A Low Temperature Nitridation Route for Nanocrystalline AlN

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6 nm crystalline AlN has been synthesized through a simple reaction between commercial Al and NH_4Cl in an autoclave at 580 ℃ which is much lower than those of traditional methods. X-ray diffraction result indicates the formation of hexagonal AlN nanocrystallites. Transmission electron microscopy image shows that the average size of the crystallites is 6 nm. The possible synthetic mechanism of AlN is proposed.

Nanometer-scale structures have attracted great interests as potential building blocks for future devices of greatly reduced size.[1] Their physical and chemical properties are very distinguished and depend on the grain size and shape significantly.[2] Thus the synthesis of uniform nanocrystallites is of interest to many materials scientists.[3]

Aluminum nitride is an important material due to its high thermal conductivity, high electric resistivity, low thermal expansion coefficient that matches well with that of silicon, and high mechanical strength. It has been considered for many applications, such as electronic substrates, cutting tools, and refractory applications.[4,5]

Conventional process for AlN powders is the direct nitridation of aluminum powders at 1200 -1400 ℃ or carbothermal reduction nitridation of aluminum oxide at 1200 - 1750 ℃ in flowing nitrogen or ammonia.[6,7,8] Haber *et al.* developed a method for nanocrystalline AlN (25 nm - 50 nm mean coherence length by XRD) at 1000 ℃ or 1100 ℃ through the nitridation of nanocrystalline Al that was the pyrolysis product of precursor $H_3Al(NMe_2Et)$.[9] Recently, AlN powders have also been prepared by self-propagating high-temperature synthetic method.[10,11] Ohhashi *et al.* synthesized AlN powders by the reaction of ammonia with a mixture of aluminum chloride vapor species ($AlCl_x$; x=1, 2 and 3) in a flow-tube reactor at 720 ℃ - 920 ℃. The produced particle size was in the range of 200 - 400 nm.[12]

Herein, we report a one-step method for nanocrystalline AlN by using commercial Al powders as Al-source and NH_4Cl as N-source. The synthesis of AlN is associated with the following chemical reaction.

$$2Al(s) + 2NH_4Cl(s) \longrightarrow 2AlN(s) + 2HCl(g) + 3H_2(g) \qquad (1)$$

The reaction was carried out in an autoclave at 580 ℃ and maybe involved the chloridization of Al powders and subsequent nitridation. The prepared AlN powders consist of uniform particles, which may relate to the gas-gas reaction between the intermediate products $AlCl_3$ and NH_3.

All manipulations were carried out in a dry glove-box with Ar gas flowing. Appropriate amounts of commercial aluminum powders and NH_4Cl were mixed and then put into a stainless steel autoclave with silver-liner. The autoclave was kept at 580 ℃ for 12 h and then cooled to room temperature. After washed with absolute alcohol and drying in vacuum at 50 ℃ for 4 h, a gray-white product was collected.

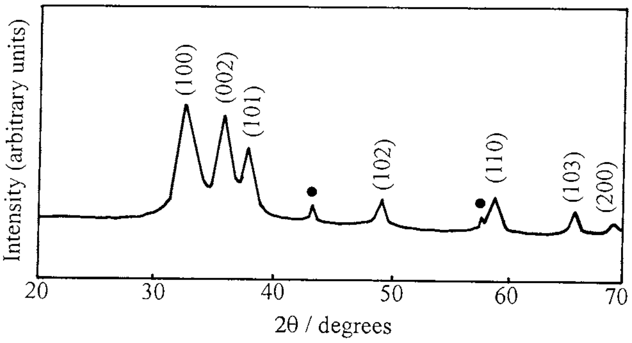

Figure 1. X-Ray diffraction pattern of the obtained sample.

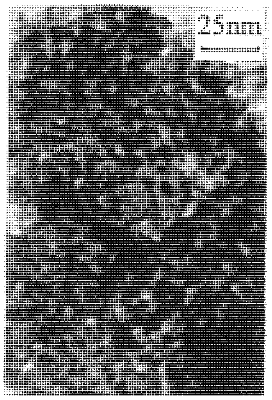

Figure 2. Transmission electron microscopy image of the obtained sample.

X-Ray powder diffraction (XRD) patterns were carried out on a Rigaku DmaxγA X-ray diffractometer with Cu Kα radiation (λ=1.54178 Å). Figure 1 shows the XRD pattern of the sample prepared at 580 ℃ with the molar ratio of NH_4Cl to Al of 3 : 1. All strong peaks can be indexed to hexagonal AlN with lattice constants a = 3.11 Å and c = 4.98 Å, which are near the reported values (a = 3.1114 Å, c = 4.9792 Å JCPDS, No. 25-1133). From this figure, we also detect a small amount of Al_2O_3 that maybe come from the surface oxidation of commercial Al powders. (The reflections of Al_2O_3 are marked with circles in Figure 1.) The broadening of the peaks in XRD pattern reveals that the grain is in nanometer-scale. The average particle size of the product, calculated by the Scherrer formula, is 6 nm.

Figure 2 shows a transmission electron micrograph (TEM) image of the sample, taken with a Hitachi H-800 transmission electron microscope. From this figure, we can find that the product consists of uniform spherical particles with the average

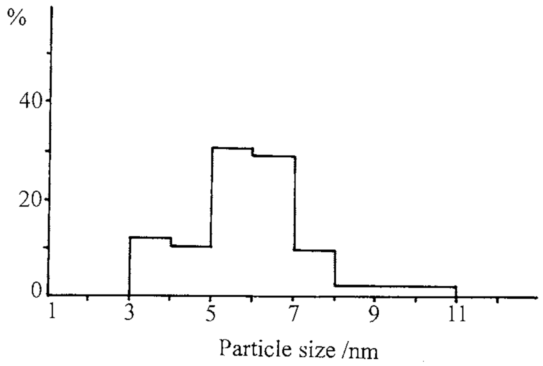

Figure 3. Histogram of AlN particle size in the obtained sample.

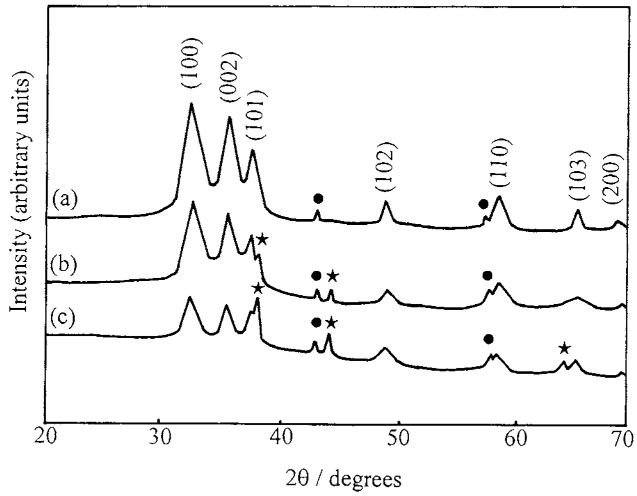

Figure 4. X-Ray diffraction patterns of the samples prepared with different molar ratios of NH_4Cl to Al. (a) NH_4Cl : Al = 3 : 1; (b) NH_4Cl : Al = 2 : 1; (c) NH_4Cl : Al = 1 : 1.

size of 6 nm, which is in agreement with the XRD result. Figure 3 is a histogram of the AlN nanoparticles, obtained by PDS 1010 M Microdensitometer, showing a distribution of particle sizes ranging from 3 nm to 11 nm. The average particle size calculated by the reported method was 5.85 nm, with a standard deviation of 0.57.[13]

During the synthesis process of AlN powders, the amount of NH_4Cl has a significant effect on the formation of nanocrystalline AlN. Figure 4 shows the XRD patterns of the products prepared with different molar ratios of NH_4Cl to Al ((a): NH_4Cl : Al = 3 : 1; (b): NH_4Cl : Al = 2 : 1; (c): NH_4Cl : Al = 1 : 1). The peaks marked with stars are the reflections of Al resulted from the incomplete reaction. The peaks marked with circles are the reflections of α-Al_2O_3 maybe due to the surface oxidation of commercial Al powders. From this figure, one can see that, to make the synthetic reaction complete, the molar ratio of NH_4Cl to Al should be no less than 3:1. This ratio is consistent with the molar ratio of HCl to Al in the chloridizing reaction. On the other hand, the amount of NH_4Cl also has an effect on the crystallinity of the produced AlN. With the increase of the amount of NH_4Cl, the pressure in the autoclave increases, which is beneficial to the crystallization of AlN. The processing temperature is another influence factor to the crystallinity and the particle size of the product. At about 500 ℃, the synthesis reaction also occurred but the crystallinity of the produced AlN was very poor. With the increase of the processing temperature, the particle grew and its crystallinity became better. The synthesis temperature we chose for nanocrystalline AlN is 580 ℃.

The possible reaction path is proposed here. With the increase of the temperature, NH_4Cl would decompose into NH_3 and HCl (NH_4Cl: decomposition temperature of 339 ℃)[14]. In view of the fact that one of the conventional methods for $AlCl_3$ is using HCl to make Al powders chloridize at moderate temperature[15], we believe that the chloridization of Al powders can occur under our synthesis conditions. Although best result was obtained with NH_4Cl : Al (molar ratio) = 3 : 1, we think that, besides $AlCl_3$, $AlCl_x$ (x<3) compounds were also involved in the synthetic reaction due to the presence of the following equilibrium reaction under our experimental conditions: [16].

$$Al(l) + AlCl_3(g) \rightleftharpoons AlCl_2(g) + AlCl(g) \qquad (2)$$

The produced aluminum chlorides were so active that they could directly react with NH_3 at temperatures above 500 ℃. So nanocrystalline AlN was produced through what may be a gas-gas reaction. The reaction path can be summarized as follows:

$$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g) \qquad (3)$$

$$2Al(l) + 2xHCl(g) \longrightarrow 2AlCl_x(g) + xH_2(g) \quad (x<3) \qquad (4)$$

$$\text{or } 2Al(l) + 6HCl(g) \longrightarrow 2AlCl_3(g) + 3H_2(g) \qquad (5)$$

$$3AlCl_x(g) + xNH_3(g) \longrightarrow xAlN(s) + 3xHCl(g) + (3-x)Al(l) \qquad (6)$$

$$\text{or } AlCl_3(g) + NH_3(g) \longrightarrow AlN(s) + 3HCl(g) \qquad (7)$$

In summary, to prepare nanocrystalline AlN, a low temperature nitridation route has been designed. The reaction conditions in our route are very easy to maintain and the gas-gas synthetic reaction results in the formation of uniform AlN crystallites (6 nm). In this process, a single nitrogen source, NH_4Cl, has been used for the preparation of AlN crystallites. It's maybe a useful nitrogen source for many other nitrides such as Si_3N_4, BN and GaN.

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