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Morphology-controlled synthesis of quasi-aligned AlN nanowhiskers by combustion method: Effect of NH_4Cl additive

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Abstract

Uniform quasi-aligned AlN nanowhiskers grown in the reacting Al particles have been successfully prepared in high content by combustion synthesis using NH_4Cl as a morphology-controlled promoting additive. FE-SEM and TEM images show that the nanowhiskers, which are single-crystalline hexagonal wurtzite AlN growing along [0 0 1] direction, have diameters in the range of 80–170 nm and a length of several to several tens of micrometers. The effect of NH_4Cl on the growth of nanowhiskers was discussed. It was found that NH_4Cl not only controlled the products' morphology, but also changed the combustion behavior and nitridation mechanism in the combustion synthesis process.

Keywords: D. Nitrides; Nanowhiskers; Ammonium chloride; Combustion synthesis

1. Introduction

In recent years, research on the controlled synthesis of one-dimensional (1D) inorganic nanomaterials has attracted increasing attention because of their importance in both scientific research and technological applications [1–3]. Aluminum nitride (AlN), an important III–V group wide band-gap semiconductor, has aroused great interest due to its high thermal conductivity, good electrical resistance, low dielectric constant, and low thermal expansion coefficient, matching that of silicon [4]. Recently, 1D AlN nanostructures, such as nanowhiskers [5], nanorods [6] and nanobelts [7] were found to process promising applications in both electronics and photonic devices. To date, 1D AlN nanostructures such as nanofibers [8], nanowhiskers [9], nanowires [10–12], nanotubes [13] and nanobelts [7], have been synthesized by several methods, including chemical vapor deposition (CVD), carbothermal reduction and nitridation (CRN), direct nitridation (DN) and DC arc discharge. For these methods, high temperature, catalysts, substrates or long-term production cycle tend to be required, which will increase the cost and limit the applications. From this point of view, it is imperative to further exploit some synthetic routes for preparation of 1D AlN nanostructures.

In addition to above methods, the combustion synthesis (CS, also known as self-propagating high temperature synthesis or SHS), has become a promising choice for industrial fabrication because of its low processing cost, high energy efficiency and short reaction period. To date, many CS processes have been developed for synthesis of pure AlN powders [14–17]. However, since the high thermal-gradient and fast reaction speed in the CS process, as well as the low melting temperature of metal Al (~660 °C), the morphology of the AlN product was difficult to control and often consists of various grain morphologies such as agglomerated particles, whiskers, faceted particles, rods, pyramids, etc. [18–21]. Although a uniform morphology is very important to engineer the properties of AlN-based materials or devices, a morphology-controlled synthesis condition is still difficult to realize, which prevents the CS process from wide application. It has been reported that the addition of ammonium halides (NH_4X, X = F, Cl, Br and I)

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to the starting Al powder during CS can not only control the process parameters, but also enhance the nitridation rate as well as promote the growth of 1D structures (such as AlN fibers and whiskers) [22–25]. This indicates the possibility to achieve the morphology-controlled CS of AlN by NH_4X promoting additives.

In previous studies [26,27], we have reported the synthesis of AlN nanofibers and nanowhiskers with uniform morphologies by the CS method, where the morphologies of products were controlled through adding NH_4Cl and various oxide additives (such as Y_2O_3 and CaO). The oxide additives play an important role for the growth of 1D AlN nanostructures. However, the performances of AlN products, especially the thermal conductivity, would be decreased since the oxygen impurities introduced into the AlN lattice [28]. Moreover, the content of 1D AlN nanostructures in the product is still low.

To overcome the above-mentioned shortcomings, in present paper, uniform quasi-aligned AlN nanowhiskers were successfully formed inside the reacting Al particles by controlling the CS process just using NH_4Cl as the promoting additive. The effect of NH_4Cl on the combustion reaction process and morphology evolution of the products was investigated. Finally, by repeating the combustion reaction two times using the as-synthesized AlN powders as diluent, high content of the AlN nanowhiskers in the final products was achieved.

2. Experimental procedure

The starting materials were high-purity Al (>99.9%, ~23 μm, Toyo Aluminum K.K., Tokyo, Japan), AlN diluent powder (type H, >99.9%, ~0.5 μm, Tokuyama K.K., Hino, Tokyo, Japan), and NH_4Cl additive (>99%, Nacalai Tesque, Inc., Kyoto, Japan). The morphological characteristics of Al powders and AlN diluent are shown in Fig. 1. In a typical experimental procedure, Al and AlN powders were mixed with a molar ratio of 4:6, which was chosen according to a previous study to achieve looser and full AlN product [29]. Additionally, 6 wt% NH_4Cl was also added as a promoting additive to control the morphology of the product. The powders were lightly mixed using mortar for 10 min, and then sieved through a 212-mesh sieve to disperse any large agglomerates. The mixture (50 g) was poured into a porous graphite container (Ø 42 mm × 90 mm H) at a tapping density of 0.6 g/cm^3. Then, the container was placed into a combustion chamber, and two W-Re thermocouples protected by alumina tubes were inserted into the center of the mixture (one at the middle and the other near the top surface) at a fixed distance of 30 mm to record the temperature–time pattern of the combustion and determine the combustion speed by measuring the time lapsed for the wave passage between the two thermocouples. The chamber was evacuated and then filled with high-purity N_2 (99.99%) at the pressure of 1 MPa. The mixture was ignited from the bottom with an ignition pellet (2 g, Al/AlN = 1/1 wt%) by passing an electric current of 60 A × 20 V for 10 s through a carbon ribbon under the pellet. After the first combustion reaction, the as-synthesized AlN product, which was a loose cake composed of quasi-aligned nanowhiskers and original AlN diluent, was broken lightly by a mortar. Then, the product was sieved through 212-mesh sieve to use as the diluent for the second combustion reaction with similar conditions as the first time. The procedures were repeated for two times. Finally, AlN nanowhiskers with high content in the final product were achieved.

The phase purity of the as-synthesized products was examined by using powder X-ray diffraction (XRD; JDX-3530, JEOL, Tokyo, Japan) with Cu Kα radiation. The morphology of the as-synthesized products was observed by field emission scanning electron microscopy (FE-SEM; ERA-8800, ELIONIX, Tokyo, Japan) equipped with energy-dispersive X-ray (EDX) spectroscopy. Samples for SEM observations and EDX analyses were coated with thin films of sputtered gold to reduce electrical charge-up. Transmission electron microscopy (TEM; JEM-2010, JEOL, Tokyo, Japan) was used for further characterization of the products, where both TEM images and selected area electron diffraction (SAED) patterns were acquired.

3. Results and discussion

Fig. 2 shows a typical XRD pattern of the as-synthesized product. All the diffraction peaks can be indexed to the hexagonal wurtzite structure of AlN crystal (JCPDS No. 25-1133). No characteristic peaks of impurities were detected in the pattern. The sharp diffraction peaks indicated the good crystallinity of the product.

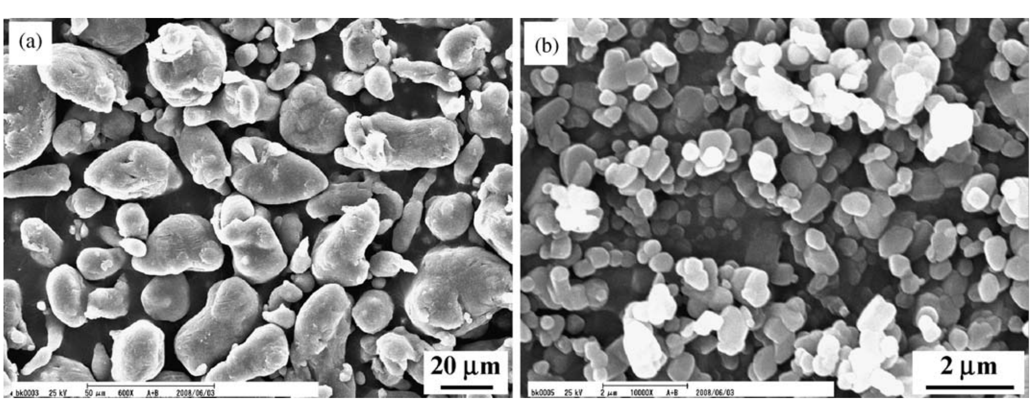

Fig. 1. Morphological characteristics of starting powders: (a) Al and (b) AlN diluent.