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Short communication

Free nucleation of aluminum nitride single crystals in HPBN crucible by sublimation

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Abstract

Clear and colorless aluminum nitride (AlN) single crystal thin platelets up to 60 mm^2 were prepared at 2100 °C and 800 Torr in hot-pressed boron nitride (HPBN) crucibles by free nucleation in a graphite furnace. Crystals grown in HPBN crucibles typically form thin platelets with the fastest growth rate (above 400 μm/h) occurring in the *c*-axis direction. Growth striations frequently run the length of the crystals, probably due to the presence of boron in the growth environment. Raman spectra and X-ray topography reveal that the crystals have good structural quality. Emissions peaks around 4.10 eV, 3.90 eV, and 3.70 eV were observed in the photoluminescence spectrum, suggesting that boron from the boron nitride crucible may incorporate into the AlN crystals as hexagonal boron nitride.

Keywords: Aluminum nitride; Crystallization; Sublimation; Boron nitride

1. Introduction

Single crystal aluminum nitride (AlN) is attractive as an excellent substrate for AlGaN-based electrical and optical devices. AlN has many desirable properties, such as a large direct band gap, high thermal conductivity and hardness, and high thermal and chemical stability [1]. The early application of AlN was as surface acoustic wave devices because of its piezoelectric properties [2]. AlN has also received attention in the field of III-nitride epitaxial applications due to its promising electrical and optical properties [1]. For instance, high quality AlGaN epitaxial layers with high Al mole fraction are necessary for fabrication of deep ultraviolet (DUV) optoelectronic devices [3], because AlGaN is the only wide band-gap semiconductor system that possesses the ability of band-gap engineering through the use of alloy and heterostructure design. Needless to say, future applications of AlN devices depend on the development of methods for producing high quality bulk AlN substrates and device structures, as well as on the full understanding of the basic properties of AlN.

Much research has been devoted to bulk AlN single crystal growth via sublimation technique [4–8], also called physical vapor transport (PVT). The most successful initial demonstration of this technology was reported by Slack and McNelly [9] in the 1970s. In the past 10 years, much development and optimization of this technology has occurred. Even so, bulk AlN substrates are currently available only in limited quantities suitable for research purpose [10].

One potentially viable candidate as a crucible material to contain the AlN source and growing crystals is boron nitride. Previous studies of AlN grown in hot-pressed boron nitride (HPBN) crucibles by vaporizing Al in nitrogen at Sitar's group [11] yielded relatively small *c*-platelet crystals with

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surface areas less than 10 mm^2. In this communication, we report AlN single crystals free nucleated from high purity AlN powders in HPBN crucibles. Large AlN single crystal platelets up to 60 mm^2 were obtained.

A prior investigation by the author's group [12] showed that needles and platelets from free nucleation (no foreign substrate employed) exhibited much better crystal quality than the crystals grown on 6H-SiC substrates. However, this is not the only advantage that free nucleation has: AlN produced from self-seeding has the lowest stress, low Si and C impurity content, and can be performed at a higher temperature to achieve a higher growth rate compare with seeded growth on 6H-SiC substrates[13].

2. Experimental procedures

A schematic diagram of a resistively heated graphite furnace for AlN sublimation growth is shown in Fig. 1. The furnace includes a growth chamber, graphite heating element, graphite foam insulation, and a temperature and pressure control system. HPBN crucibles were contained within a concentric graphite retort sitting together on a cylindrical graphite work support. The vertical temperature profile of the growth chamber was measured by an optical pyrometer focused on a movable target placed at different axial positions. The shape of the graphite heater and its material grade determined the axial temperature distribution. Fig. 2 shows the temperature profile inside the furnace measured at 50% power output. A spatially uniform high temperature zone of 2 cm long was located in the middle of the heating element. The temperature variations were less than 2 °C in this high temperature zone. By varying the height of the work support, different temperature gradients were obtained. The source material was enclosed in the HPBN crucible, and positioned at this zone. The nucleation surface, where the AlN recondensed, was about 1–2 cm above the sublimation surface with a temperature decrease less than 10 °C. The critical parameters were the growth temperature and the temperature difference between the sublimation surface and nucleation surface. The source material was AlN powder, which contains less than 0.9 wt.% of O and less than 0.4 wt.% of C according to the vender's specification.

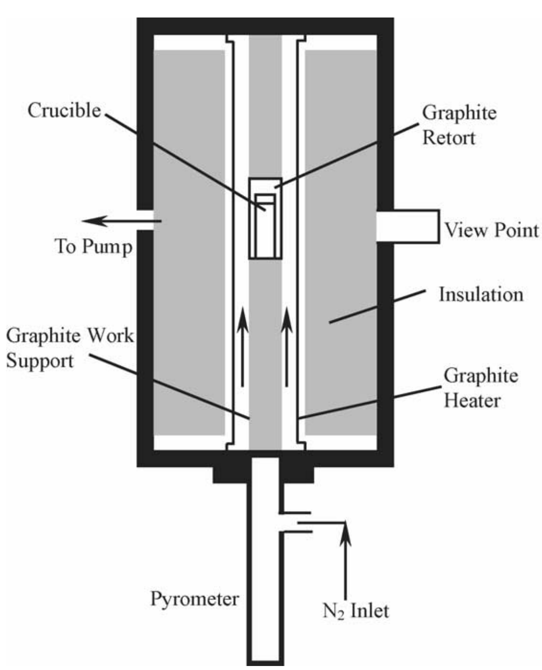

Fig. 1. Scheme of the graphite furnace for AlN sublimation growth.

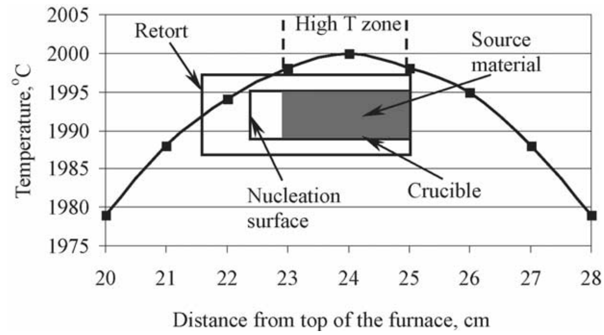

Fig. 2. Temperature profile inside the furnace at 50% of power output.

The AlN crystals produced in the HPBN crucibles were characterized by several methods. The crystal perfection was assessed by X-ray topography (XRT) taken at the Stony Brook Synchrotron Topography Station. Topographs were recorded on 8″ × 10″ Kodak Industrex SR-45-1 high-resolution X-ray film. Micro-Raman spectra were obtained using a Renishaw micro-Raman system with the 488 nm line of an Ar laser as the excitation source. The spot size and the spectral resolution were 1–2 μm and 3–4 cm^{-1}, respectively. Photoluminescence (PL) measurements were taken to determine the optical transitions in the AlN crystals. For the PL measurements, a specially designed deep UV laser spectroscopy system was utilized consisting of a frequency quadrupled 100 fs Ti:sapphire laser with excitation photon energy set around 6.28 eV (with a 76 MHz repetition rate and a 3 mW average power at 196 nm) and a monochromator (1.3 m). The time resolution of the detection system is about 20 ps [14]. Compositional analysis was carried out using inductively coupled plasma optical emission spectroscopy (ICPOES).

3. Results and discussions

At 1850 °C, transparent and colorless AlN whiskers nucleate on the sidewall and the crucible lid, with an average growth rate about 0.5 μm/h. At 2000 °C, a thin layer of individual crystals comprised of small needles and platelets, grew on the cap. The average growth rate of the crystalline layer under this temperature was about 20 μm/h. At 2080 °C, thin and narrow AlN platelets formed on the