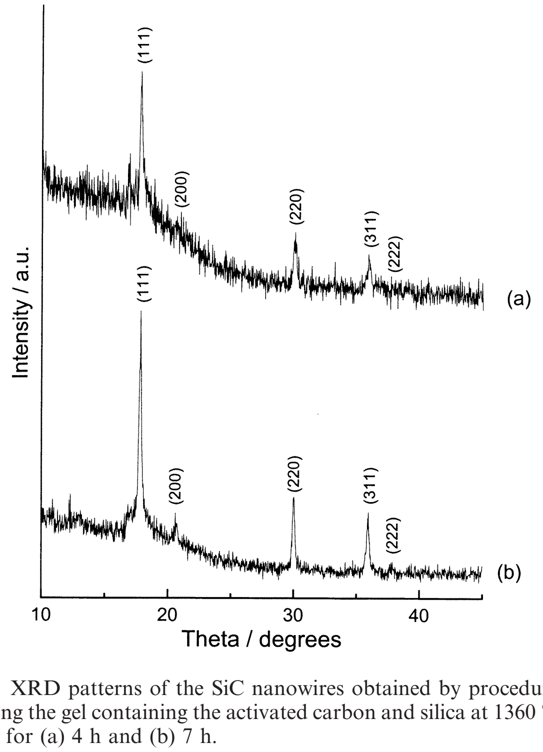

Fig. 2 XRD patterns of the SiC nanowires obtained by procedure (i) (heating the gel containing the activated carbon and silica at 1360 °C in NH_3) for (a) 4 h and (b) 7 h.

matches with that of cubic β-SiC with the unit cell parameters $a = 4.3589$ Å (JCPDS file: 29-1129). There are no reflections corresponding to α-SiC (hexagonal form) or SiO_2 in the diffraction pattern. We have carried out the same reaction for a period of 7 h (instead of 4 h) to improve the crystallinity of the SiC nanowires. The SEM image shown in Fig. 1b indicates that the nanowires so obtained have a diameter of ~40 nm with lengths of several tens of microns. The XRD pattern of this sample (Fig. 2b) is characteristic of the β-SiC phase. The pattern also shows that the crystallinity of the sample is considerably improved. The SiC nanowires did not have a silica coating as evidenced from the XRD pattern and transmission electron microscope images. Low magnification electron microscope images of the nanowires did not reveal the presence of any droplets at the ends of the nanowires. A bead-necklace morphology, similar to that reported by Wu *et al.*[17] was, however, present in the nanowires, suggesting that the growth of the nanowires probably occurs by the VLS mechanism.[18,19] In this mechanism, the SiO_2 nanoparticles form droplets that are in contact with the activated carbon to give SiO vapour. The SiO vapour further reacts with carbon to form β-SiC particles, which act as the nuclei for the growth of the nanowires. Once the droplets are saturated with β-SiC, crystallization of the β-SiC occurs, followed by growth in one direction to yield nanowires.

We have carried out the reaction of silica gel with activated carbon in the presence of H_2 gas instead of NH_3 gas. This also gives excellent yields of nanowires of β-SiC. In Fig. 3a we show the SEM image of β-SiC obtained by this method. The nanowires are thick with a uniform diameter of ~325 nm and have lengths of several tens of microns.

The HREM image of a SiC nanowire presented in Fig. 4, shows a spacing of 2.5 Å between the (111) planes. The normal to the (111) planes forms an angle of 35° with the growth direction of the nanowires. The selected area electron diffraction pattern (SAED) pattern showed Bragg spots corresponding to the (111) planes, with some streaking due to the presence of stacking faults.

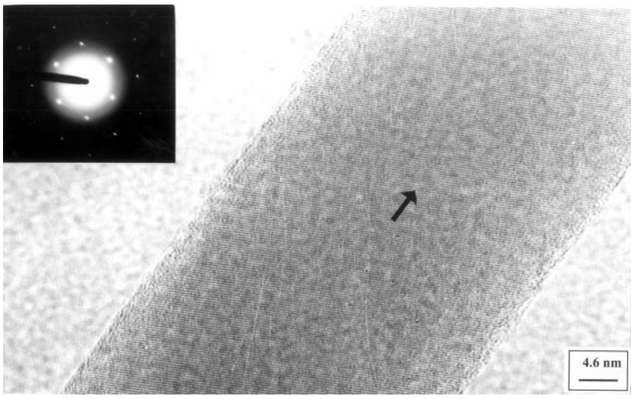

Fig. 4 HREM image of a SiC nanowire prepared by procedure (i) (heating the gel containing activated carbon and silica for 7 h at 1360 °C in NH_3). The inset shows the SAED pattern. The arrow denotes the normal to the (111) planes and the direction of growth of the nanowire.

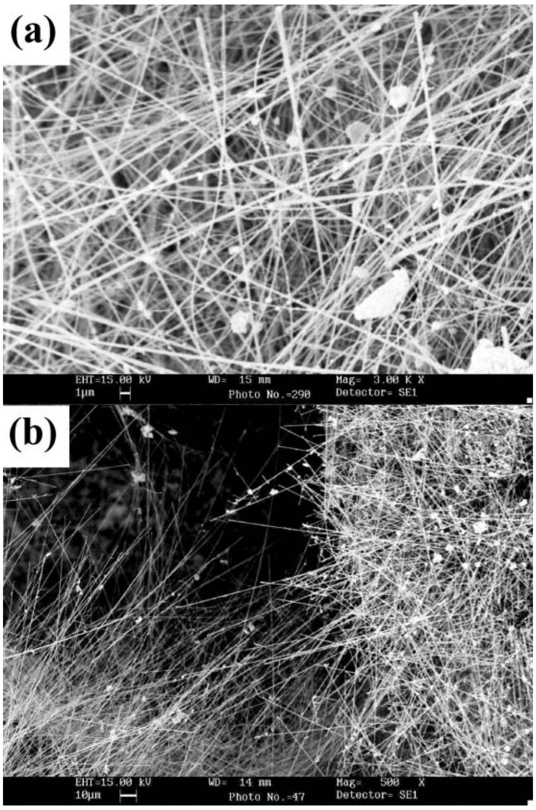

Fig. 3 SEM images of SiC nanowires obtained by (a) procedure (i) (heating the gel containing the activated carbon and silica for 7 h at 1360 °C) in the presence of H_2 gas and (b) procedure (iii) (heating the gel prepared by the reaction of ethylene glycol with citric acid in the presence of TEOS at 1360 °C for 7 h in NH_3).

The basic reactions involved in the formation of the SiC nanowires are given by,

$$SiO_2 + C \rightarrow SiO + CO$$

$$SiO + 2C \rightarrow SiC + CO$$

The NH_3 and H_2 in the gas stream favour the formation of SiO from SiO_2. The SiO reacts readily with carbon to form SiC.

In procedure (i), we have employed TEOS as the starting material since it gives fine particles of silica at low pH values. We have carried out the reaction of fumed silica (instead of a silica gel) with activated carbon by grinding the reactants in order to see if this procedure also gives us a good yield of SiC nanowires as in the case of the sol–gel route. Procedure (ii) yielded a grey, wool-like product, which had β-SiC as the major component. The diameter of the nanowires was ~500 nm and with the lengths extending to tens of microns. The XRD pattern, however, showed the presence of some silica.

We could obtain β-SiC nanowires by procedure (iii) wherein the gel formed by ethylene glycol, citric acid and TEOS was heated in a reducing atmosphere at 1360 °C. The ethylene glycol initially reacts with citric acid (in the presence of silica gel) to form silica particles embedded in carbon precursors. On treatment with NH_3 or H_2, this composite generates active carbon *in situ* which reacts with the silica nanoparticles to yield SiC. The SEM image (Fig. 3b) shows that the nanowires have large diameters (~750 nm) with lengths of up to tens of microns. The nanowires appear to be straight, unlike the ones obtained earlier, and seem to grow out from the carbon–silica composite particles.

The photoluminescence (PL) spectrum of the β-SiC nanowires synthesized by procedure (i) is shown in Fig. 5. The sample exhibits a single broad peak at 400 nm. Such a PL feature is characteristic of SiC, though there is a considerable blue shift as compared to the bulk sample.[20] The 3C form SiC shows a PL band maximum around 540 nm due to the presence of defect centres within the band gap.

Infrared spectra of the β-SiC nanowires show a strong band at 810 cm^{-1} due to the Si–C stretching band. The Raman spectrum of the nanowires is more interesting. Fig. 6 shows the room temperature Raman spectrum of the SiC nanowires with a quasi-backscattering geometry. We observe a broad band around 780 cm^{-1} corresponding to the TO phonon at the Γ point of cubic SiC. The absence of the folded modes that are related to the SiC polytypes (natural superlattices due to various stacking orders of Si–C bilayers) in the Raman

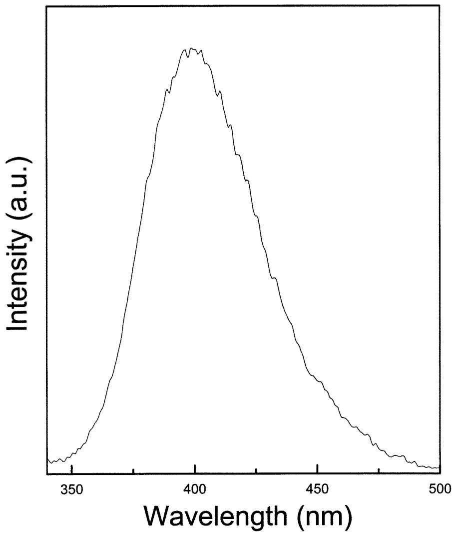

Fig. 5 Photoluminescence spectrum of SiC nanowires synthesized by procedure (i) (heating the gel containing activated carbon and silica for 7 h at 1360 °C in NH_3).

spectrum is consistent with the X-ray data, and suggests the nanowires are only cubic SiC.[21] The TO phonon line is shifted by around 16 cm^{-1} from the bulk SiC[22] towards lower energy. This is due to the small grain size of SiC and the presence of growth faults of the nanowires.

In the zinc-blende structure (as in cubic SiC) the LO phonon has a higher energy than the TO phonon near the zone center. LO phonon is around 972 cm^{-1} in bulk at ambient conditions in the bulk 3C-SiC.[22] In the Raman spectrum recorded by us, we do not see the LO phonon. As shown in Fig. 6, the LO phonon is absent even when different excitation wavelengths are used. Raman selection rules for the zinc-blende structure governs this observation as explained below. While preparing the SiC sample for Raman experiments, the nanowires are compressed to form a continuous surface. This orients the nanowires, such that the long cylindrical axes of the nanowires are parallel to the sample plane. From the TEM images it is clear that the cylindrical axis of the nanowires is [011] for the zinc-blende 3C-SiC. Raman experiments are carried out in the quasi-backscattering geometry on planes perpendicular to the (011) planes, such as $(0\bar{1}1)$. In the case of such a backscattering geometry, the incident wave vector ($\boldsymbol{k}_{\mathrm{i}}$) and scattered wave vector ($\boldsymbol{k}_{\mathrm{s}}$) are along the $[0\bar{1}1]$ direction and the polarization of the incident ($\boldsymbol{e}_{\mathrm{i}}$) and scattered ($\boldsymbol{e}_{\mathrm{s}}$) wave vectors are along the [011] direction. According to the Raman selection rules, the TO phonon is allowed whereas the LO phonon is forbidden for a zinc-blende structure.[23] This is the reason for the absence of the LO mode in the present experiment.

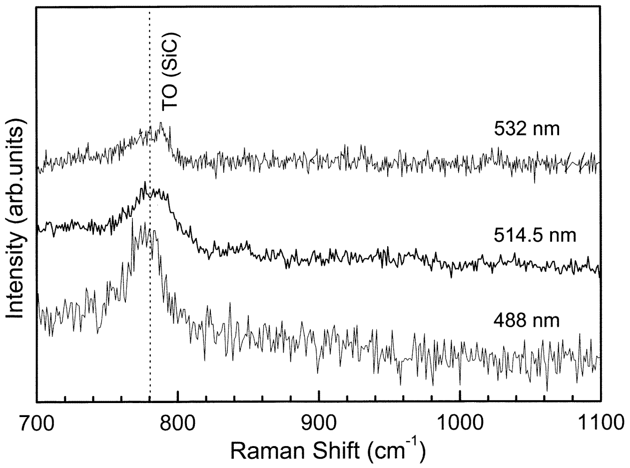

Fig. 6 Raman spectra of SiC nanowires synthesized by procedure (i) (heating the gel containing activated carbon and silica for 7 h at 1360 °C in NH_3).

Si_3N_4 nanowires

The reaction of silica gel with ammonia alone or in the presence of activated carbon in the temperature range 1100–1360 °C did not yield Si_3N_4 nanowires. However, when the reaction of silica gel was carried out with arc-generated multi-walled carbon nanotubes in an NH_3 atmosphere at 1360 °C for 4 h, we obtained a good yield of Si_2N_2O nanowires. The XRD pattern of the nanowires, shown in Fig. 7a, is characteristic of Si_2N_2O with unit cell parameters a = 8.868 Å, b = 5.497 Å, c = 4.854 Å, $\alpha = \beta = \gamma = 90°$ (JCPDS file: 47-1627). The SEM image of the Si_2N_2O nanowires shown in Fig. 8a reveals the diameter of the nanowires to be ~300 nm with lengths of up to tens of microns.

When the reaction of arc-generated multi-walled carbon nanotubes with silica gel was carried out at 1360 °C for longer periods ($\geqslant$7 h), the product contained mainly Si_3N_4 nanowires. The XRD pattern of the sample, shown in Fig. 7b, establishes the nanowires to be predominantly of the hexagonal α-Si_3N_4

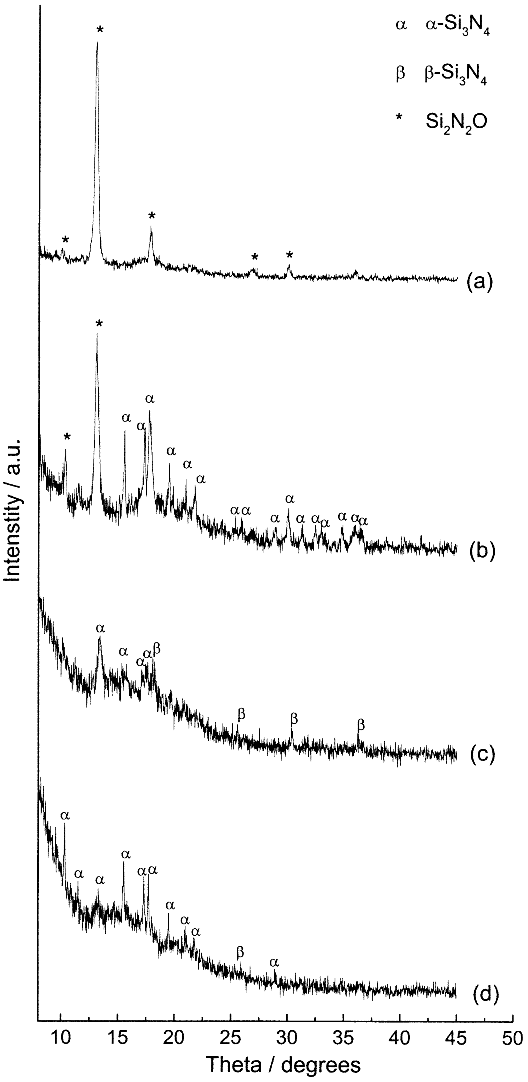

Fig. 7 XRD patterns of the products obtained by the reaction of multi-walled carbon nanotubes with silica gel at 1360 °C in an NH_3 atmosphere: (a) for 4 h, (b) for 7 h, (c) for 4 h in the presence of 0.1 mol% Fe, and (d) for 4 h in the presence of 0.5 mol% Fe. Relative intensities of the α-Si_3N_4 peaks show variations due to the orientational effects.

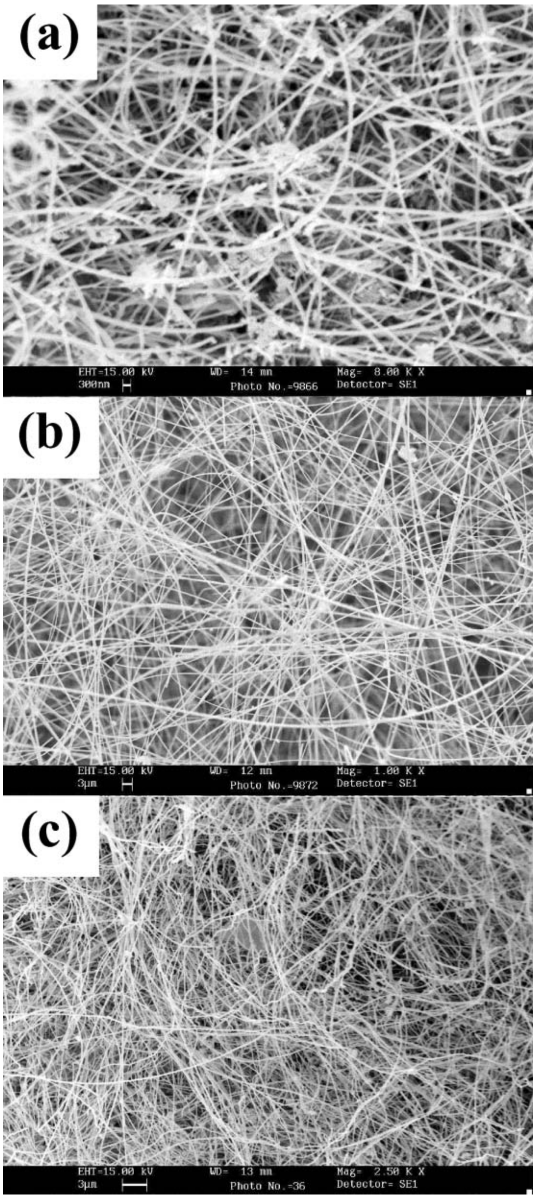

Fig. 8 SEM images of (a) Si_2N_2O nanowires obtained by the reaction of silica with NH_3 in the presence of multi-walled carbon nanotubes with silica at 1360 °C for 4 h, (b) Si_3N_4 nanowires prepared by the reaction of silica with NH_3 in the presence of multi-walled carbon nanotubes with at 1360 °C for 7 h and (c) Si_2N_2O nanowires obtained by the reaction of silica with NH_3 at 1100 °C in the presence of activated carbon and 0.5% Fe catalyst.

phase with unit cell parameters $a = 7.7541$ Å, $c = 5.6217$ Å (JCPDS file: 41-0360), with a minor component of Si_2N_2O. The composition of the final product was dependent on the duration over which the reaction was carried out. Fig. 8b shows an SEM image of these nanowires, which have diameters of between 150 and 175 nm. In the presence of catalytic Fe particles, the reaction of silica gel with carbon nanotubes occurs within 4 h giving a good yield of nanowires of pure Si_3N_4 with no Si_2N_2O. Fig. 7c and d show the XRD patterns of the products obtained in the presence of 0.1% and 0.5% Fe catalysts. While the 0.1% Fe catalyst gives a mixture of the α-phase with the hexagonal β-phase with unit cell parameters $a = 7.6044$ Å, $c = 2.9075$ Å (JCPDS file: 33-1160), the 0.5% Fe catalyst yields almost monophasic α-Si_3N_4 nanowires, as can be seen from Fig. 7d. Fig. 9a shows an SEM image of the Si_3N_4 nanowires obtained with 0.1% catalyst. The diameter is ~400 nm and the length extends to hundreds of microns. The nanowires prepared with the 0.5% Fe catalyst however have larger diameters (~700 nm) as can be seen from Fig. 9b. It should be noted that both the length and diameter of the Si_3N_4 nanowires are generally larger than those of the carbon nanotubes.

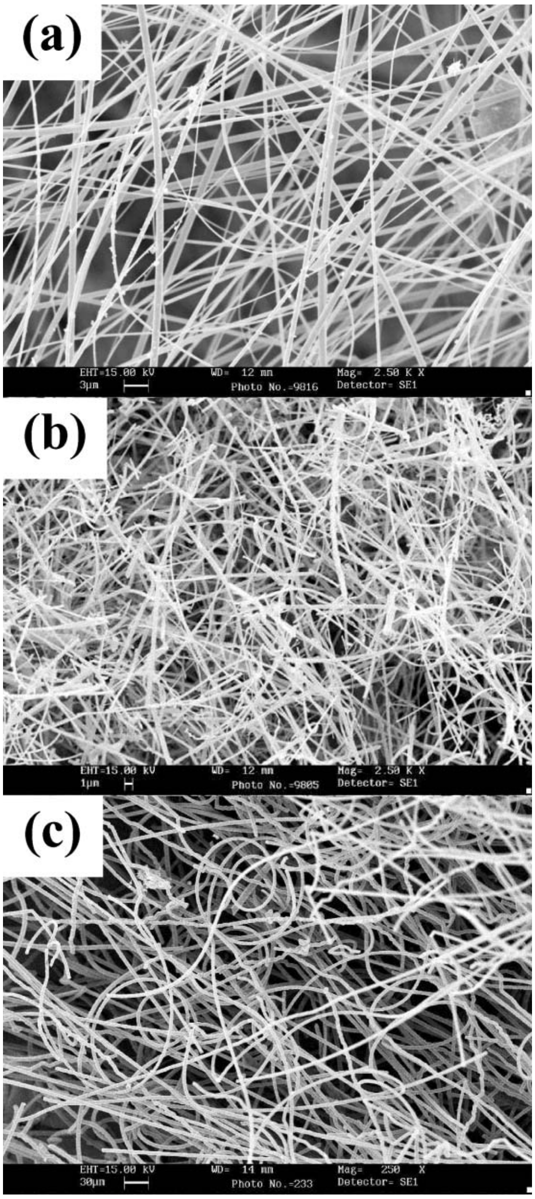

Fig. 9 SEM images of the Si_3N_4 nanowires prepared by the reaction of multi-walled carbon nanotubes with silica at 1360 °C for 4 h in the presence of (a) 0.1% Fe and (b) 0.5% Fe catalysts, respectively. (c) SEM image of the Si_3N_4 nanowires prepared by the reaction of aligned multi-walled carbon nanotubes with silica at 1360 °C for 4 h.

The reaction involved in the formation of Si_3N_4 nanowires in the presence of carbon nanotubes can be represented as,

$$3SiO_2 + 6C + 4NH_3 \rightarrow Si_3N_4 + 6H_2 + 6CO$$

The role of the catalytic iron particles is likely to be in facilitating the removal of oxygen from the silica. The iron oxide formed in such a reaction would readily get reduced back to metal particles in the reducing atmosphere. The formation of Si_2N_2O is given by the reaction

$$2SiO_2 + 3C + 2NH_3 \rightarrow Si_2N_2O + 3CO + 3H_2$$

Carbon nanotubes prepared by precursor pyrolysis get oxidized at a relatively low temperature (~550 °C) compared to the nanotubes prepared by arc evaporation (which oxidize at around 700 °C). We have carried out the reaction of silica and NH_3 with multi-walled carbon nanotubes prepared by the

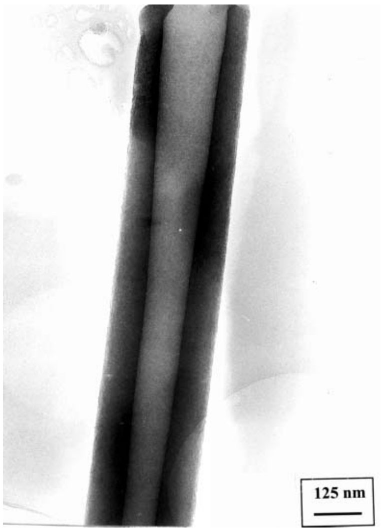

Fig. 10 TEM image of Si_3N_4 nanotubes obtained by the reaction of aligned multi-walled nanotubes with silica gel at 1360 °C.

decomposition of ferrocene. The reaction of these nanotubes with silica gel and NH_3 at 1360 °C yields a mixture of α- and β-Si_3N_4. Fig. 9c shows the SEM image of the product obtained by this reaction. The nanowires have a large diameter (5–7 μm), with lengths of the order of hundreds of microns. Activated carbon has a larger surface area than the nanotubes produced from hydrocarbon pyrolysis and gets oxidized at temperatures as low as 500 °C (compared to 800 °C for graphite). We would therefore expect activated carbon to yield Si_3N_4 by reacting with silica gel in the presence of NH_3 under milder conditions. However, as mentioned earlier, we did not obtain Si_3N_4 nanowires with activated carbon. In the presence of 0.5% Fe, however, the reaction of silica gel with activated carbon at 1200 °C for 8 h yielded α-Si_3N_4. The same reaction at 1360 °C for 4–7 h yields β-SiC nanowires. When the reaction was carried out at 1100 °C for 4 h, it gave Si_2N_2O nanowires. We show an SEM image of these nanowires in Fig. 8c.

Infrared spectra of the Si_3N_4 nanowires show a prominent band around 825 cm^{-1} due to the Si–N stretching vibration. There were no bands due to Si–O stretching.

In the synthesis of Si_3N_4 nanowires using aligned multi-walled nanotubes as the carbon source, we occasionally obtained nanotubes of α-Si_3N_4 along with the nanowires. The outer diameter of the nanotubes is ∼200 nm as seen in the low resolution TEM image in Fig. 10.

Conclusions

The present study establishes that pure β-SiC (cubic) nanowires are easily obtained by reacting silica gel with activated carbon in a reducing atmosphere at 1360 °C. This procedure eliminates the need to use SiO as the starting material. Furthermore, carbon nanotubes are not necessary to produce SiC nanowires. The reaction of activated carbon with silica gel and NH_3 in the presence of catalytic iron particles yields α-Si_3N_4 nanowires at 1200 °C, and Si_2N_2O nanowires at 1100 °C. The reaction of multi-walled carbon nanotubes with silica at 1360 °C in an atmosphere of NH_3 also yields pure Si_3N_4 nanowires, while the same reaction at 1100 °C gives Si_2N_2O nanowires. The presence of catalytic iron particles favours the formation of nanowires of α-Si_3N_4.

Acknowledgement

The authors thank DRDO (India) for support and Dr. Chandrabhas Narayana for help with the Raman spectra.

References

1 S. Iijima, *Nature (London)*, 1991, **345**, 56.
2 (*a*) C. N. R. Rao, B. C. Satishkumar, A. Govindaraj and M. Nath, *ChemPhysChem*, 2001, **2**, 78; (*b*) Y. Feldman, E. Wasserman, D. J. Srolovitch and R. Tenne, *Science*, 1995, **267**, 222; (*c*) M. Nath, A. Govindaraj and C. N. R. Rao, *Adv. Mater.*, 2001, **13**, 283; (*d*) C. N. R. Rao, A. Govindaraj, F. L. Deepak, N. A. Gunari and M. Nath, *Appl. Phys. Lett.*, 2001, **78**, 1853.
3 H. Dai, E. W. Wong, Y. Z. Lu, S. Fan and C. M. Lieber, *Nature (London)*, 1995, **375**, 769.
4 W. Han, S. Fan, Q. Li, W. Liang, B. Gu and D. Yu, *Chem. Phys. Lett.*, 1997, **265**, 374.
5 G. W. Meng, L. D. Zhang, C. M. Mo, S. Y. Zhang, Y. Qin, S. P. Feng and H. J. Li, *J. Mater. Res.*, 1998, **13**, 2533.
6 X. T. Zhou, N. Wang, H. L. Lai, H. Y. Peng, I. Bello, N. B. Wong, C. S. Lee and S. T. Lee, *Appl. Phys. Lett.*, 1999, **74**, 3942.
7 C. H. Liang, G. W. Meng, L. D. Zhang, Y. C. Wu and Z. Cui, *Chem. Phys. Lett.*, 2000, **329**, 323.
8 J. Q. Hu, Q. Y. Lu, K. B. Tang, B. Deng, R. R. Jiang, Y. T. Qian, W. C. Yu, G. E. Zhou, X. M. Liu and J. X. Wu, *J. Phys. Chem. B*, 2000, **104**, 5251.
9 Y. Zhang, N. Wang, R. He, X. Chen and J. Zhu, *Solid State Commun.*, 2001, **118**, 595.
10 Z. Pan, H. L. Lai, F. C. K. Au, X. Duan, W. Zhou, W. Shi, N. Wang, C. S. Lee, N. B. Wong, S. T. Lee and S. Xie, *Adv. Mater.*, 2000, **12**, 1186.
11 W. Han, S. Fan, Q. Li, B. Gu, X. Zhang and D. Yu, *Appl. Phys. Lett.*, 1997, **71**, 2271.
12 M. J. Wang and H. Wada, *J. Mater. Sci.*, 1990, **25**, 1690.
13 X. C. Wu, W. H. Song, B. Zhao, W. D. Huang, M. H. Pu, Y. P. Sun and J. J. Du, *Solid State Commun.*, 2000, **115**, 683.
14 R. Seshadri, A. Govindaraj, H. N. Aiyer, R. Sen, G. N. Subbanna, A. R. Raju and C. N. R. Rao, *Curr. Sci.*, 1994, **66**, 839.
15 M. Nath, B. C. Satishkumar, A. Govindaraj, C. P. Vinod and C. N. R. Rao, *Chem. Phys. Lett.*, 2000, **322**, 333.
16 C. N. R. Rao, R. Sen, B. C. Satishkumar and A. Govindaraj, *Chem. Commun.*, 1998, 1525.
17 X. C. Wu, W. H. Song, W. D. Huang, M. H. Pu, B. Zhao, Y. P. Sun and J. J. Du, *Mater. Res. Bull.*, 2001, **36**, 847 and references therein.
18 E. I. Givargizov, *J. Cryst. Growth*, 1975, **31**, 20.
19 R. S. Wagner and W. C. Ellis, *Appl. Phys. Lett.*, 1964, **4**, 89.
20 A. O. Konstantinov, A. Henry, C. I. Harris and E. Jansén, *Appl. Phys. Lett.*, 1995, **66**, 2250.
21 (*a*) T. Tomita, S. Saito, M. Baba, M. Hundhausen, T. Suemoto and S. Nakashima, *Phys. Rev. B*, 2000, **62**, 12896; (*b*) S. Nakashima, H. Katashama, Y. Nakamura and A. Mitsuishi, *Phys. Rev. B*, 1986, **33**, 5721.
22 D. Olego and M. Cardona, *Phys. Rev. B*, 1982, **25**, 3889.
23 P. Y. Yu and M. Cardona, in *Fundamentals of Semiconductors*, Springer-Verlag, Berlin, 1996, p. 366.