Microanalysis of single-phase AlN nanocrystals and AlN-Al nanocomposites prepared by DC arc-discharge

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Abstract

AlN nanocrystals and AlN-Al nanocomposites of < 100 nm size were prepared by the direct current (DC) arc-discharge plasma evaporation of aluminum in an ambient of N₂ + NH₃. The analysis of these two kinds of nanoparticles revealed that the AlN nanocrystals were single phase and single crystal. The AlN-Al nanocomposites were composed of AlN single-crystals embedded in amorphous aluminum phase. The crystallographic features and formation mechanisms for these two kinds of nanoparticles are discussed. © 1998 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Aluminum nitride (AlN) has numerous attractive properties including high thermal conductivity (319 W/m K), low thermal expansion coefficient (4.4 × 10⁻⁶/°C), high electrical insulation (> 10¹³ Ω cm), high dielectric breakdown strength, good mechanical strength, ease for cutting and polishing, excellent chemical stability and nontoxicity [1, 2]. A number of processing methods used to synthesize AlN powders have been reported in the recent literature. They mainly involve carbothermal reduction and nitrating of Al₂O₃ [3], arc-plasma methods and the methods based on chemical vapor deposition [4-6]. Established uses for AlN powders include electronic substrates, packaging materials for integrated circuits, ignition modules, RF/microwave packages, optoelectronics parts, heat sinks, cutting tools, laser heat spreaders, and fillers for polymer and glass materials [7, 8]. Although some applications of AlN powders have been realized to a large extent, several problems with AlN powders, such as the phase purity, chemical impurities, surface absorption of oxygen and moisture, crystal quality and particle size distribution still challenge researchers.

Phase-pure AlN single-crystal particles of < 100 nm range can be pressureless sintered in the
manufacture of fully dense AIN components of high thermal conductivity [8]. As described by Kuramoto et al. [9] and Inoue et al. [5], the thermal conductivity is expected to increase significantly by synthesis of nanoscale composites and compositional gradient materials consisting of AIN and Al [9].

In this paper, single-phase AIN nanocrystals and nanocomposites of AIN-Al were prepared by the DC arc-discharge method. The morphology, crystallographic habit, microstructure, and chemical composition of these two kinds of particles were investigated. The formation process for these two kinds of nanoparticles are discussed.

2. Experimental procedure

The samples reported here were all prepared by the DC arc-discharge evaporation of metallic aluminum in an ambient of N₂ + NH₃. The DC arc-discharge system was the same as that described in another paper [10]. The purity of the starting materials was aluminum 99.999% and ammonia 99.95%. The experimental parameters were as follows: ambient pressure 10–100 kPa, DC arc-current 100–500 A. The volume ratio of NH₃/(N₂ + NH₃) is a crucial factor for the crystallographic habit of the as-grown nanoparticles. Single-phase AIN nanocrystals usually formed in the ratio range 5–50%. AIN-Al nanocomposites were formed at a slightly lower ratio of less than 5%. The typical value is about 3% for the nanocomposites reported in this paper. The as-grown particles were collected from the water-cooled wall.

Microanalysis of the particles was carried out by using transmission electron microscope (TEM), selective-area diffraction (SAD), and energy dispersive spectroscopy (EDS) in the nanoprobe electron-beam mode using a HITACHI-8100IV transmission electron microscope with a 200 kV accelerating voltage and a PHILIPS DX-4 energy dispersive spectroscopy attached with a super-ultra-thin-window (SUTW) capable of detecting elements down to boron. The crystallographic habit and phase purity were investigated by X-ray diffraction (XRD) using Cu Kα radiation line as an X-ray source. Microanalysis samples were prepared by spraying the as-grown particles onto an amorphous carbon film supported on a copper grid. The impurity concentration analysis of EDS was carried out on ion-milled films of cold-pressed plates of AIN nanocrystals and AIN-Al nanocomposites.

3. Results and discussion

The as-grown single-phase AIN nanocrystals are white in color. Fig. 1 shows the bright-field TEM micrograph and XRD pattern of these crystals. The XRD peaks (Fig. 1b) of the well-faceted, hexagonal-shaped nanocrystals of AIN (Fig. 1a) match well with the AIN wurtzite phase. No aluminum metal was detected in these samples. A bright-field TEM micrograph and SAD pattern of an individual nanocrystal of AIN (Fig. 2) show that the crystal is a well-faceted hexagonal plate with (1 1 0), (1 2 0) and (2 1 0) crystallographic planes, which is in agreement with Wulfs polyhedron [11] and is very similar to the results reported by Inoue and co-workers [5]. In order to obtain accurate chemical composition and impurity data for the single-phase AIN nanocrystals (based on the thin-sample approximation), EDS analysis was carried out on an ion-milled thin sample from the cold-pressed plates of the as-grown AIN nanocrystals. The results showed that the atomic ratio of aluminum/nitrogen in AIN was 43/57. The excessive nitrogen proportion detected is assumed to be absorbed nitrogen on the crystal surface, which passivate and stabilize the crystals. No impurity and absorbed moisture and/or oxygen were detected in the sample within the detection limit (0.1% for the thin-sample approximation). AIN-Al nanocomposites could be prepared with a low ammonia addition to the ambient-gas mixture. Fig. 3 shows the bright-field TEM micrograph and SAD pattern corresponding to AIN-Al nanocomposite. The nanocomposites, composed of AIN + Al contained AIN crystals embedded in an amorphous Al matrix. The crystal size of AIN in the composites was also in the <100 nm range which is similar to that of AIN nanocrystals mentioned above. Based on the symmetry analysis of the SAD pattern in Fig. 3c,
the surfaces of the hexagonal AlN crystal in the composite are crystallographic planes of (1 0 0), (0 1 0) and (1 1 0), which is different from that of single-phase AlN nanocrystals. That is to say, the AlN nanocrystals embedded in amorphous aluminum do not obey Wulff's polyhedron. The phase distribution of AlN and Al in the composites were confirmed further with the use of EDS and nanoprobe (<3 nm) electron beam illumination. Fig. 4 shows the typical EDS data obtained for the core AlN and Al matrix in the composites. It can be seen that the atomic ratio of nitrogen/aluminum is about 1 for the core AlN (Fig. 4a) and that only the peak for aluminum can be seen in the matrix (Fig. 4b). The small peak in Fig. 4b is assigned to nitrogen signal from adjacent AlN core irradiated by the multi-reflection electrons from the aluminum matrix.

In the discharge plasma, the nitridation process involves evaporation of aluminum, decomposition of N₂ and NH₃, and the formation of stoichiometric AlN crystals. The reactive precursors, including atoms, ions and radicals came from the evaporation of aluminum and decomposition of nitrogen gas and ammonia. The chemical reaction and aggregation of the precursors occurs from the random collisions in the gas phase. The only dominant factor is the free-energy, not only inside the as-grown particles but at interface and surface as well.

In the case of complete nitridation, the aggregated precursors tend to exist in a lowest free-energy state, while they fly toward the water-cooled wall along a temperature gradient path. Obviously, the highly arranged lattice structure in the single crystals with well-faceted surfaces in Wulff's polyhedron have the lowest free-energy. Therefore, the only reasonable equilibrium state for the final product is single-crystalline AlN nanocrystals. On the other hand, for the AlN-Al nanocomposites formation, co-aggregation of AlN and Al molecules, atoms, ions, and radicals occurs simultaneously in the plasma. The precursors in the AlN structure tend to develop single-crystal lattice arrangement for the
sake of minimizing it's free-energy. The reaction of the molecule formation and crystallization of AlN is a highly exothermic process [12] releasing an extensive heat, which caused the aggregated Al to melt and cover the AlN crystals with liquid aluminum. Sudden cooling on the water-cooled wall make the liquid aluminum coatings to become amorphous. In fact, the whole process of AlN formation was undertaken in the liquid aluminum environment in this case. So, the final crystal shapes of AlN nanocrystals embedded in the aluminum were determined by the interface energy between AlN and aluminum.

The dependence of aluminum nitridation on the addition of NH₃ is attributed to the decomposition of NH₃ into atoms or ions of nitrogen and hydrogen, and reactive N–H radicals, which is supposed to enhance the process of aluminum nitridation. Moreover, the hydrogen introduced into the plasma from the decomposition of NH₃ maybe another important factor that needs to be studied further.

4. Conclusions

Nanosized single crystals of single-phase AlN and AlN-Al nanocomposites were prepared by DC arc-discharged plasma-evaporating aluminum in the ambient of N₂ + NH₃. The AlN nanocrystals produced were well-faceted single crystals of sub-100 nm size with definite crystallographic faces. The AlN-Al nanocomposites prepared at reduced partial pressure contained AlN single crystals embedded in an amorphous aluminum phase. AlN nanocrystals in these two cases have different equilibrium shapes, which is due to different free-energy conditions on surface and interface.

References
