

Facile Synthesis of Si₃N₄ Nanocrystals Via an Organic–Inorganic Reaction Route

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Silicon nitride (Si₃N₄) nanocrystals were synthesized at about 250°C by a simple organic–inorganic reaction between CH₃SiCl₃ and NaN₃. The yield of Si₃N₄ is no < 70 wt% based on the amount of precursor CH₃SiCl₃ used in the reaction and TGA analysis. X-ray diffraction indicates the formation of a mixture of α- and β-Si₃N₄. Particles with size from 40 to 100 nm are dominant in the products examined by transmission electron microscopy. X-ray photoelectron spectroscopy gives an atomic ratio of Si:N around 0.75:1. The formation of nanocrystalline Si₃N₄ during the organic–inorganic reaction goes through an intermediate product of NaSi₂N₃, which is important for understanding the reaction mechanism.

I. Introduction

THE high mechanical properties, thermal shock resistance, wear resistance, corrosion resistance, chemical stability, and excellent creep resistance of silicon nitride (Si₃N₄) make it an attractive material in many fields, especially for high-temperature engineering applications.^{1–3} The excellent performances and wide applications stimulate the exploitation in synthesis methods, and a lot of methods have so far been developed to prepare Si₃N₄, such as direct nitridation,^{4–6} carbothermal reduction,^{7,8} vapor phase reaction,⁹ thermal decomposition,^{10–12} silicon diimide pyrolysis,¹³ combustion synthesis,^{14,15} and solvothermal synthesis.¹⁶

Very recently, several new routes have been proposed to prepare Si₃N₄. Zhu *et al.*¹⁷ fabricated Si₃N₄ nanorods through nitridation of silica using NaNH₂ as a reduction–nitridation reagent at 700°C. Yang *et al.*¹⁸ synthesized crystalline Si₃N₄ via a one-step sulfur-assisted route. Crystalline Si₃N₄ could also be prepared by the metathesis reaction between SiCl₄ and NaN₃ at temperatures from 150° to 450°C.¹⁹ However, owing to the violent reaction between SiCl₄ and NaN₃, it is quite difficult to control the reaction rate, and the reaction mechanism cannot be understood throughout.

In this research, an organosilicon compound of CH₃SiCl₃ was used to react with NaN₃. It is interesting to detect an intermediate product of NaSi₂N₃ at a low reaction temperature during the mild reaction between CH₃SiCl₃ and NaN₃, which is of great

significance for insight into the reaction mechanism not only for the reactions reported here but also for the reaction between SiCl₄ and NaN₃.

II. Experimental Procedure

The analytically pure grade CH₃SiCl₃ and NaN₃ were used as starting materials in this work. A series of experiments were conducted for better understanding the reaction mechanism. These include the reactions at 200°, 250°, 300°, 400°, and 550°C for 0, 1, 2, and 5 h, respectively.

In a typical procedure, 4.32 mL (0.037 mol) analytical pure-grade methyltrichlorosilane (CH₃SiCl₃, SIGMA-ALDRICH, Inc., St. Louis, MO) and 7.5 g (0.115 mol) sodium azide (NaN₃, from Tianjin Chemical Reagent Corp., Tianjin, China) were put into a stainless steel autoclave with a capacity of 30 mL. All the manipulations were carried out in a protecting N₂ gas flow. After the autoclave was sealed, it was heated in an electric oven to 250°C, and held at this temperature for 2 h. And then the autoclave was allowed to cool to room temperature in the furnace. The product was collected and washed several times with diethyl ether anhydrous ((CH₃CH₂)₂O, from Laiyang Chemical Reagent Corp., Laiyang, China), and deionized water successively to remove CH₃SiCl₃, NaN₃ remained, and by-product NaCl. The final product was dried at 70°C for 6 h and gray-black powder was ultimately obtained.

X-ray powder diffraction (XRD) patterns were obtained on a Rigaku Dmax-rc diffractometer (Tokyo, Japan) with Ni-filtered CuKα radiation (V = 50 kV, I = 80 mA) at a scanning rate of 4°min⁻¹. The morphology of Si₃N₄ nanocrystals was examined using a Hitachi H-800 transmission electron microscope (TEM; Tokyo, Japan) at an accelerating voltage of 150 kV. The chemical composition of the product was analyzed by X-ray photoelectron spectroscopy, the data were recorded on a KARTOS XSAM800 X-ray photoelectron spectrometer (XPS; Kratos Analytical Ltd., Manchester, U.K.), AlKα (hν = 1486.6 eV) radiation was used as the excitation source with an anode voltage of 12 kV and an emission current of 10 mA. The resulting yield of Si₃N₄ was determined based on the amount of precursor CH₃SiCl₃ used in the reactions and with the help of DTA–TGA analysis in a SDT Q600 (TA Instruments Ltd., New Castle, Delaware) thermal-microbalance apparatus at a heating rate of 10°C/min in air atmosphere.

III. Results and Discussion

From series of experiments, no reactions occur at temperatures below 200°C. When holding at 250°C for <2 h, the reaction is incomplete with a low yield of product. However, higher yields

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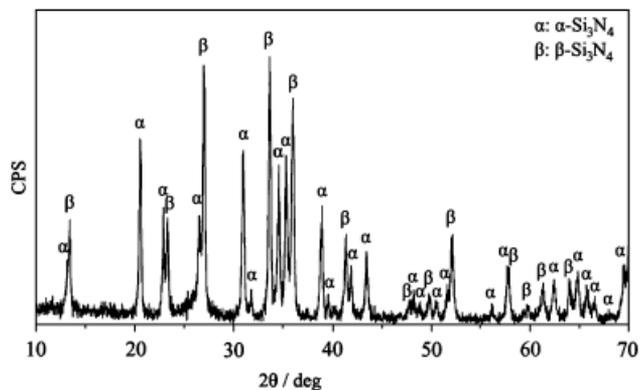


Fig. 1. X-ray powder diffraction pattern of the resulting product obtained from the reaction at 250°C for 2 h.

can be achieved either with holding for more than 2 h at 250°C or at temperatures above 300°C with any durations. Figure 1 is the XRD pattern of the resulting product obtained from the reaction at 250°C for 2 h. The peaks marked with α can be identified as α - Si_3N_4 with lattice parameters $a = 7.770$ and $c = 5.631$ Å, which are in good agreement with those in JCPDS 9-0250. The other peaks marked with β can be indexed to β - Si_3N_4 with lattice constants $a = 7.624$ and $c = 2.911$ Å, which match well with those in JCPDS 33-1160. So the resulting product is a mixture of α - and β - Si_3N_4 . The intense diffractions in the pattern imply the high crystallinity of both α - and β - Si_3N_4 . The XRD patterns for the products obtained from the reactions at 300°, 400°, and 550°C are very similar to that in Fig. 1.

Figure 2 shows the representative TEM image of the products obtained from the reaction at 250°C for 5 h. The products are comprised dominantly of particles with size from 40 to 100 nm, which are Si_3N_4 phases. A small amount of flakes may also be observed in the products. However, the flakes can't be observed in the sample after TGA analysis. Taking into account of the following XPS and TGA analysis, the flakes are carbon. So the carbon in the resulting product from the reaction of CH_3SiCl_3 with NaN_3 can be simply removed by heating the product to about 700°C. By comparison with the products obtained from the reactions at 250°C for 2 h and above 300°C for any duration, it was found that the morphology and size is independent on the synthesis temperature and holding time.

XPS was used to derive overall compositional information of the obtained products. Figure 3 gives the XPS spectra of the

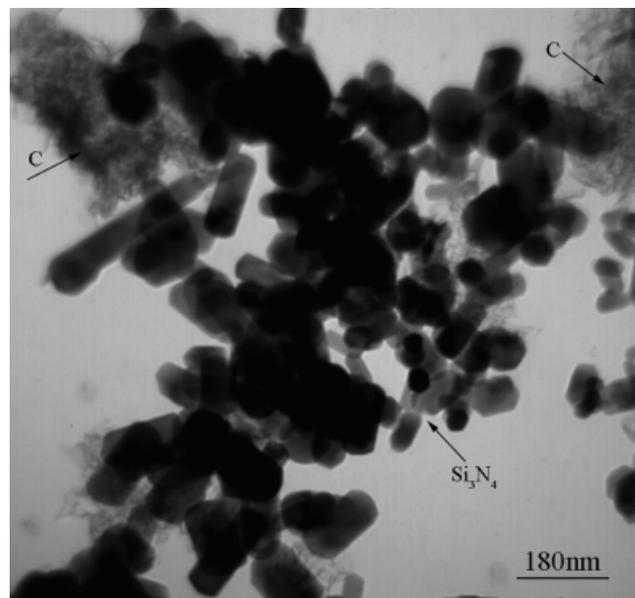


Fig. 2. Transmission electron microscopic images of the products obtained from the reaction at 250°C for 5 h.

product, indicating the presence of Si, N, O, and C elements, while no chlorine can be detected. The oxygen is due to the absorption of CO_2 , H_2O , and O_2 on the surface of the samples and the slight surface oxidation. The binding energy of $\text{Si}2p$ and $\text{N}1s$ are 101.79 and 397.64 eV, which agree well with those of Si_3N_4 (101.3 and 397.7 eV, respectively).²⁰ The quantification of the peaks gives a Si:N ratio around 0.75, confirming the formation of Si_3N_4 .

Figure 4 shows the IR spectrum of the product obtained from the reaction at 250°C for 2 h. According to literature,²¹ the absorption band around 950 cm^{-1} is a fundamental vibration due to the Si–N–Si antisymmetrical stretching mode and the absorption at 494 cm^{-1} is the symmetrical stretching mode for the Si–N–Si molecular group. The bands at 968, 939, 904, 893, 869, 852, 684, 494, 461, and 406 cm^{-1} are the distinct absorptions of α - Si_3N_4 , whereas those at 578, 443, and 376 cm^{-1} are the strong absorptions of β - Si_3N_4 . The superposed IR spectrum of α - and β - Si_3N_4 further confirms the formation of their mixture. The peak at 1165 cm^{-1} is the stretching mode of Si–O bonds owing to the slight surface oxidation. The IR spectra of the products obtained from other experiments are similar to that in Fig. 4.

The actual yield of Si_3N_4 can be determined with the help of TGA analysis. Based on the amount of precursor CH_3SiCl_3 used in the reaction and the TGA analysis, the yield of Si_3N_4 is no < 70 wt% at 250°C for more than 2 h or above 300 for any durations. According to the conservation of mass, the weight percent of carbon in the resulting product was 20.4% if the element of C in CH_3SiCl_3 translated into carbon completely. However, the weight losses of the products obtained at all reaction temperatures are lower than 20.4% during the TGA analysis, demonstrating that there are other products during the reaction between CH_3SiCl_3 and NaN_3 besides Si_3N_4 , carbon, and NaCl.

The formation mechanism of the nanocrystalline Si_3N_4 was investigated. In the course of heating, CH_3SiCl_3 vaporizes above its boiling point ($\text{bp} = 66^\circ\text{C}$) and gas–solid interfaces form between CH_3SiCl_3 and NaN_3 particles. However, when the temperature is lower than 200°C, no reaction takes place between CH_3SiCl_3 and NaN_3 . The reactions occur when the temperature is above 250°C. Figure 5 shows the XRD pattern of the product obtained from the reaction at 250°C without holding, which is greatly different from that in Fig. 1. Besides a small amount of α - and β - Si_3N_4 , the other strong peaks can be indexed to NaSi_2N_3 according to JCPDS 48-1431, indicating the formation of an intermediate product of NaSi_2N_3 when the reactions are incomplete.

Figure 6 shows the typical TEM image of the product obtained from the reaction at 250°C without holding and the selected area electron diffraction (SAED) pattern. Besides a small quantity of rods and particles, plates are the dominant morphology, which can be determined to be NaSi_2N_3 by calculating the interplanar spacings and the angle of the corresponding SAED pattern.

TGA and DTA experiment was conducted to determine the role of NaSi_2N_3 during the reaction. Figure 7 is the DTA curve of the product obtained at 250°C without holding, from which no reaction is revealed, indicating that NaSi_2N_3 is stable below 800°C and cannot transform into Si_3N_4 .

As stated above, NaSi_2N_3 is the intermediate product during synthesizing Si_3N_4 via the reaction of CH_3SiCl_3 and NaN_3 . When the hold time is more than 2 h at 250°C, or the reaction temperature is higher than 300°C with or without holding, no NaSi_2N_3 can be detected, demonstrating that further reaction may occur between NaSi_2N_3 and the reactants to form Si_3N_4 . It can be noted that the reaction temperature of 250°C is much lower than the decomposition temperature of NaN_3 (365°C),²² so it is reasonable to believe that a metathesis reaction may occur between CH_3SiCl_3 and NaN_3 , leading to the generation of the intermediate product of NaSi_2N_3 and byproduct NaCl. The methyl radicals ($-\text{CH}_3$) generated during the reaction may bind by twos into gaseous ethane (CH_3CH_3) molecules. Prolonging the hold time at 250°C, NaSi_2N_3 reacts continuously with

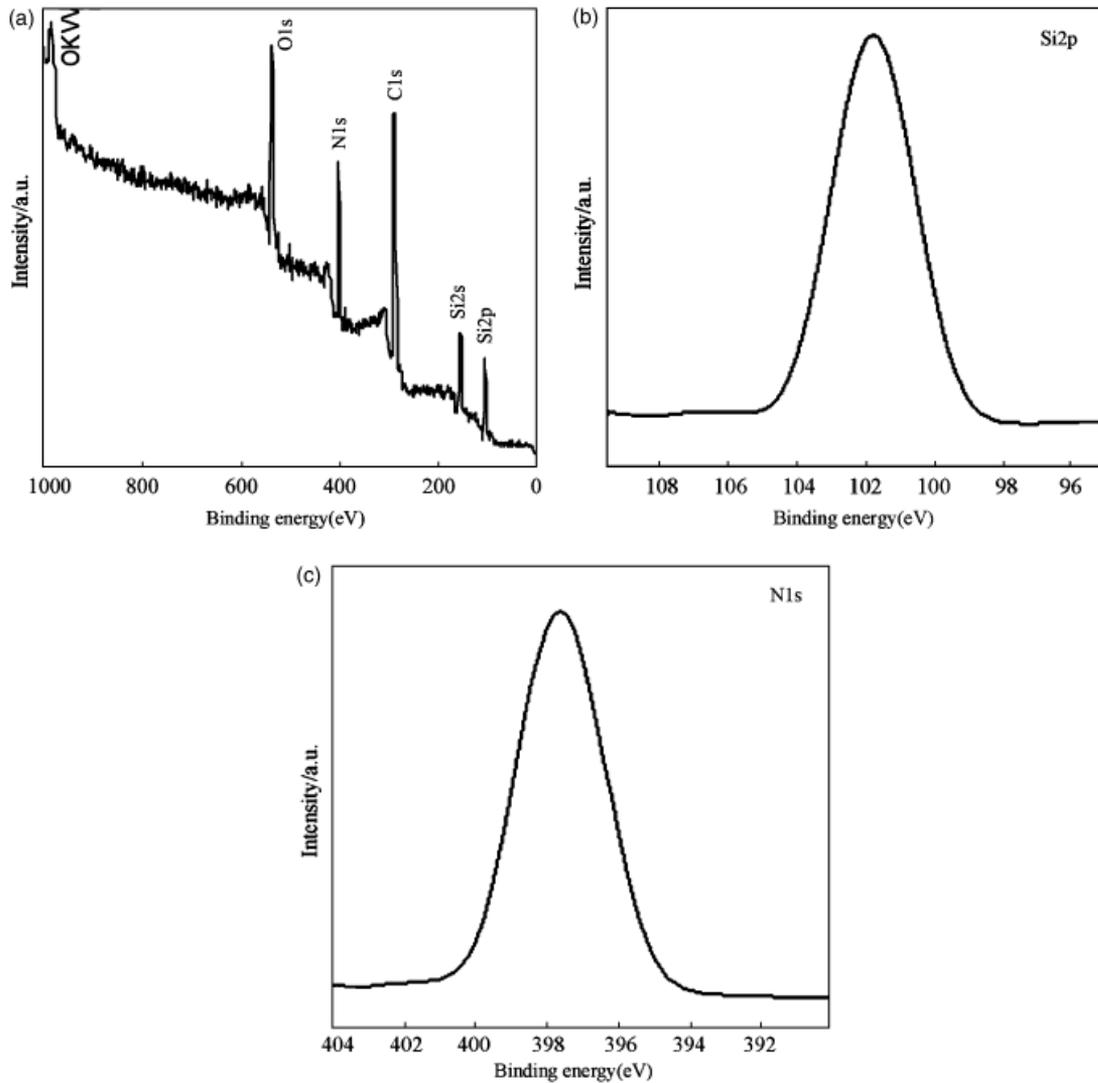


Fig. 3. X-ray photoelectron spectrometer (XPS) spectra of the product obtained from the reaction at 250°C for 2 h. (a) The overall XPS (b) Si2p, and (c) N1s.

CH_3SiCl_3 and NaN_3 to form Si_3N_4 . The reaction temperatures higher than 300°C promote the reactions involved, giving rise to the rapid formation of Si_3N_4 within a very short duration. So the reactions between CH_3SiCl_3 and NaN_3 can be divided into two steps as follows:

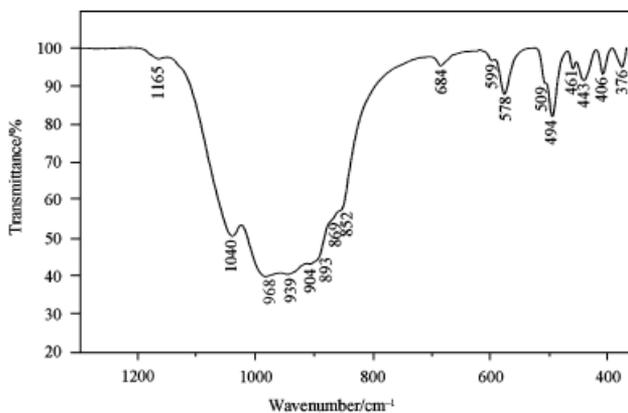
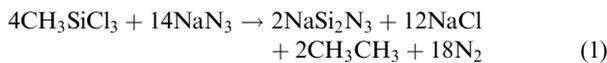
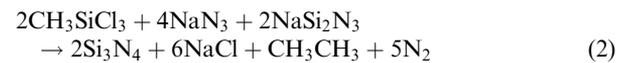


Fig. 4. Infrared spectra of the product obtained from the reaction at 250°C for 2 h.



The energy resulted from the formation of NaCl facilitates not only the large-scale nucleation of Si_3N_4 within a short duration, but also the carbonization of partial ethane into carbon, so nanocrystalline Si_3N_4 containing some carbon was ultimately achieved. The generation of gaseous ethane is similar to the result in literature that the dechlorination of CH_3SiCl_3 at 900°C in ammonia results in the gaseous reaction product of CH_4 and H_2 .⁹

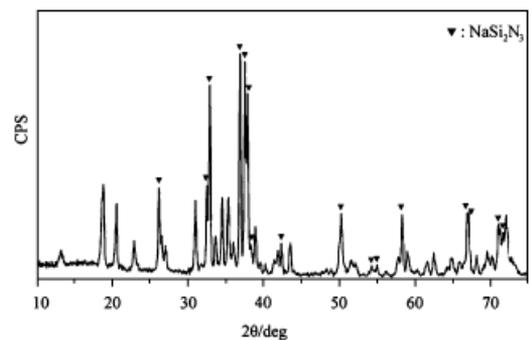


Fig. 5. X-ray powder diffraction pattern of the resulting product obtained from the reaction at 250°C without holding.

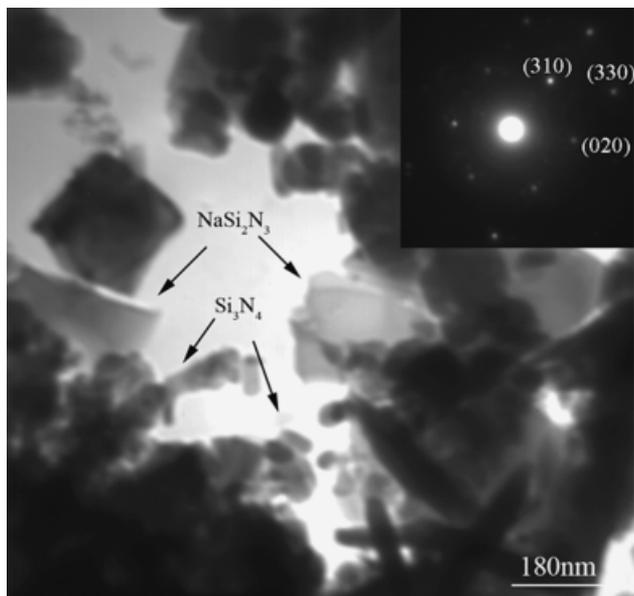


Fig. 6. Transmission electron microscopic image of the products obtained from the reaction at 250°C without holding, and the SAED pattern of the plates.

IV. Conclusions

A mixture of α - and β - Si_3N_4 with high crystallinity can be prepared by the reaction of CH_3SiCl_3 and NaN_3 at a temperature as low as 250°C. The resultant is composed dominantly of Si_3N_4 particles with an average size of 80 nm, and a small amount of carbon. The carbon can be removed simply by heating the product to about 700°C in air atmosphere. The low reaction temperature provides some unique advantages such as energy

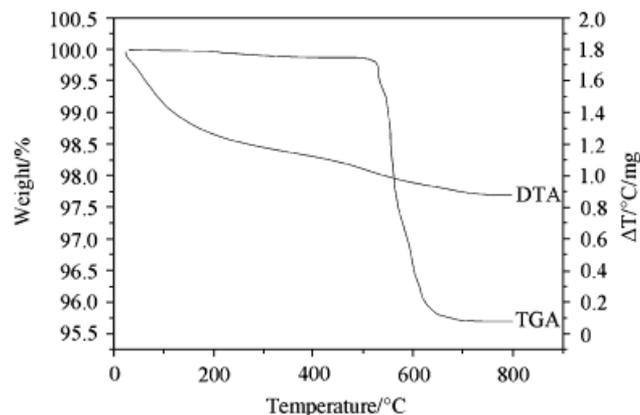


Fig. 7. TGA and DTA curve of the product obtained at 250°C without holding.

saving, easily controlling, and high yield of Si_3N_4 . We are exploring whether the similar organic-inorganic reactions can be used to rapidly synthesize other inorganic materials at low temperatures.

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