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Growth of AlN crystals on AlN/SiC seeds by AlN powder sublimation in nitrogen atmosphere

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AlN single crystals were grown on AlN/SiC seeds by sublimation of AlN powder in TaC crucibles in a nitrogen atmosphere. The seeds were produced by metallorganic chemical vapor deposition (MOCVD) of AlN on SiC crystals. The influence of growth temperature, growth time and source-to-seed distance on the crystallinity and the crystal growth rate were investigated. Crystals were grown in an RF heated sublimation reactor at growth temperatures ranging from 1800-2000°C, at a pressure of 600 Torr, nitrogen flow-rate of 100 sccm and source-to-seed distances of 10 and 35 mm. At 1870°C and a source-to-seed distance of 35 mm, isolated crystals were observed with few instances of coalescence. At 1930°C, a source-to-seed distance of 10 mm and longer growth times (~30 hrs), crystal coalescence was achieved. Above 1930°C, the decomposition of SiC was evidently affecting the growth morphology and resulted in growth of polycrystalline AlN. After an initial nucleation period, the observed growth rates (10-30 μm/hr) were in close agreement with predictions of a growth model that assumed gas-phase diffusion controlled growth. Optical and electron microscope observations revealed step-flow growth, while X-ray diffraction results showed the single crystal nature of the grown material. Single crystalline AlN was grown over surface areas of 200-300 mm^2 and was transparent and essentially colorless.

1 Introduction

AlN has been identified as a promising material for a wide range of electronic, optoelectronic and acoustic applications, due to its chemical, mechanical and thermal stability, wide direct bandgap (6.2 eV), high thermal conductivity (3.2 W/cmK), high sound velocity ($\sim 10^5$ cm/sec), and high electron drift velocity (1.7 10^7 cm/sec). Furthermore, AlN is interesting because it can be alloyed with GaN over the whole composition range, and can be used as a substrate for growth of optoelectronic devices emitting at wavelengths ranging from blue to deep UV [1] [2] [3] [4].

Epitaxial growth techniques have been routinely used to grow group III-N device structures, however, the grown layers contain high concentrations of defects ($\sim 10^{10}$ cm^{-2}) that originate from substrate materials (SiC, Al_2O_3) as well as from the growth process as a result of lattice and thermal mismatch [5] [6] [7] [8]. As a result, the lifetime and performance of present devices are limited. Successful reduction of dislocation density by a few orders of magnitude (to10^6 cm^{-2}) has been achieved by the use of alternative methods such as Lateral Epitaxial Overgrowth (LEO) and Hydride Vapor Phase Epitaxy (HVPE). AlN single crystal substrates are expected to substantially decrease defect density in the overgrown films for additional 3-4 orders of magnitude ($<10^3$ cm^{-2}), by eliminating thermal and mechanical stresses and by drastically decreasing the dislocation density in the substrate material itself. This will contribute to improved III-N device performance [9].

AlN crystal growth by sublimation has been extensively studied during the past four decades [10] [11] [12] [13] [14] [15] [16] [17] [18] [19] [20]. Growth is performed in a nitrogen atmosphere at temperatures above 1800°C. Despite continuing efforts reported in the literature, AlN crystals are not yet available in commercially interesting sizes or quantities [12] [13] [14] [15] [16] [17] [18]. The major challenges in the sublimation growth of AlN have been: 1) crucible material, 2) high temperature reactor stability, 3) availability of native

AlN seeds with pre-defined crystallographic orientation, and 4) presence of oxygen and other impurities.

In this study, we focus on fabrication of c-plane AlN crystals that can be used as substrates, by optimizing the growth of AlN on 6H-SiC seeds coated with MOCVD AlN epilayers. The effect of SiC orientation, as well as an alternative nucleation layer scheme on SiC, can be found elsewhere in the literature [19] [20] [21]. Prior studies indicated that seeded growth of bulk AlN on SiC is a viable option for achieving large area bulk AlN crystals with specific crystallographic orientation [22]. However, the instability of crucible materials at growth conditions and presence of impurities have been major drawbacks [19] [20] [21] [22]. In this work we demonstrate the growth of bulk AlN by using a new crucible material and an inductively heated reactor with custom-designed features that enable high-temperature stability and low concentration of unwanted impurities.

In the following, paper discusses the effects of growth temperature, source-to-seed distance and growth time on crystal morphology, crystallinity and growth rate.

2 Experimental set-up and procedure

A schematic of the reactor used in these experiments is shown in Figure 1. The reactor was water cooled by means of a double walled quartz tube and cooling baffles at the top and bottom of the hot zone. An inductively heated crucible was surrounded by graphite foam insulation to minimize thermal losses. High-resolution control of the output power within ±3.125 W of the air-cooled induction heating inverter (Mesta Electronics) provided crucible temperature stability of ±1-3°C over 36 hours of growth.

The temperature gradient along the crucible was controlled by appropriate dimensioning of insulation and by the position of the inductive coil relative to the crucible. Two infra red (IR) pyrometers were used to monitor the temperatures at the bottom (T_b) and at the top (T_t) of the crucible. The growth temperature (T_G) at the crystal growth surface was estimated by finite element analysis using T_b and T_t as boundary conditions. The process nitrogen gas was flown in the upward direction at a flow rate of 100 sccm and was controlled by a mass flow controller. An upstream pressure controller was used to control the process pressure. Base pressure of 10^{-6} Torr was achieved before each experimental run by pumping the system with a turbo-molecular pump.

Optical and scanning electron microscopes (SEM) were used to characterize the crystal surface morphology. X-ray diffraction (XRD) equipped with a two-dimensional detector system (Bruker AXS/GADDS) was used to determine crystallinity and crystallographic orientation of the grown crystals.

Sublimation growth of AlN is a challenging process from both technological and scientific aspects. The materials used in the reaction zone need to be chemically inert and thermally stable in presence of Al vapor at temperatures above 1800°C. The selection of proper crucible material has been identified as a crucial issue. In the initial studies reported in the literature, tungsten crucibles were employed [10]. However, the short crucible lifetime led to a search for improved materials. SiC coated graphite crucibles were used in other studies, but the Si and C impurities lowered the crystal quality [13]. High-quality AlN crystals were grown by spontaneous nucleation in BN crucibles, but presence of B was found to induce high growth rate anisotropy at high temperatures [14] [15]. In our recent investigation, alternative crucible materials were tested, including Re, TaC, and TaN [18]. High-temperature sintered TaC and TaN crucibles exhibited the highest chemical stability under the applied growth conditions. TaC crucibles, used in this study were approximately 65 mm long and had an inner diameter of 25 mm.

6H-SiC has been commonly used as a substrate material in MOCVD growth of III-N epilayers. SiC has a hexagonal crystal structure and lattice mismatch with AlN on the basal plane of ~1 %. The growth of bulk AlN directly on SiC seed crystals by sublimation/recondensation is challenging, primarily because of the high process temperature (T>1800°C) and the presence of Al vapor, both of which tend to deteriorate SiC. Therefore, seeded growth on SiC requires an extra effort to achieve a delicate balance between the two competitive processes, i.e., AlN deposition and SiC decomposition. An epitaxial layer of AlN was first deposited on the Si face of 6H-SiC templates at T~1100°C using the established MOCVD process. The epilayer is used as a nucleation layer and to help preserving the integrity of SiC seeds in the early stages of growth. The epi layer thickness varied from 0.4 to 4 µm. The seeds were sugar-glued onto a cap, which was placed on the top of the crucible. Caramelized sugar, kept at 150°C for 15-20 min, was applied on the C-face of the SiC seed, which was then attached to the crucible cap and annealed at the same temperature until it was transformed into a dark solid adhesive layer. A small gap between the crucible and the cap connected the inside of the crucible to the outside. Therefore, the nitrogen pressure in the crucible was equal to the controlled nitrogen process gas pressure in the reactor.

The effect of temperature on growth was studied using 36 hour-long runs and approximately constant source-to-seed separation distance of ~35 mm. The effect of source-to-seed distance on growth was studied at a constant growth temperature, T_G~1930°C, in 15-20 hour-long runs. Crystal development as a function of growth time was studied at a 10 mm source-to-seed distance and growth temperatures between 1920 and 1930°C.

3 Results

Based on prior experience in sublimation growth of AlN, the process pressure and nitrogen flow rate were kept fixed at 600 Torr and 100 sccm, respectively. A series of initial experiments was completed with varying temperature gradients. In the temperature range of 1800-2000°C and a separation distance between the source and seed of 10 to 35 mm, a temperature difference (T_b-T_t) of 100°C provided sufficient driving force for the sublimation growth single crystalline material. Table I summarizes the growth results as a function of process parameters. Observations showed that TaC crucibles exhibited very good performance at the growth temperature, and no reaction between the crucible and Al vapors could be detected.

The estimated growth temperature was approximately 20-30°C higher than the temperature measured at the top of the crucible, Figure 1. The growth temperature and temperature gradient are crucial parameters for both the mass transfer of source material to the seed surface and the rate of nucleation. At a source-to-seed distance of 35 mm, increasing the temperature resulted in decreased number of nuclei. Hexagonal features were grown on the seeds at growth temperatures of 1820-1830°C, as shown in Figure 2a. Based on the EDX analysis, they were identified as an alloy of AlN and SiC. Once a temperature of about 1870-1880°C was reached, discrete single-crystalline islands of AlN were observed, as shown in Figure 2b. They grew at a growth rate of ~5 μm/hr; after a growth period of ~36 hours, they measured ~8 mm across and were ~190 μm thick. Cracking evident in Figure 2b occurred due to thermal stress generated during cool-down. The single crystalline nature of these islands was confirmed by XRD. By increasing the growth temperature to 1920-1930°C, the island density increased and a number of single crystalline AlN islands with well-defined facets were grown at a rate of 20 μm/hr. However, the coalescence of these islands was incomplete. An increase of growth temperature above 1930°C resulted in severe SiC decomposition, followed by growth of polycrystalline AlN. These effects limited the growth of AlN on SiC seeds to an estimated seed temperature of 1920-1930°C.

Due to the highest temperature limit of AlN growth on SiC seeds, the effect of source-to-seed distance on coalescence and crystal growth rate was investigated at an estimated growth temperature of 1930°C. Decreasing the source-to-seed distance from 35 mm to 10 mm resulted in an increase of the growth rate from 20 μm/hr to 25-30 μm/hr, accompanied by coalescence of the grown AlN crystal, as shown in Figure 3. Cracks and pinholes in the material grown at 10 mm distance for 15 hrs can be observed in Figure 3 (left). Complete coalescence of individual islands was achieved at the same growth temperature by increasing the growth time from 15 to 28 hours. Pinholes and cracks that originally existed in the earlier stages of growth were overgrown by single crystalline AlN, as shown in Figure 3 (right). All the features seen in this image (cracks, holes) are below the top surface of the crystal and can be seen because of the high transparency of single crystalline AlN. This was observed by translating the focal plane of the optical microscope through the crystal. Optical images of the crystal surface revealed steps indicative of step-flow growth, as seen in Figure 4. The growth steps are evident at higher magnifications (Figure 4 (left)), while the cracks in the material can be observed at lower magnification (Figure 4 (right)). An SEM image of the cross-section obtained by cleaving is shown in Figure 5 (left). The image shows well-aligned cleavage facets and stepped growth surface confirming the step-flow growth mechanism. XRD analysis showed that the grown material was single crystalline and epitaxially grown on the AlN/SiC seed. The 2θ scan showed a reflection peak at 36.32°, corresponding to the expected position of the (0002) reflection of the wurtzitic AlN, Figure 5 (top right), which confirmed the epitaxial relationship of AlN with SiC in the c-direction. The (0002) rocking curve shown in Fig, 5 (bottom right) had a FWHM of 0.8°. High density of defects that originate from both the SiC substrate and the growth process contributed to the width of the peak.

4 Discussion

Based on the EDX analysis, the hexagonal features that appeared at the surface of the seed at low temperature and large source-to-seed distance were an alloy of AlN and SiC. In the regions of the seed without growth, the epitaxial MOCVD AlN layer could not be detected. This implied that the MOCVD-grown AlN nucleation layer sublimed from the substrate, followed by the sublimation and re-deposition of SiC. This observation emphasizes that two competitive processes occur in the initial stage, i.e., (1) AlN deposition on the SiC seed, and (2) sublimation of the AlN epilayer and the SiC crystal substrate. Although SiC is a thermally stable material, in the presence of Al vapors, it decomposes at temperatures as low as 1700°C. The SiC decomposition rate was slow enough up to a temperature of 1930°C to allow growth of single crystalline AlN. Above this temperature limit, decomposition of SiC became severe and prevented growth of single crystalline AlN.

Better crystal coalescence, although still incomplete, was achieved at a short source-to-seed distance, which resulted in a ~50% higher growth rate. This result is consistent with the notion that growth was controlled by the gas-phase mass transfer processes (diffusion). If the vapor-phase diffusion is the rate-controlling factor, then one would expect the growth rate to increase with decreasing source-to-seed separation distance. Such analysis is presented elsewhere [18]; it shows that the growth rate is well-described by a vapor phase diffusion controlled model, which takes into account the equilibrium of the gas phase above the source and considers only axial concentration and temperature gradients in the vapor phase [18]. Predictions made by the diffusion model at a 10 mm source-to-seed distance were consistent with the actual growth rate, while at a distance of 35 mm, the model underestimated the growth rate. In this case, the axial temperature gradient induces buoyant forces and the resulting convective flow augments the growth beyond that predicted by the diffusion model.

Finally, coalescence was achieved at a growth temperature of ~1930°C and a growth time of 28 hours. Pinholes and cracks that originally existed in the earlier stages of growth were overgrown by single crystalline AlN. Crack formation is attributed to thermally induced stresses as a result of the thermal and lattice mismatch between the SiC and AlN. Pinholes observed in Figure 3 could result from two sources: 1) micropipes present in SiC substrates, and 2) growth conditions. Two distinct situations could arise during growth over the existing micropipes in SiC. Some micropipes are associated with screw dislocations having a large Burgers vector [23]. It can be argued that they would be replicated into the overgrowth and would not be covered. However, if micropipes were to emit dislocations into the adjoining matrix, they could be overgrown. Pinholes could also result from non-optimal initial growth conditions, preventing the coalescence of growth fronts form different islands. Pinhole-free growth in our process was achieved only by reducing the source-to-seed distance and by increasing the growth rate and time at a seed temperature below the onset of severe SiC decomposition.

5 Summary

Growth of bulk AlN crystals was achieved on SiC seeds by sublimation of AlN powder in a nitrogen atmosphere. The benefit of using TaC crucibles for growth of bulk AlN was also demonstrated. The growth temperature, source-to-seed distance and growth time were very important parameters in the growth. The growth temperature was found to affect the nucleation stage and the mass transfer rate. The nucleation stage was very sensitive to the appropriate choice of process parameters, and was complicated due to the instability of SiC in the presence of Al vapors. Hexagonal features that initially nucleated on the substrate surface were identified as an alloy of SiC and AlN. This indicated two competing processes exist: (1) sublimation of SiC and the MOCVD-grown AlN epilayer, and (2) deposition of AlN and re-deposition of sublimed SiC. AlN growth was achieved above 1920-1930 °C. By decreasing the source-to-seed distance the crystal growth rate increased and AlN single crystals with coalesced areas of 200-300 mm^2 were grown. Pinholes and cracks, which are characteristic of seeded growth on SiC, were overgrown by single crystalline material in long growth runs. Optical microscopy and SEM cross sectional imaging revealed the step-flow growth mechanism after initial nucleation. XRD analysis confirmed that the deposited material was single crystalline and oriented in the same sense as the SiC seeds.

This work demonstrates the use of new reaction crucibles and the feasibility of SiC seeded growth for preparation of single crystalline, crack-free AlN seeds with pre-defined crystallographic orientation, which can be used for high-temperature AlN bulk growth. The high-temperature growth process yields significantly larger growth rates, as well as high uniformity required for fabrication of AlN boules. At the same time, dislocation density is anticipated to gradually decrease with boule length, thus enabling the growth of single crystalline material of higher quality than the AlN/SiC seeds. However, seeded growth technique still needs additional optimization of the crucible configuration and process parameters in order to achieve larger area and thicker crack-free AlN single crystals.

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FIGURES

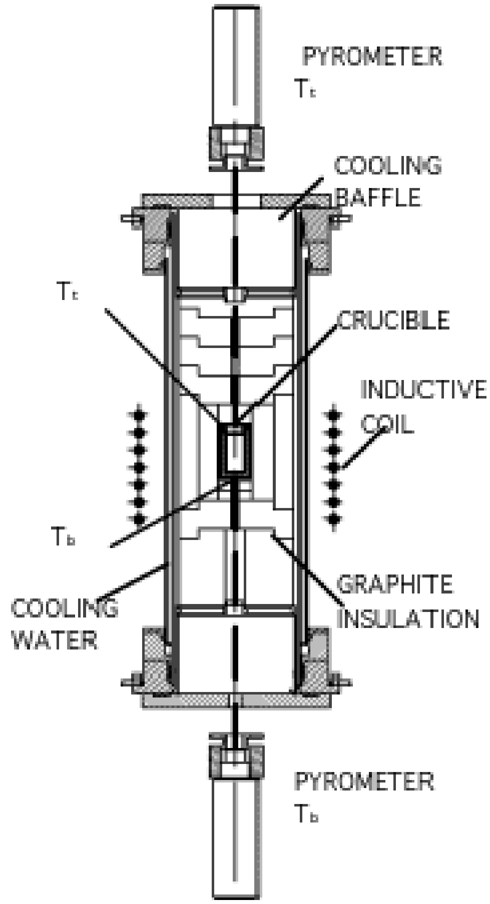

Figure 1. Schematic diagram of the inductively heated sublimation reactor. T_t and T_b refer to the top and bottom crucible temperatures, respectively.

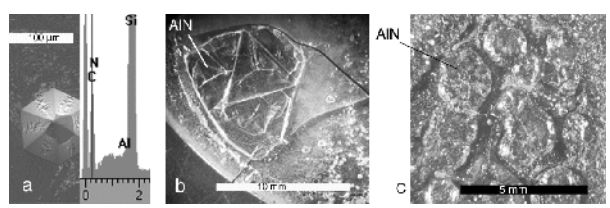

Figure 2. The effect of temperature on AlN growth observed in three samples: a) SEM image of the hexagonal features grown at T_G=1820-1830°C, EDX of these features (AlN_xSiC_y); b) AlN single crystal growth at T_G=1870-1880°C; cracks due to thermal and mechanical stresses are evident; c) colorless and transparent AlN islands with flat c-faces grown at T_G=1920-1930°C.

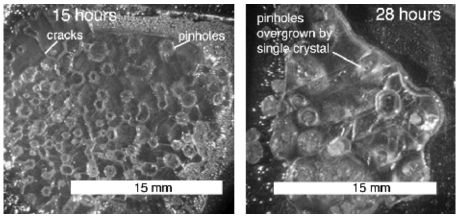

Figure 3. The effect of growth time on AlN crystal morphology at T_G=1930°C and a source-to-seed distance of 10 mm. Left: AlN single crystal, 200-300 mm^2 large and 300-350 µm thick, after 15 hours of growth; Right: AlN single crystal, 200-300 mm^2 large and 650-700 µm thick, after 28 hours of growth.

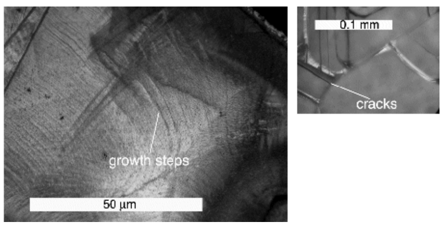

Figure 4. Growth steps on the c-plane observed by an optical microscope.

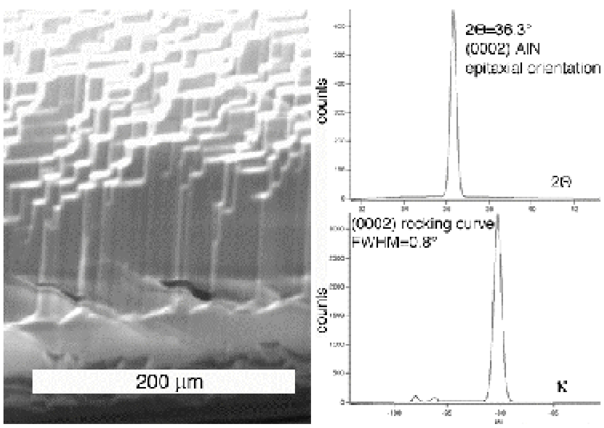

Figure 5. SEM image of a cleaved cross-section of an AlN crystal (left) and XRD analysis (right).

TABLES

Table 1. Summary of growth results

T_G (°C)	Growth time (hrs)	Source-to-seed distance (mm)	Growth rate (µm/hr)	Observations
1820–1830	36	35	0	No growth
1870-1880	36	35	5	Discrete growth of large islands, cracks
1920-1930	20	35	20	Discrete growth of mm-size single crystalline islands
1920-1930	15	10	25-30	Single crystal growth, pinholes, cracks and incomplete coalescence
1920-1930	18	10	25-30	Single crystal growth, complete coalescence