Sulfur-assisted Fabrication of Silicon Nitride Nanorods in Autoclaves at 250 °C

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Silicon nitride nanorods were fabricated from Si, NaN_3, and sulfur powder at 250 °C. XRD patterns show that the final product is mixed α- and β-Si_3N_4. SEM, TEM, and HRTEM images reveal that the product was composed of crystalline Si_3N_4 nanorods with diameters in the range of 70–400 nm and lengths up to 3 μm. It is found that sulfur plays a crucial role in the low-temperature formation of Si_3N_4 powders. Low reaction temperature and cheap raw materials make it possible for large scale synthesis of Si_3N_4 nanomaterials.

Silicon nitride (Si_3N_4) is an important material for many high-temperature engineering applications owing to its interesting mechanical and physical properties.[1] Traditionally, Si_3N_4 powder is prepared by direct nitridation of Si powder,[2] carbothermal nitridation of silica[3] or aluminosilicates,[4] thermal decomposition of polyureasilazane,[5] and silicon diimide synthesis.[6] In early research, a Si–H_2S–NH_3 reaction (SiS_2 is an intermediate) was applied for the synthesis of Si_3N_4.[7] Lately, Si_3N_4 was prepared through combustion synthesis by using Si and NaN_3 as the agents, NH_4Cl as an assistant agent, Ti and C as the igniting agents.[8] Previous work in this field has been focused on the fabrication of 1D Si_3N_4 nanocrystals, such as Si_3N_4 nanorods,[9] nanowires,[10] nanoneedles,[11] and nanobelts.[12] In all of the above processes, either reaction temperature or posttreatment temperature must be above 1200 °C in order to obtain crystalline Si_3N_4.

Recently, Si_3N_4 powders were prepared via solvothermal method: nanocrystalline Si_3N_4 was synthesized from excessive $SiCl_4$ with NaN_3 at 670 °C,[13] or 100–150 °C via increasing the amount of NaN_3,[14] or 200–300 °C via adding metallic Mg.[15] Si_3N_4 nanomaterials were also prepared by using Mg_2Si, $SiCl_4$, or SiO_2 as silicon sources and NH_4Cl, Mg_3N_2, or $NaNH_2$ as nitrogen sources in 450–70 °C, respectively.[16] All these experiments were carried out in sealed autoclaves, which would maintain a certain high pressure to promote the crystallinity of Si_3N_4.[17]

Herein, mixed α- and β-Si_3N_4 nanorods were obtained at 250 °C via a one-step sulfur-assisted route. The yield of Si_3N_4 was 42% (calculated according to the amount of Si) and the α/β phase ratio was 9.[18] The overall favorable reaction could be written as follows:

$$3Si + 6S + 12NaN_3 \xrightarrow{250\,^\circ C,\ 8\,h} Si_3N_4 + 6Na_2S + 16N_2 \quad (1)$$

All the chemicals were obtained from Shanghai Chemical Co. and were directly used. In a typical experimental procedure, Si powder (200 mesh, 0.02 mol), NaN_3 (0.08 mol), and sublimed sulfur (0.04 mol) were mixed and put into a 20-mL stainless-steel autoclave. The autoclave was sealed, then heated from room temperature to 250 °C at a rate of 10 °C min^{-1} and maintained at 250 °C for 8 h in a furnace. After it was allowed to cool to room temperature, the raw product was washed with dilute hydrochloric acid, dilute hydrofluoric acid and distilled water and finally dried in a vacuum oven at 60 °C for 6 h. The final product was characterized by X-ray powder diffractmetery (XRD; Bruker D8 with Cu Kα radiation), scanning electron microscopy (SEM; JSM-6700F) and high-resolution transmission electron microscopy (HRTEM; JEOL 2100; 200 kV).

XRD pattern analysis is used to determine the phases of the samples (Figure 1A). All the peaks that marked with "α" can be indexed to α-Si_3N_4 with lattice constant: $a = 7.7464$ Å, $c = 5.6166$ Å, the values agree well with that of the α-Si_3N_4 (JCPDS Card No. 41-0360); while those peaks that marked with "β" can be attributed to β-Si_3N_4 with lattice parameters: $a = 7.5965$ Å, $c = 2.9031$ Å, consistent with that of the β-Si_3N_4 (JCPDS Card No. 33-1160). No evidence of cubic Si_3N_4 or impurities is observed in this pattern.

The SEM image (Figure 1B) indicates that the product is mainly composed of one-dimensional nanorods with diameters in the range of 70–400 nm and lengths up to 3 μm. The magnified SEM images (Figures 1C and 1D) confirm the product composed of nanorods. Figure 1D shows that a typical SEM image of a nanorod with a hexagonal prism morphology in the body and sharp ends in both of its tips, as indicated by the white line.

Figure 2A depicts a typical TEM image of a single α-Si_3N_4 nanorod with a diameter of 70 nm. HRTEM image (inset of Figure 2A) reveals that the clearly resolved interfringe distances

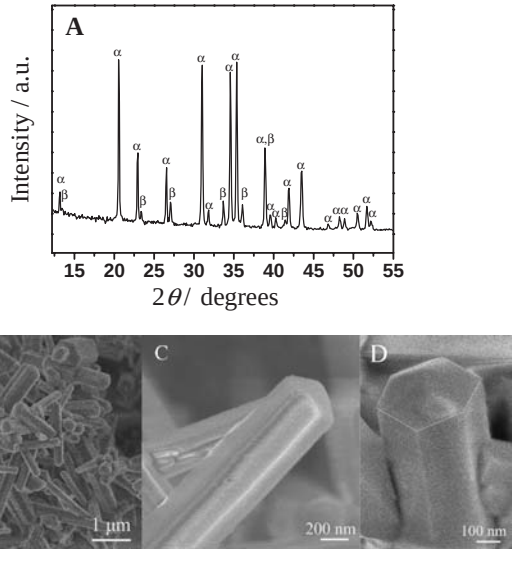

Figure 1. (A) A typical XRD pattern of the product obtained at 250 °C for 8 h, and (B) its SEM image. (C and D) Magnified SEM images of individual Si_3N_4 nanorods.

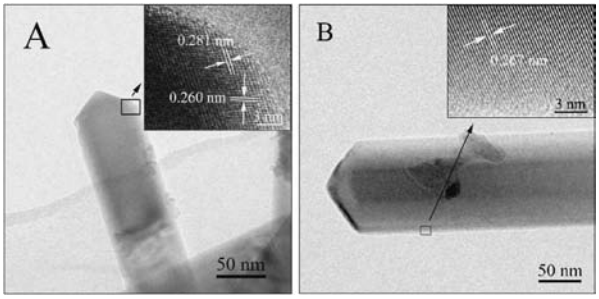

Figure 2. (A and B) Typical TEM images and HRTEM images (inset) of a single α-Si_3N_4 nanorod and a single β-Si_3N_4 nanorod, respectively.

were 0.260 and 0.281 nm, which are coincide with the (102) and (002) lattice spacings of α-Si_3N_4 (JCPDS Card No. 41-0360), respectively. Figure 2B shows a typical TEM image of a single β-Si_3N_4 nanorod with a diameter of 110 nm. HRTEM image (inset in Figure 2B) shows that the average interplanar distance is 0.267 nm, which is consistent with (101) planes of β-Si_3N_4 (JCPDS Card No. 33-1160).

We call this approach "sulfur-assisted," because sulfur used in this experiment plays a crucial role in the formation of Si_3N_4 nanorods at relative low temperature. In the absence of sulfur, no Si_3N_4 was obtained even if the temperature was increased to 600 °C. Mixed phases of α-Si_3N_4 and β-Si_3N_4 powders were obtained when the molar ratio of $Si/S/NaN_3$ was 1:2:4. Decreased sulfur amount resulted in the appearance of $NaSi_2N_3$, while excessive sulfur was not favorable for the formation of Si_3N_4. It is considered that SiS_2 might be an intermediate during the formation of Si_3N_4, although it was not detected in the whole process. The calculated thermodynamic factor values might partly support this assumption: the reaction (eq 1) is thermodynamically spontaneous ($\Delta G = -779$ kcal/mol) and exothermic ($\Delta H = -954$ kcal/mol);[19] while the values calculated for eq 2 (without sulfur) are $\Delta G = -157$ kcal/mol; $\Delta H = -243$ kcal/mol, which are smaller than those of the calculated values for eq 1. It is obvious that the reaction in eq 1 is more prone to occur than that in eq 2.

$$3Si + 4NaN_3 \rightarrow Si_3N_4 + 4Na + 4N_2 \quad (2)$$

It was also found that Si_3N_4 could not be obtained if the reaction temperature was below 250 °C or the reaction time was shorter than 4 h at 250 °C. Moreover, Si_3N_4 could be obtained within shorter time if the reaction temperature was elevated further, for instance, crystalline Si_3N_4 was formed at 300 °C for 30 min and the α/β phase ratio would fall and stay at 5. In this experiment, NaN_3 was used as the nitrogen source in the mean time to sustain a high pressure (23.2 MPa, calculated by the ideal gas law). However, the excess molar ratio of NaN_3 to sulfur (2.5, 2.75, or 3) led to the preferenercial formation of $NaSi_2N_3$ rather than Si_3N_4.

The exothermic reaction between NaN_3 and S would occur at 250 °C. With the increasing temperature, NaN_3 spontaneously decomposed to produce Na and N_2 and released lots of energy,[20] which would support the transformation from Si to silicon sulfides (such as SiS_2).[21] Si_3N_4 might be formed via a chemical metathesis reactions from a $SiS_2/N_2/Na$ mixture system. However, the exact formation mechanism of Si_3N_4 nanorods is not very clear, which might be similar to Tang's model.[13]

In summary, silicon nitride nanorods were prepared from Si powder and NaN_3 with the assistance of sulfur at 250 °C under an estimated pressure of 23.2 MPa. The as prepared Si_3N_4 nanorods are composed of α- and β-phases and well crystallined. The sulfur-assisted technique might be extended to prepare other nitrides.

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