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Aligned ultra-long single-crystalline α -Si₃N₄ nanowires

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Abstract

We report the synthesis of aligned ultra-long single-crystalline α -Si₃N₄ nanowires by pyrolysis of a polymeric precursor without any template. The length of the wires is up to several centimeters, which is significantly longer than that of any Si₃N₄ wires reported previously. Microscopy characterization reveals that the wires are single crystals, with a uniform diameter of \sim 200 nm. Intense visible photoluminescence was observed between 1.3 and 3.7 eV. The wires could be useful in the fabrication of optoelectronic nanodevices and nanocomposites.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Silicon nitride (Si₃N₄) is an important engineering ceramic for a variety of applications due to its excellent thermo-mechanical properties and chemical stability [1]. The material is also a wide-band-gap semiconductor with a band gap of 5.3 eV. Mid-gap levels can be introduced in Si₃N₄ by properly doping in order to tailor its electronic/optic properties [2]. Similar to the group III–V compounds, such as GaN and AlN, Si₃N₄ is an excellent host material and is promising for applications in optoelectronic devices for high temperature and radiation environments.

Recently, one-dimensional Si₃N₄ has attracted extensive attention because of its potential application in nanodevices and nanocomposites. To date, one-dimensional Si₃N₄ in the shapes of wires, rods and belts has been synthesized by methods such as confined reaction [3], combustion [4, 5] sol–gel [6], plasma-assisted hot-filament CVD [7], reduction–nitridation [8], vapor–solid thermal reaction and thermal decomposition/nitridation [9]. In spite of these tremendous efforts, the growth of aligned ultra-long one-dimensional Si₃N₄ nanostructures, which can be used directly as devices [10],

has not been reported. In addition, ultra-long one-dimensional Si₃N₄ could be more useful compared to short wires in some particular applications, such as connections for devices and reinforcements for composites.

In this paper, we report, for the first time, the growth of aligned ultra-long single-crystalline α -Si₃N₄ nanowires. The wires were synthesized via pyrolysis of a polymeric precursor. The aligned wires, which possess perfect single-crystal structures, uniform diameter and a smooth surface, are up to several centimeters in length and perpendicular to the substrate. Photoluminescence measurements reveal that the Si₃N₄ wires exhibit a broad intense light emission in the range 1.3–3.7 eV.

2. Experimental details

Aligned Si₃N₄ nanowires were synthesized via pyrolysis of a polyaluminasilazane precursor. The precursor was obtained by reaction of commercially available polyureamethylvinylsilazane (Cereset, Kion Corporation, USA) and 0.5 wt% aluminum isopropoxide (AIP, Beijing Bei Hua Fine Chemicals Company, Beijing, China). The obtained polyaluminasilazane,

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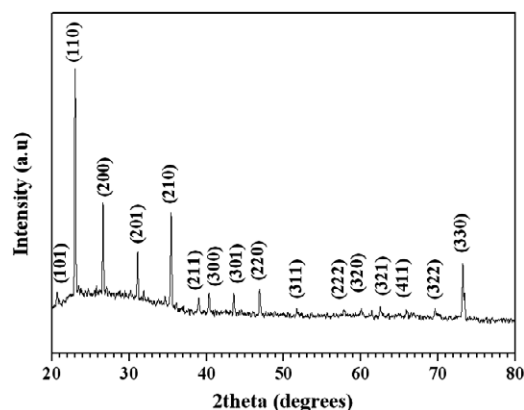


Figure 1. A representative XRD pattern of the as-synthesized α - Si_3N_4 nanowires.

which is liquid as synthesized, was then solidified by heat treatment at 260 °C for 0.5 h in N_2 . The obtained solid was crushed into a fine powder by high-energy ball milling for 24 h, with 3 wt% of Cu (Beijing Bei Hua Fine Chemicals Company, Beijing, China) added as a catalyst. The powder mixture was then loaded into a high-purity alumina crucible with a graphite sheet (Beijing Bei Hua Fine Chemicals Company, Beijing, China) as a cover. The pyrolysis was carried out in a conventional tube furnace with flowing ultra-high purity nitrogen at 0.1 MPa. The powder mixture was heated to 1550 °C at 4 °C min^{-1} and held there for 2 h, followed by furnace cooling. An experiment with similar conditions was also carried out without the Cu additive for comparison.

The products were characterized using field emission scanning electron microscopy (SEM, JSM-6301, JEOL, Tokyo, Japan), x-ray diffraction (XRD, Automated D/Max-RB, Rigaku, Tokyo, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$), and high-resolution transmission electron microscopy (HRTEM, JEOL-2011, JEOL, Tokyo, Japan) equipped with energy-dispersive spectroscopy (EDS). The photoluminescence (PL) spectrum of the wires was recorded using a UV-lamp microzone Raman spectrometer under the excitation of a 325 nm HeCd laser at room temperature.

3. Results and discussion

After removing the sample from the furnace, a large amount of pyrolysis products was found on the graphite sheet which was placed on top of the alumina crucible as a cover. The x-ray diffraction pattern of the products (figure 1) reveals that the products are hexagonal α - Si_3N_4 . All diffraction peaks correspond to hexagonal α - Si_3N_4 , suggesting that there are no other crystalline phases in the products.

Figures 2(a) and (b) are the optical images of the products taken with a digital camera (Canon, IXUS 800IS, Japan). It is seen that the wires are very long, up to several centimeters (figure 2(a); the wires are detached from the graphite sheet), and are well aligned along the direction perpendicular to the graphite sheet (figure 2(b)). To the best of our knowledge, this is the first time that Si_3N_4 wires have been grown so long and in an aligned manner. Figures 2(c)–(f) are typical SEM images of the obtained products under different magnifications. These images reveal that (i) the wires are well aligned (figures 2(c) and (d)); (ii) the wires exhibit a cylindrical shape (figures 2(e) and (f)); (iii) the diameters of the wires are narrowly distributed around 200 nm and within each individual wire the diameter is uniform along its entire length; and (iv) the surfaces of the wires are smooth and clean, without any attached particles. It is estimated that ~ 35 wt% of the raw materials has been converted to the aligned nanowires. The process is highly repeatable.

Further characterization of the morphology and crystalline structure of the synthesized wires was carried out using TEM and HRTEM. Figure 3(a) is a typical TEM image of the Si_3N_4 wires. The energy dispersive spectroscopy (EDS) spectrum (figure 3(b)) obtained from an individual wire reveals that the compositions of the wire are Si and N (the Cu signals in the EDS spectrum come from the TEM grid used to support the sample), confirming that the products are Si_3N_4 . Figure 3(c) is the selected area electron diffraction (SAED) pattern, which is identical over the entire wire, indicating that the wire is a single crystal. Figure 3(d) is the HRTEM image of the wires. The HRTEM image reveals that the wires possess a perfect crystal structure with few structural defects such as dislocations and

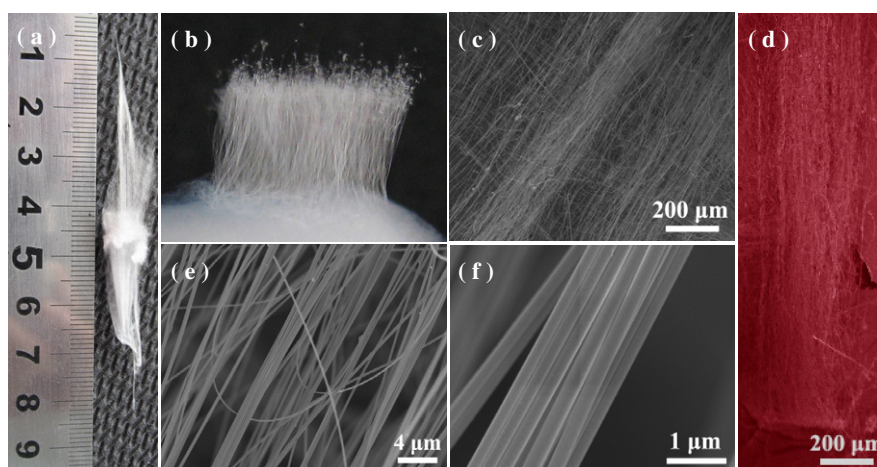


Figure 2. (a) and (b) images of the products recorded using a digital camera. (c)–(f) typical SEM images of the wires under different magnifications.

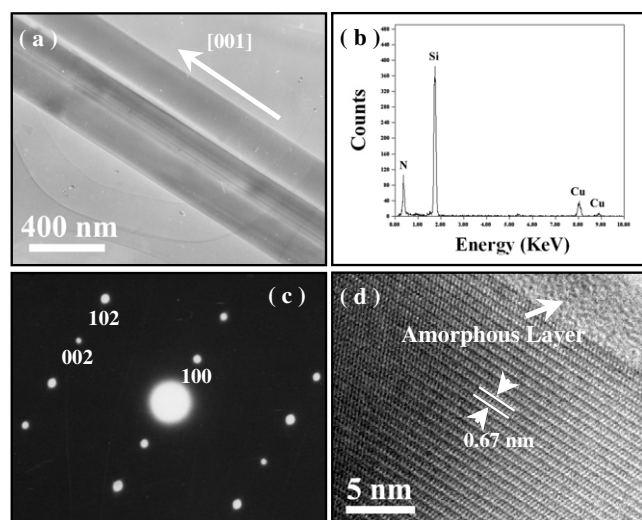


Figure 3. (a) A typical TEM image of the aligned Si_3N_4 nanowires. (b) A typical EDS spectrum obtained from an individual wire recorded under TEM. (c) The SAED pattern recorded from a single wire. (d) An HRTEM image of the Si_3N_4 wires. Both the SAED pattern and the HRTEM image suggest the single-crystalline nature of the as-grown wires with the growth direction along [001].

stacking faults. The surface of the wire possesses a ~ 5 nm amorphous layer, which is amorphous SiO_x , as is often observed in the synthesized Si_3N_4 nanowires [4]. The lattice fringe spacing of 0.67 nm in figures 3(d) agrees well with the spacing of (100) planes of bulk $\alpha\text{-Si}_3\text{N}_4$, where $a = 0.77541$ nm and $c = 0.56217$ nm (JCPDS Card No. 41-0360). Both the HRTEM image and the SAED pattern suggest that the wire is $\alpha\text{-Si}_3\text{N}_4$ phase and that it grew along the [001] direction.

Careful examination of the tips and roots of the wires reveals that there are no catalytic droplets at either position, suggesting that the growth mechanism of the wires is not vapor–liquid–solid (VLS) [11] or solid–liquid–gas–solid (SLGS) [12]. The fact that the wires are only found on the graphite sheet cover and not on the bottom of the crucible suggests that the ultra-long wires reported here grow via a vapor–solid (VS) process [13]. In this process, the precursor was first decomposed into amorphous SiCN containing a small amount of O at a temperature $\sim 1000^\circ\text{C}$ [14]. The amorphous SiCN(O) was further decomposed and released CO and SiO gases (the formation of oxide gases is due to the presence of O) when pyrolyzed at 1550°C [15]. These gaseous phases then reacted with N_2 to form Si_3N_4 wires and CO_2 via reaction (1) [16, 17]. The CO_2 further reacted with the solid C resulting from the decomposition of SiCNs to form CO via reaction (2), which, in turn, was involved in reaction (1). SiC is formed via reactions (3) [17] and (4) [18] when the temperature is higher than $\sim 1480^\circ\text{C}$. However, only Si_3N_4 was obtained in the current paper. This can be attributed to the low $P_{\text{CO}}/P_{\text{SiO}}$ ratio, which can shift the equilibrium boundary between Si_3N_4 and SiC so that Si_3N_4 is stable up to higher temperatures [15]. The length of the wires (figure 2(a)) can be up to ~ 4 cm after being grown for 2 h, which corresponds to a growth rate of ~ 0.33 mm min^{-1} . Such a high growth rate

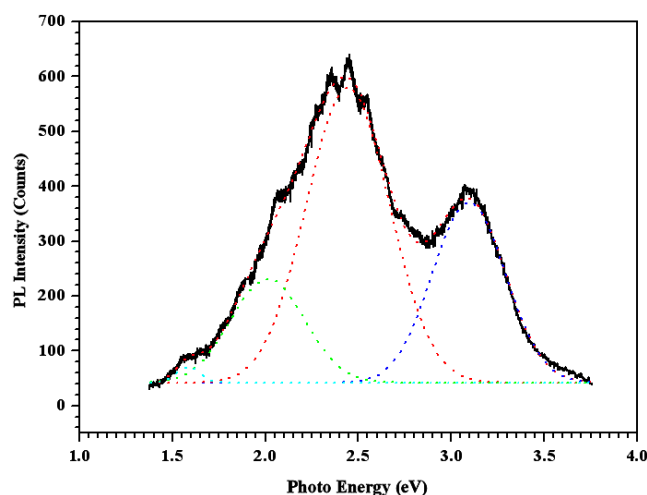
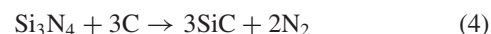
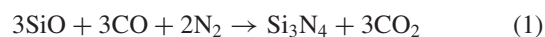


Figure 4. PL spectrum of $\alpha\text{-Si}_3\text{N}_4$ wires under excitation of a 325 nm He–Cd laser at room temperature.

could be due to the high processing temperature (1550°C), which can significantly accelerate the vapor transportation and precipitation processes. This point was confirmed since nanowires synthesized at 1350°C can only grow up to a few millimeters. All possible reactions involved are listed below:



It is worth noting at this stage that the current result is different from those we reported previously. In the previous studies, pyrolysis of polymeric precursors with FeCl_2 as the catalyst resulted in the formation of nanobelts/nanowires, via the solid–liquid–gas–solid (SLGS) mechanism [12]. Two things are different between the current study and the previous ones: (i) Cu instead of FeCl_2 was used as the catalyst, and (ii) a small amount of aluminum isopropoxide was added to the raw materials. To examine the effect of Cu powder, the precursor used here was also pyrolyzed in the same conditions without Cu catalyst. In that case, no Si_3N_4 wire was grown, which suggested that the Cu played a key role in the growth of the ultra-long Si_3N_4 wires. Since no catalyst droplets were observed at either the tips or the roots of the wires, we believe that the Cu likely helped to generate Si-containing vapor during pyrolysis.

The photoluminescence (PL) spectrum of the Si_3N_4 wires was measured using a UV-lamp microzone Raman spectrometer under the excitation of a 325 nm HeCd laser for 200 s at room temperature. The power output of the laser is 35 mW and the beam focus diameter is 2–5 μm . Two strong and broad peaks were observed between 1.3 and 2.9 eV and between 2.9 and 3.7 eV, respectively (figure 4). These broad bands can be further split into four peaks, centered at 1.56, 2.01, 2.45 and 3.1 eV, respectively. Previous studies suggested that there are four types of defect in Si_3N_4 : Si–Si and N–N

bonds, and Si and N dangling bonds [19]. The Si–Si bond forms a bonding orbital and an antibonding orbital, which form an optical band gap of ~ 4.5 eV. The silicon dangling bond forms a state at about mid-gap, and the two nitrogen defect states that give rise to levels within the gap, namely, N_4^+ and N_2^0 , are near the conduction and valence bands, respectively. Based on our previous work [20], the main broad PL peak at 2.45 eV arises from recombination processes at the silicon dangling bonds, similar to those in amorphous silicon nitride. The peak at 3.1 eV has a contribution from the recombination between the Si–Si σ^* level and the N_2^0 level or between the N_4^+ and the intrinsic valence band edge. The PL peaks at 1.56 and 2.01 eV can be attributed to the following recombination processes: between the conduction edge of the intrinsic band and N_4^+ level, and between N_4^+ and N_2^0 states.

4. Conclusion

In summary, we report for the first time the growth of aligned ultra-long α - Si_3N_4 nanowires on a graphite sheet. The wires were synthesized by pyrolysis of polymeric precursors with Cu as the catalyst. The length of the Si_3N_4 wires is up to several centimeters. The wires possess a perfect crystal structure and are uniform in size. Intense visible photoluminescence was observed from the wires, which can be attributed to defects in the α - Si_3N_4 structure. The wires could be useful in the fabrication of optoelectronic nanodevices and nanocomposites.

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