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Growth of AlN crystals by a sublimation process and their optical properties

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We have grown AlN crystals by a sublimation process. As grown AlN boules were grown as polycrystals because a seed crystal was not used. The size of the crystallites was 0.2-1 mm and the color was dark green. The as-grown AlN boule had a length of about 2-3 mm. Carbon impurities were observed on its surface while they could not be inside the as-grown AlN boule. The growth behavior and the morphology of the crystallites were investigated by an optical microscope, SEM observations and X-ray diffraction(XRD). Photoluminescence (PL) measurements were carried out in order to characterize the optical properties. We could obtain a 204 nm deep UV emission peak from an excitation wavelength of 202 nm.

Key words: AlN, LEDs, crystal growth, sublimation process, photoluminescence (PL).

Introduction

AlN has the wurtzite crystal structure, a large band gap of about 6.2 eV, a high decomposition temperature (ca. 2400 °C), and good chemical stability. The preparation of aluminum nitride (AlN) crystals has received much attention due to potential applications in electronic and optoelectronic devices such as power devices and UV LEDs. AlN is a promising material for electronic substrates such as passivation and dielectric layers, protective coatings, and optical devices [1].

In the bulk crystal growth of AlN, little attentions has been given due to the high growth temperature [2-4]. In this study, we tried to grow AlN crystals using a sublimation process [5-8] which is a particular method used for the growth of materials a having high decomposition temperature such as SiC. Although the fine crystallites of AlN were grown randomly because a non-seeded growth process was applied, the optimum growth conditions for AlN crystals were established. Furthermore we report the PL (Photoluminescence) emission results in the UV region for the grown AlN crystals.

Experimental Procedure

A schematic diagram of the crucible inside the graphite support located in the bottom of the reactor used in these experiments is shown in Fig. 1. The reactor was air cooled by means of a single walled quartz tube and the both the top and bottom were made to be vacuum tight assemblies. A crucible inductively heated by a radio frequency (RF) induction heater at a frequency of 20 kHz, was insulated by graphite insulation to minimize thermal losses. The temperature gradient for crystal growth inside the crucible was controlled by appropriate dimensions of the insulation and adjustment of the position of the inductive coil relative to the crucible. One 2-ray infra red (IR) pyrometer was used to monitor the growth temperatures (T_g) at the top of the crucible. Through preliminary experiments in order to obtain the growth temperature (T_g) and temperature gradient, the appropriate temperature gradient was established to be 20-30 Kcm^{-1}. In the growth process, argon gas flowed in the upward direction at a flow rate of 500 sccm and was controlled by a mass flow controller. The growth pressure was controlled at 1.013 ×

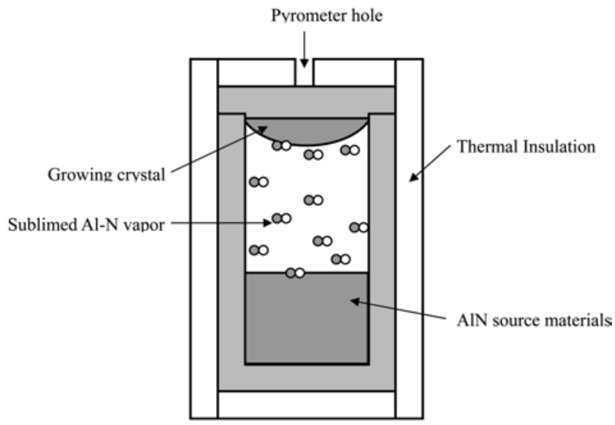

Fig. 1. Schematic diagram of the crucible inductively heated by an RF generator and the thermal shield applied to the sublimation growth reactor system.

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10^{-6} Mpa at the time of the periodic purging procedure and atmospheric pressure and was kept at a value of 0.399×10^{-6}-0.533×10^{-6} MPa for the practical growth period.

An optical microscope and a scanning electron microscope (SEM) were used to characterize the crystal surface morphology and the size and shape of the crystallites. A x-ray diffractometer (XRD) was used to identify the AlN phase and the crystallinity of the grown crystals. In particular, in order to characterize the optical properties of the grown AlN crystals, photoluminescence (PL) measurements were carried out at room temperature under a vacuum.

Furthermore, sublimation growth of AlN has been a challenging process from both technological and scientific viewpoints. The materials applied for the growth assemblies in the facility need to be chemically and thermally stable in the presence of Al vapor as the temperature is increased. So, the proper crucible material for high temperature endurance has been evaluated as an important role. In this study, high purity graphite crucibles that had been designed especially and had an inner diameter of 26 mm were used.

Results and Discussion

We have grown the AlN crystals as shown in the photograph of Fig. 2. The as-grown boule had a length of 2-3 mm long(central part was 3 mm) and a diameter of 26 mm and the growth time was 4 h. From these dimensional aspects, we could estimate the growth rate which was about 0.5-0.7 mmh^{-1}. The boule was composed of small size AlN crystallites (as shown in Fig. 3) because a seed crystal was not used in the growth process. The color of the boule was slightly dark green, although the crystallites were transparent green as shown in Fig. 3. Although carbon particles were covered in the surface of the as-grown boule, they could not be observed inside of the crystallites. A possible explanation is the carbon particles which were evaporated from the heated graphite crucible were deposited together with Al-N vapor phase at the growth interface but could not react with the Al-N bonding. The crystallites in the as-grown crystal had an hexagonal plate shape reflecting the basic morphology of the crystallographic structure of the AlN (Wurtzite structure). This is shown in Fig. 4 which represents the hexagonally shaped crystallites observed in the scanning electron microscope (SEM).

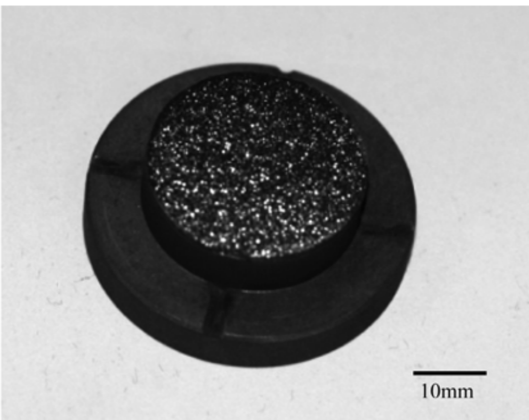

Fig. 2. The as-grown AlN crystals were grown at a growth temperature of 2020 °C on the top of the crucible without a seed crystal.

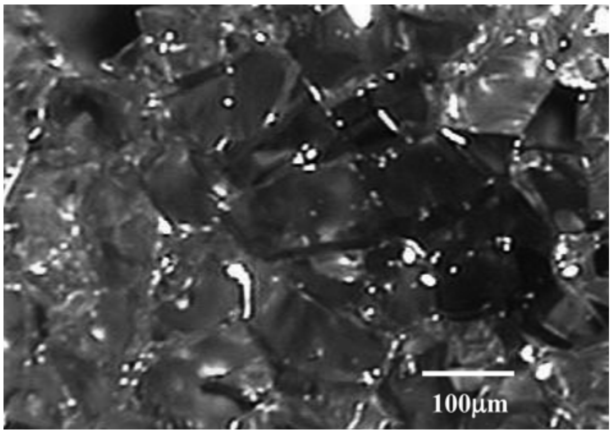

Fig. 3. An optical micrograph of the as-grown AlN crystal surface is shown. Each crystallites has a size in the range of about 60-130 μm.

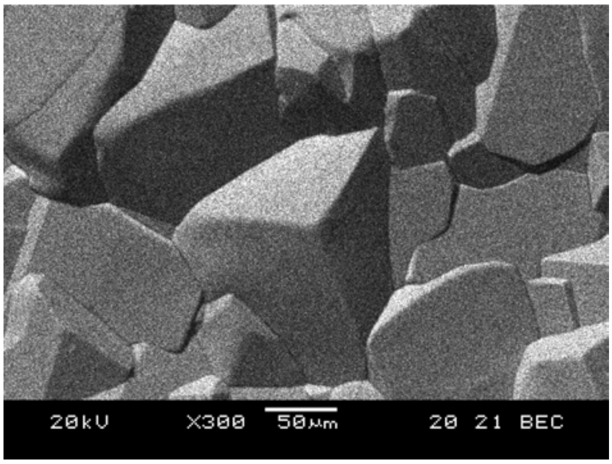

Fig. 4. SEM micrograph of the crystallites in the as-grown boule showing the hexagonal shape reflecting the crystallographic morphology.

The X-ray diffraction (XRD) pattern for the as-grown crystals is shown in Fig. 5. According to the XRD pattern, no secondary peaks were detected. Thus secondary phases were not formed from the sublimed Al-N vapor phase in the growth cavity. This fact came from the optimum growth conditions for AlN crystals which had been established.

Fig. 6 shows the room temperature photoluminescence (PL) emission spectrum measured using a vacuum spectrophotometer with a deuterium lamp (> 100 nm possible excitation). The measurement was done in the vacuum state at a basic pressure of about 4×10^{-5} MPa. A broad emission peaks at 204 nm in Fig. 6(a) was measured from the as- grown crystals. This peak was estimated to

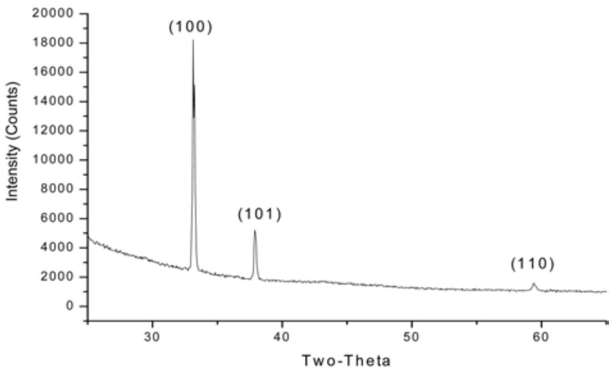

Fig. 5. X-ray diffraction pattern for the as-grown AlN crystals.

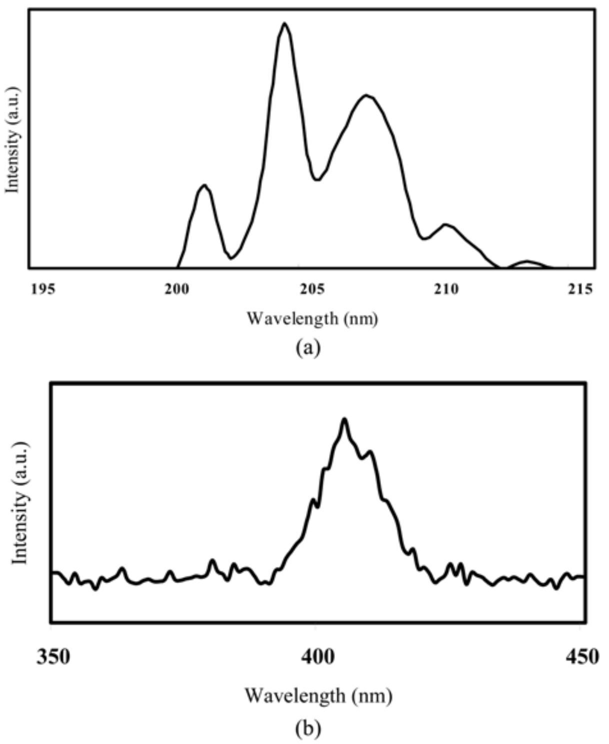

Fig. 6. Photoluminescence (PL) spectra that were measured at room temperature under a vacuum in the range of (a) around 205 nm and of (b) 350-450 nm are shown. The light source wavelength of these emission peaks was 202 nm.

have come from the micro-crystals grown naturally and corresponded to the AlN bandgap energy of 6.2 eV. The peak position at about 204 nm was due to the well-crystallized state of the AlN grown crystals even though non-seeded growth was used. Also, an emission peak coming from near 405 nm (E_g = 3.1 eV) shown in Fig. 6(b) was considered to arise from nitrogen vacancies or oxygen vacancies. We have grown AlN crystals in an atmosphere of Ar, so we think that the 3.1 eV peak is attributed to nitrogen vacancies, not oxygen impurities. There is a report that the 405nm peak is attributed to native defects [9]. By contrast with the previous report, the emission spectrum near 405nm is attributed to defects in the inside of the crystals or to the grain boundaries of the grown polycrystal of AlN in our case.

Conclusions

Growth of AlN crystals was achieved by sublimation of AlN powder in an argon atmosphere. The growth temperature, source-to-seed distance and growth time were very important parameters in this experiment. The optimum growth conditions in our growth facility were set up with a growth temperature of 2010-2030 °C at the upper position of the crucible and the growth pressure of 0.399×10^{-6}-0.533×10^{-6} MPa respectively. It was realized that the hexagonal features of the nucleus initially nucleated continued to grow throughout the growth period which was confirmed through optical microscopy and by SEM. It was recognized that a near UV emission could be possible from the result of the broad PL spectrum having a peak value of 204 nm peak excited from a 202 nm wavelength light source. A peak at 405 nm was seen that may have come from nitrogen vacancies or the polycrystalline nature of the grown boule.

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