

Challenges in AlN Crystal Growth and Prospects of the AlN-based Technology

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Keywords: AlN, AlGa_xN, crystal growth, physical vapor transport, epitaxy

Abstract

Any crystal growth from the vapor phase relies on one of the two strategies to achieve large-area wafers: growth of thick layers on non-native seeds and subsequent seed removal, or gradual crystal-size expansion through an iterative re-growth process. While the former technique produces large diameter wafers faster, the latter approach yields crystals of much higher quality.

This paper focuses on the latter approach. From the equilibrium crystal shape, it was determined that the stable facets were *c*-, *m*-, and *r*-. Single crystalline AlN boules were grown in polar and non-polar crystallographic orientations; they exhibited high crystalline quality as evidenced by x-ray rocking curved below 20 arc sec and dislocation density $<10^3 \text{ cm}^{-2}$.

AlN and AlGa_xN films with varying compositions and doping levels were deposited on single crystal AlN substrates. A hydroxide passivation layer that could be removed *in situ* prior to MOCVD growth was crucial for achieving homoepitaxial growth. TEM studies confirmed epitaxial relationship and absence of interfacial oxide or defects; Al_xGa_{1-x}N films with a thickness of 0.5 μm and $x \geq 0.7$ grew pseudomorphically on AlN substrates.

INTRODUCTION

Due to their exceptional properties (direct bandgap spanning a wide range from 6.1 to 0.8 eV, high breakdown voltage (several MV/cm), high electron mobility (several $1000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$), and high saturation velocity ($>10^7 \text{ cms}^{-1}$)), the semiconducting III-nitride compounds have become the base for a new multi-billion US dollar device market over the past two decades. Although the worldwide demand for native substrates exceeded \$400M in 2010, GaN substrates are being used only in commercial fabrication of laser diodes, while AlN substrates are under development and available in limited quantities.

Due to the limited availability or prohibitive pricing, the III-nitride device technology is strongly relying on foreign substrates, which in most cases limit the quality of device layers and ultimately device performance. It has been widely recognized that the lack of thermally and lattice-matched substrates presents a major roadblock in the development of

high-performance devices with improved efficiency, reliability, and long lifetime.

Although the first AlN was synthesized in 1862 [1] by the reaction between molten aluminum and nitrogen, it took more than a century before any sizeable single crystals of AlN were grown [2]. Past efforts to grow AlN bulk crystals have explored sublimation of AlN [3], vaporization of Al [4], and solution routes [5], with sublimation yielding the most voluminous and the best quality AlN single crystals to date [6]. In recent years, several research groups [7-10] independently developed processes and models for growth of AlN crystals via physical vapor transport (PVT), which all converge to the same basic growth principle and process parameter space. All these efforts clearly demonstrated that AlN bulk crystals of very high quality and of sizes appropriate for use as III-nitride substrates can be produced by PVT.

With the availability of native AlN substrates, several studies of AlN homoepitaxy [11, 12] and AlGa_xN heteroepitaxy [13] have been reported. AlN possesses high hardness and chemical stability, and forms a stable native hydroxide surface layer upon exposure to ambient air or water [14], necessitating the development of proper surface polishing and preparation processes in order to enable high quality epitaxy. Nikishin *et al.* [15] grew AlN/Al_{0.08}Ga_{0.92}N short-period superlattices on AlN substrates and attributed the higher dislocation density observed in the superlattices to incomplete oxide removal, performed under ammonia nitridation conditions at 800 °C, prior to epitaxy. In other studies, AlN films were grown on substrates showing remnant surface scratches after chemo-mechanical polishing (CMP), evidence of incomplete removal of residual work damage. Improved surface processing is critical for achieving high-quality epitaxy on AlN. Furthermore, studies of strain relaxation in AlGa_xN alloys grown on AlN are necessary to guide device design and ensure low defect densities of the substrate are preserved in heterostructure active layers. Grandusky *et al.* [13] reported that pseudomorphic n-type Al_{0.6}Ga_{0.4}N layers up to 0.5 μm thick may be grown on AlN.

In this paper, we address AlN crystal growth, surface preparation and growth of AlN and AlGa_xN epitaxial films on native AlN substrates.

EXPERIMENTAL PROCEDURE

AlN boule expansion was pursued in an inductively-heated reactor, capable of temperatures in excess of 2400°C. Sintered AlN powder was used as a source material and growth was performed in a nitrogen atmosphere. Detailed finite element analysis was used to design radial and axial gradients to follow the desired boule expansion. Further details of the AlN boule growth have been published elsewhere (12, 13).

The *c*-plane, Al-polar, epi-ready AlN substrates were processed from AlN boules. Substrates were sliced from boules using a diamond wire saw and subsequently lapped and mechanically polished using decreasing abrasive sizes in order to remove the plastically damaged subsurface layer caused by slicing. Epi-ready surfaces, free of remnant subsurface damage from mechanical polishing, were obtained by a final CMP step in a proprietary alkaline slurry of sub-micron sized abrasives. Prior to epitaxy, as-polished substrates were ultrasonically cleaned in organic solvents and wet etched in a 3:1 solution of sulfuric and phosphoric acids for 10 minutes at 90 °C. Wet etched substrates were then rinsed and dried, and transferred into a vertical, cold-walled, rf-heated, low-pressure MOCVD reactor. The reactor was back-filled with ammonia and substrates were ramped within 5 minutes to a temperature of 1250 °C under flowing ammonia, at which point they were annealed at 1250 °C and 60 Torr for an additional 15 minutes, in order to nitride the AlN surface hydroxide and provide a surface suitable for epitaxy. More details on the AlN substrate surface preparation and chemistry can be found in [18]. AlN epitaxial layers were deposited using trimethylaluminum (TMA) and ammonia as the aluminum and nitrogen precursors, respectively, at 1100-1250 °C under 20 Torr total pressure, with V/III ratios of 180-300 in either N₂ or H₂ diluent. AlGaN films of different compositions were grown at a temperature of 1100 °C by first depositing a 200 nm thick AlN homoepitaxial layer.

High-resolution X-ray diffraction (HRXRD) was performed on a Philips X'Pert Materials Research Diffractometer using Cu *K*α radiation. On-axis RCs were recorded from the symmetric (00.2) reflection, while off-axis RCs were recorded from the skew-symmetric (10.2) reflection. Surface morphology was characterized by AFM using a JEOL JSPM-5200 in tapping mode. Electron-transparent foils, ~140 nm thick, were prepared for STEM analysis using a focused ion beam (FIB) with a Ga⁺ primary beam. Carbon (C) and Platinum (Pt) layers were applied to the film surface prior to FIB processing. STEM imaging was performed in a Hitachi HD-2300 operated at 200 kV and equipped with a high angle annular dark field (HAADF) detector for elemental contrast (Z-contrast) imaging.

RESULTS AND DISCUSSION

ALN BOULE GROWTH

Stable facets observed in AlN crystals grown close to the thermal equilibrium are *-c*, *m* and *r*, as shown in Figure 1.

Single crystalline AlN boules were grown on *+c*, *-c*, *a* and *m* oriented high-quality AlN seeds. The growth on the N-polar seeds was controlled by one growth center leading to a mirror-like growth facet, while the growth on the Al-polar seeds resulted in numerous competing growth centers. A surface energy model in conjunction with the BCF theory, developed as a framework for AlN crystal growth on different facets, supported experimental observations [ref]. AlN boule growth on non-polar seeds was controlled by step-flow growth emanating from one to a handful of growth centers and was always terminated with *m*-facets, regardless of seed orientation, as shown in Figure 2. AFM measurements were performed on the as-grown *-c* and *m*-surfaces and showed step-flow growth mechanism.

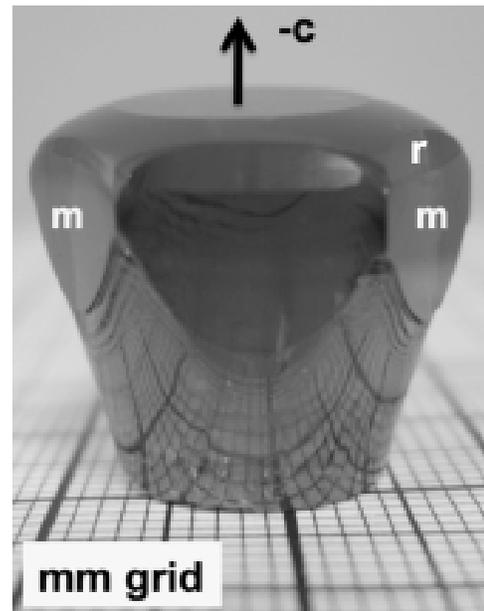


Figure 1: A single crystalline AlN boule expanded from a smaller seed; the top half of the boule was grown close to the equilibrium conditions and shows stable *-c*, *m*, and *r* facets.

Despite the excellent FWHM of x-ray rocking curves and low dislocation density, which were typically below 20 arcsec and 10³ cm⁻², respectively, formation of low-angle grain boundaries during crystal expansion and control of point defects (intrinsic and extrinsic) seem to be the remaining issues.

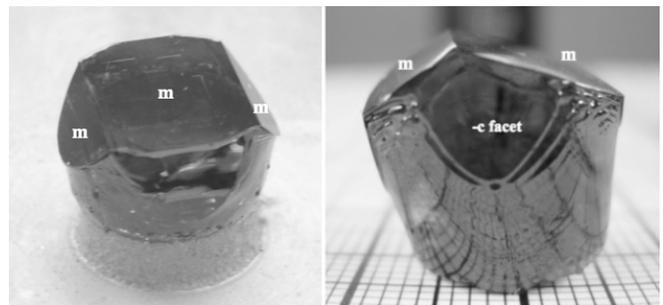


Figure 2: Boules grown on non-polar seeds: left *m*-seed, right *a*-seed. Although the seed orientation was different, both boules are terminated with *m*-facets.

AlN EPITAXY

The preparation of epi-ready AlN wafers presents unique challenges due to the polar nature of AlN, as well as its strong affinity to oxidation, and was critical for obtaining epitaxial films that maintained the crystalline quality of the substrates. While the oxide thickness on the surface of a chemo-mechanically polished AlN wafer can be controlled, the oxide cannot be removed under atmospheric conditions. We have solved these issues for polar, +*c*-oriented substrate surfaces through the use of a hydroxide passivation layer (Patent pending, US 2010/0025823). Unlike the aluminum oxide, which is thermodynamically more stable than the nitride, aluminum hydroxide can be transformed into nitride within the parameters of a commercial MOCVD process.

Typical RC widths of AlN substrates were 12-40 arcsec for the (00.2) reflection and 12-60 arcsec for the (10.2) reflection, demonstrating excellent crystalline quality. The RCs were symmetric and single-peaked. Films deposited on mechanically damaged or improperly-prepared substrate surfaces were characterized by rough surfaces, random nucleation on scratches, cracks, and asymmetric shoulders in triple axis $2\theta-\omega$ scans, indicating the films were strained due to re-nucleation on these surfaces (14). In contrast, films deposited on substrates processed by CMP and *in situ* nitridation were smooth and crack-free. HRXRD analysis indicated the films reproduced the crystalline structure of the substrates. Figure 3 shows the triple axis $2\theta-\omega$ scans of the (00.2) reflection, which are highly sensitive to lattice dilation, from an AlN substrate prior to epitaxy and the AlN film deposited at 1100 °C. The lack of any peak shifts or shoulders in the film scan indicated that the film was epitaxial and strain-free.

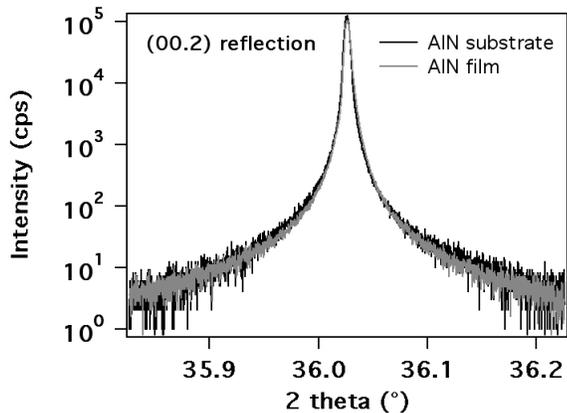


Figure 3: HRXRD scans of the AlN substrate and homoepitaxial AlN film; the two peaks are perfectly aligned, indicating a true, strain-free homoepitaxy.

Figure 4 shows a Z-contrast cross-section STEM image of an AlN/AlGaN/AlN structure grown on an epi-ready and passivated AlN substrate. The passivation layer was removed *in situ* prior to growth. Note that, remarkably, the

interface between the bulk crystal and homoepitaxial layer remains invisible, as the AlN thin film grew perfectly epitaxially on the substrate; no defects were found to emanate from the bulk/film interface. These results clearly document the importance of proper surface preparation of AlN prior to growth.

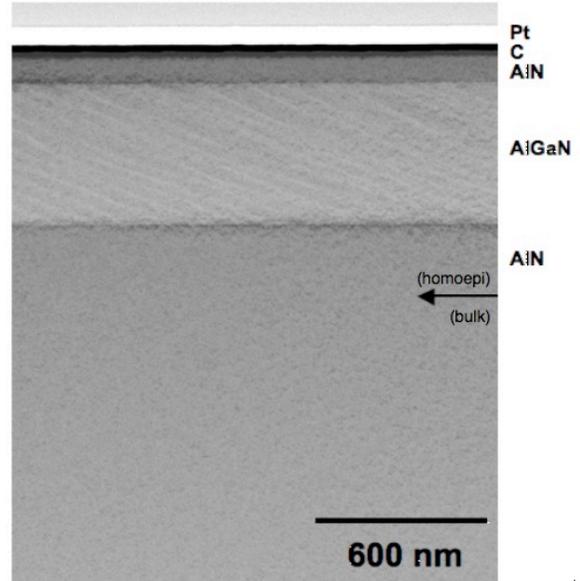


Figure 4: A Z-contrast STEM image of an epilayer heterostructure grown on an AlN substrate. No dislocations were observed in the foil. The location of the interface between the AlN substrate and AlN homoepilayer is indicated by the arrow. Note the complete absence of interface features between the bulk and homoepitaxial AlN. The AlGaN layer appears lighter due to its larger average atomic number.

CONCLUSIONS

Presently, the PVT approach to AlN crystal growth on native seeds seems to be the most promising: it delivers high-quality, low dislocation density substrates, $<10^3 \text{ cm}^{-2}$, but still requires a lot of tedious engineering work to increase the yield and scale the process beyond 1 inch. HRXRD and STEM analyses of epi heterostructure verified that CMP produced epi-ready substrate surfaces free of subsurface polishing damage, that high temperature substrate nitridation resulted in a clean surface suitable for epitaxy, and that AlN and high aluminum content AlGaN films with abrupt interfaces were grown pseudomorphically on AlN wafers, without introduction of new extended defects.

ACKNOWLEDGEMENTS

Support from ARL and DARPA through the contract # W911QX-10-C-0027 is greatly acknowledged; Dr. A. Hung program monitor.

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ACRONYMS

MOCVD: Metalorganic Chemical Vapor Deposition
 TEM: Transmission Electron Microscopy
 UV: Ultraviolet
 LED: Light Emitting Diode
 PVT: Physical Vapor Transport
 CMP: Chemo-Mechanical Polishing
 TMA: Trimethylaluminum
 HRXRD: High-Resolution X-ray Diffraction
 RC: Rocking Curve
 AFM: Atomic Force Microscopy
 STEM: Scanning Transmission Electron Microscopy
 HAADF: High-Angle Annular Dark Field
 FWHM: Full Width at Half Maximum