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Chemical Synthesis of Aluminum Nitride Nanorods in an Autoclave at 200 °C

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Hexagonal phase aluminum nitride (AlN) nanorods have been prepared via a chemical reaction from Al, I_2, and NaN_3 in an autoclave at 200 °C. Electron microscopy investigations show that the nanorods have diameters ranging from 50 to 100 nm and lengths up to several micrometers. Thermal gravimetric analysis reveals that the sample has good thermal stability below 600 °C, and room-temperature photoluminescence (PL) of the sample shows a strong emission peak centered at 397 nm.

The wide band gap semiconductor aluminum nitride (AlN) has attractive properties including relatively low dielectric constant (8.5), high thermal conductivity ($320\,W\,m^{-1}\,K^{-1}$), low thermal expansion coefficient (ca. $4 \times 10^{-6}\,K^{-1}$) that matches well with that of silicon, and high mechanical strength.[1] It has various applications, such as electronics substrates and packaging for electronic components,[2] UV photo detectors, pressure sensors, thermal radiation sensors, and field-effect transistors.[3]

A conventional synthesis technique for AlN powders is the carbo-thermal reduction of alumina at temperatures around 1700–1900 °C[4] or direct nitridation of Al in N_2 or NH_3 atmosphere at temperatures above 1150 °C.[5] AlN powders also have been prepared by self-propagating high-temperature synthetic methods[6] or by the reaction of ammonia with aluminum chloride vapor in a flow-tube reactor at 720–920 °C.[7]

Preparation of AlN nanocrystals in an autoclave or steel tube has been reported to be an effective route at low temperatures. For example, AlN spherical nanoparticles with an average size of 6 nm were obtained by using Al and NH_4Cl as reactants at 580 °C[8] or AlN nanocrystals with a grain size less than 10 nm prepared at 500 °C,[9] AlN nanowhiskers with diameters from 10 to 80 nm and length up to several micrometers were synthesized by directly reacting $AlCl_3$ with NaN_3 in a solvent-free system at 450 °C.[10]

Here, we report a simple route for the synthesis of hexagonal AlN nanorods by using Al, I_2, and NaN_3 at 200 °C for 48 h in an autoclave. The overall reaction could be formulated as follows:

$$Al + 3NaN_3 + 3/2I_2 \rightarrow AlN + 3NaI + 4N_2 \qquad (1)$$

In a typical process, Al powder (200 mesh, 0.4 g), NaN_3 (4 g), and I_2 (5.7 g) were mixed and loaded into a stainless-steel autoclave with a capacity of about 20 mL. The autoclave was sealed, kept at 200 °C for 48 h, and then cooled to room temperature. After washed with absolute ethanol, 1.0 M HCl, distilled water and drying under vacuum at 70 °C for 5 h, a grey-white product was collected.

The final product was characterized by X-ray powder diffraction (XRD; Bruker D8 with Cu Kα radiation), transmission electron microscopy (TEM; Hitachi H-7000; 100 kV), high-resolution transmission electron microscopy (HRTEM; JEOL 2100; 200 kV), and scanning electron microscopy (SEM; JSM-6700). Thermal gravimetric analysis (TGA) was taken on a SDT Q600 V8.0 Build 95 thermal analyzer apparatus. Photoluminescence (PL) spectrum measurement was performed on an Edinburgh instruments FLS920 fluorescence spectrophotometer with a Xe lamp at room temperature.

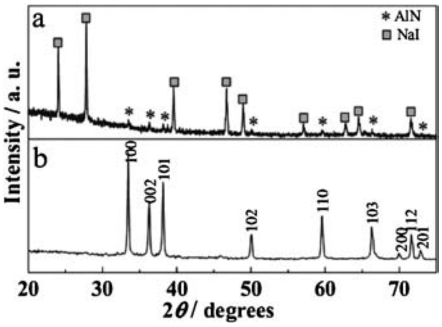

Figure 1. Typical XRD patterns of the product obtained at 200 °C for 48 h: (a) before treatment, (b) after treatment.

Figure 1a shows the XRD pattern of the product without any treatment, in which NaI was observed besides the hexagonal AlN. Figure 1b shows the XRD pattern of the same sample after acid treatment. The sharp peaks with strong diffraction intensity in this pattern can be indexed to hexagonal AlN, with lattice constants $a = 3.098$ and $c = 4.963$ Å, which are near the reported values ($a = 3.111$, $c = 4.979$ Å, JCPDS, card No. 25-1133).

The morphology of the final product was determined by TEM and FESEM images (Figures 2a and 2b). It can be seen that the sample mainly consists of nanorods with diameters ranging from 50 to 100 nm and lengths up to several micrometers. The HRTEM image (Figure 2c) of a part of a single AlN nanorod reveals that the interplanar spacing of the two adjacent fringes is about 0.263 nm, which corresponds to the (100) spacing of hexagonal AlN (JCPDS card no. 25-1133). The corresponding SAED patterns reveal that the nanorods are single crystals. In addition, the ⟨100⟩ direction is parallel to the axis of the nanorod indicating their growth direction was along the ⟨100⟩ direction. EDS spectrum (inset in Figure 2b) of the AlN nanorods indicates that the final product is composed of Al and N elements, with negligible oxygen content (ca. 2 wt % analyzed by EDS), indicating their slight surface oxidation. The appearance of Cu signal is from the TEM grid.

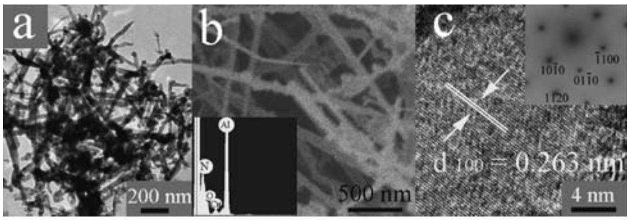

Figure 2. (a) Typical TEM, (b) FESEM (inset: EDS analysis), and (c) HRTEM (inset: SAED) images of the nanorods.

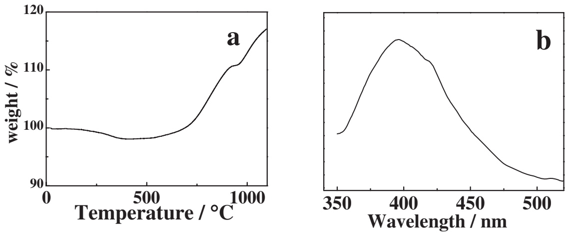

Figure 3. (a) TGA analysis of the sample, carried out under a stream of air, with a heating rate of 10 °C min^{-1}. (b) Room-temperature photoluminescence spectrum of the sample.

In order to study the thermal stability of the sample, TGA was carried out in the temperature range of 30–1100 °C (Figure 3a). Initially, it was observed that there is a slight weight loss (ca. 2%), which might be attributed to the loss of water absorbed on the surface of the sample. An obvious weight gain was observed above 600 °C, suggesting that AlN has been oxidized in air and that a protective oxide layer might form on their surfaces.[11] The room-temperature photoluminescence (PL) spectrum of the sample is shown in Figure 3b, which was obtained with an excitation wavelength of 330 nm. As the energy of the exciting light is below the band gap (6.2 eV) of AlN, the near-band-edge emission cannot be excited in this study.[12] It was clearly observed that a strong emission peak centered at about 397 nm. This result is in good agreement with the previous reports.[13,14] In our experiment, the appearance of the broad blue band could be attributable to the existence of oxygen impurities which has been detected by EDS analysis.

In the experimental process, I_2 was found to be crucial for the formation of the AlN nanomaterials at a relatively low temperature. In the absence of I_2, no AlN products are produced even if the temperature is elevated up to 650 °C in an autoclave.[10] AlN powders were obtained when the molar ratio of $Al/I_2/NaN_3$ was 1:3:4. Decrease in the amount of I_2 or NaN_3 lowers the yield of AlN nanomaterials. In addition, AlI_3 can be obtained if appropriate amounts of Al and I_2 powders are put into an autoclave and maintained at 200 °C for 16 h. It is supposed that an intermediate of AlI_3 occurred during the formation of AlN, although it has not been currently proven by the XRD pattern (Figure 1a).

The reaction between I_2 and NaN_3 was found to occur at 200 °C, producing NaI, N_2, and releasing lots of energy. Due to the higher activity of newly formed AlI_3, crystalline AlN may form via a chemical metathesis reaction from $AlI_3/Na/N_2$ under a high pressure, which is similar to the reaction between $AlCl_3$ and NaN_3.[10] The calculated thermodynamic factor values might partly support this assumption: the reaction of eq 1 is thermodynamically spontaneous and highly exothermic at 200 °C with the calculated values of $\Delta G = -1514\,\text{kJ·mol}^{-1}$ and $\Delta H = -1347\,\text{kJ·mol}^{-1}$, while those of eq 2 (without I_2) are $\Delta G = -280\,\text{kJ·mol}^{-1}$ and $\Delta H = -342.2\,\text{kJ·mol}^{-1}$.[15] It is obvious that the reaction in eq 1 is more prone to occur than that in eq 2.

$$Al + NaN_3 = AlN + Na + N_2 \tag{2}$$

It was also found that AlN could not be obtained if the reaction temperature is below 200 °C or if the amount of NaN_3 was decreased to 1 g. In our experiment, the autoclave used as the reaction vessel provided a sealed atmosphere, and NaN_3 was used as the nitrogen source in the mean time to sustain a high pressure (16.1 MPa. calculated by the ideal gas law). Excessive NaN_3 was necessary for the formation of AlN nanocrystals in high yield. The yield of AlN obtained at 200 °C based on the amount of Al powder was ca. 50%.

In summary, hexagonal AlN nanorods were synthesized via a simple chemical route at 200 °C. TGA curve reveals that the as-prepared sample has good thermal stability and oxidation resistance below 600 °C. Room-temperature photoluminescence shows a broad blue band that could attribute to the existence of oxygen impurities.

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