

A Comparison of Aluminum Nitride Freely Nucleated and Seeded on 6H-Silicon Carbide

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Abstract The crystal quality, vibrational and luminescence properties of AlN crystals prepared by the sublimation-recondensation method with free nucleation on the crucible walls or seeded growth on 6H-SiC wafers were compared. Freely nucleated needles and platelets exhibited near-band-edge cathodoluminescence, narrow Raman peak widths, and a relatively low dislocation density as revealed by synchrotron white-beam x-ray topography. In contrast, thick films deposited on on-axis, (0001) 6H-silicon carbide wafers exhibited luminescence only at 3.5 eV, had much broader Raman peak widths, and a mosaic crystal structure.

Introduction

Aluminum nitride, a wurtzite structure wide band gap (6.2 eV) semiconductor, is a good candidate substrate for GaN epitaxial films due to its relatively small lattice constant mismatch along the a-axis (-3.5%), good thermal stability (melting point >2500 °C), high resistivity, and similar coefficients of thermal expansion [1]. Bulk crystals are grown by the sublimation-recondensation technique, most successfully developed by Slack and McNelly [2] in the mid-1970's, and further advanced more recently by Balkas *et al* [3] and Tanaka *et al* [4]. In this technique, a temperature gradient is established to decompose the polycrystalline or powder source via the reaction $\text{AlN} = \text{Al}(\text{v}) + \frac{1}{2} \text{N}_2$ in a hot sublimation zone, and the vapors are recondensed (driving the reaction in the reverse direction) as single crystals, in the cooler recondensation zone. Previous researchers have either freely nucleated the crystals on the crucible walls [2,4] or on a 6H-SiC seed crystal to better control the crystal orientation [3]. The present study was undertaken to compare the crystal quality, vibrational and luminescence properties of the AlN crystals nucleated by these two different techniques.

Sample Growth

Crystals were grown in a resistively heated furnace using tungsten wire mesh heating elements. The growth ambient was pure nitrogen, maintained at pressures between 4.0×10^4 Pa and 1.11×10^5 Pa. Pure AlN sintered into a solid form was used as a source. The source and the growing crystals were contained in a cylindrical shaped pyrolytic boron nitride crucible. The freely nucleated crystals were formed on the crucible walls, subliming from a source temperature held between 2000 °C and 2200 °C. The temperature of the recondensation zone was roughly 150 °C lower. For seeded growth, silicon-face, on-axis (0001) 6H-SiC crystals roughly 2.0 cm² were employed. AlN growth on 6H-SiC was limited to a seed temperature of 1750 °C or lower, to reduce the decomposition of the SiC substrate. Typically, runs were 20 hours in duration.

Materials Analysis

Raman spectra of the samples were excited by the 514.53 nm line of an Ar⁺ laser. Raman spectra line widths were determined by curve-fitting to a sum of Gaussian lineshapes. The instrumental linewidth of the Raman spectrometer is 3.5 cm⁻¹ to 4.0 cm⁻¹. The incident laser light was plane-polarized and the polarization of the scattered light was analyzed. The Raman scattering geometries are described by the Porto notation, for example x(zz)y, where the symbols outside the parentheses (xy in the example) refer to the propagation directions of the incident and scattered light, the symbols inside the parentheses refer to the polarizations of the incident and scattered light, z refers to the crystal (0001) direction, and x,y are orthogonal to (0001). In our experiments, the incident propagation direction was neither parallel nor perpendicular to (0001), thus the experimental geometries are described by a “mixed” notation, for example x(zz)x + x(zz)y. CL spectra of the samples were obtained in a scanning electron microscope with incident electron energy of 20 keV at a temperature of T=12 K. Synchrotron white beam x-ray topographs (SWBXT) of AlN both freely-nucleated and on the 6H-SiC substrates were taken in both Laue transmission and reflection modes at the Stanford Synchrotron Radiation Laboratory, Stanford, CA. Double crystal x-ray rocking curves of the AlN/6H-SiC samples were taken at WSU.

Results and Discussion

The freely nucleated samples produced included needles up to 4 mm in length and 0.5 mm in diameter, and thin platelets up to 2 mm x 2 mm. The majority of freely nucleated samples were needle shaped, with the longitudinal axis oriented in the <0001> crystallographic direction. Occasionally, the needles had hexagonal cross-sections; more frequently, the cross-sections were incompletely formed hexagons with deep striations running along the length of the crystal. The freely nucleated samples were either colorless or slightly amber colored, possibly a consequence of residual oxygen incorporation.

On bare 6H-SiC, the AlN nucleated as islands, forming spiral patterns, suggesting that growth was enhanced at screw dislocations present in the SiC substrate. In some cases, the AlN islands would not completely coalesce, even with a relatively large c-axis growth rate. Despite undertaking growth at a low temperature (1750 °C), some decomposition of the SiC substrate occurred, and was most rapid at the micropipes. The AlN films were frequently cracked, probably as a consequence of the small difference between the thermal expansion coefficients of AlN and SiC, combined with the large temperature span (about 1800 °C) of the sublimation growth process. The characterization reported below was on a continuous AlN film approximately 100 μm thick.

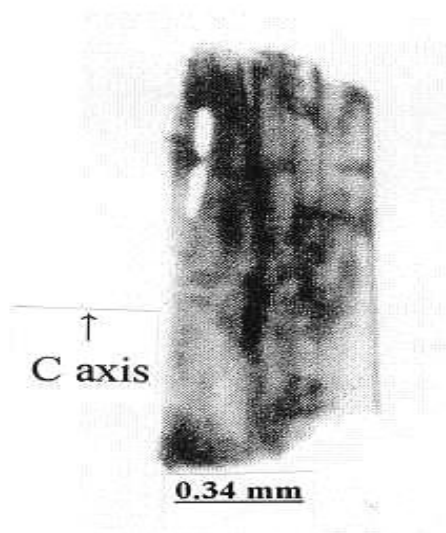


Figure 1 Synchrotron white beam x-ray topograph in Laue transmission mode from an AlN single crystal needle, diffraction vector $g = -246$, wavelength = 0.0298 nm.

Both needles and platelets were single crystal, with the wurtzite structure, as confirmed by the Laue transmission and back reflection synchrotron x-ray pattern, and contained

regions of lower amounts of defects mixed with regions of low angle grain boundaries. Figure 1 shows a SWBXT of an AlN needle in Laue transmission mode. The low transmission parts of the topograph (white regions) shows relatively lower amounts of defects while the curved black lines are low angle grain boundaries. The grains are elongated along the c-axis and the length of individual grains varies between 0.1 mm to 1.0 mm. Unfortunately, due to the small size of the needles and platelets, x-ray rocking curves could not be taken from these samples. The x-ray double crystal rocking curves for the AlN films on 6H-SiC indicated a mosaic structure with multiple grains and a full width at half maximum from an individual AlN (0002) peak of 150 arc sec.

Five of the six Raman allowed modes of AlN were observed (Figure 2(a)) in the needle shaped samples, and identified by reference to a previous Raman study of single crystal AlN [5]. The observed modes, ordered by increasing wavenumber, were: E_2 at 247 cm^{-1} , strongest for $x(yy)x + z(xx)y$ geometry; $A_1(\text{TO})$ at 609 cm^{-1} to 612 cm^{-1} , strongest for $x(zz)x + x(zz)y$ geometry; E_2 at 656 cm^{-1} , strongest for $x(yy)x + z(xx)y$ geometry; $E_1(\text{TO})$ at 669 cm^{-1} , strongest for $x(yy)x + z(xx)y$ geometry; and $E_1(\text{LO})$ at 909 cm^{-1} to 912 cm^{-1} , strongest for $x(zy)x + x(zx)y$ geometry. A distinct $A_1(\text{LO})$ peak, predicted at $\sim 890\text{ cm}^{-1}$, was not observed, but that mode is allowed only in $z(xx)z$ geometry which was not accessed in our experiments. The mode frequencies were consistently lower, by 2 cm^{-1} to 7 cm^{-1} , for our sample than reported by McNeil [5]. The reason for the discrepancy is not known; one possible cause is a difference in the concentration of oxygen or other impurities.

For the AlN on 6H-SiC, the observed modes, were (Figure 2(b)): E_2 at approximately 247 cm^{-1} , $A_1(\text{TO})$ at 601 cm^{-1} to 603 cm^{-1} , E_2 at 654 cm^{-1} to 657 cm^{-1} , a broad peak, possibly $E_1(\text{TO})$ at 647 cm^{-1} to 657 cm^{-1} , and a peak at 893 cm^{-1} to 898 cm^{-1} , which is likely a superposition of $E_1(\text{LO})$ and $A_1(\text{LO})$ lines, unresolved due to the broadening of each of these lines. The FWHM of the high-frequency peak (tentatively identified as $E_1(\text{LO})+A_1(\text{LO})$) in the AlN/6H-SiC films is much wider (29 cm^{-1}) than the FWHM of the $E_1(\text{LO})$ peak in the freely nucleated crystals (7 cm^{-1} to 8 cm^{-1}). The E_2 modes at 247 cm^{-1} and 656 cm^{-1} do not show any shift of the peak position

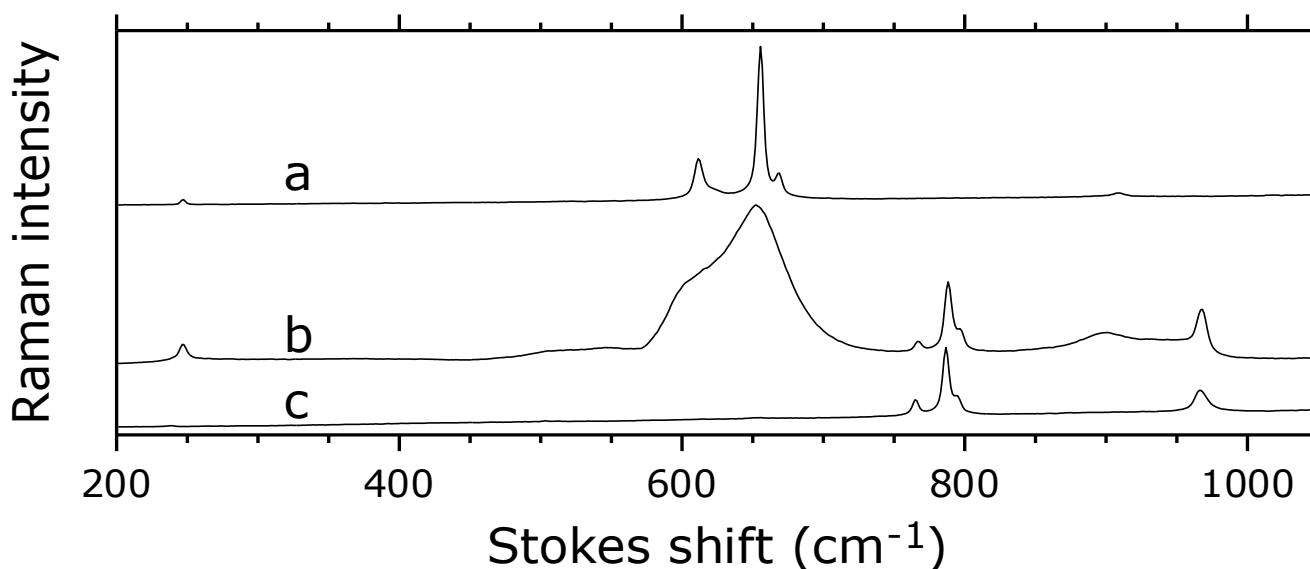


Figure 2. Raman scattering spectra of AlN from (a) a freely nucleated AlN crystal, (b) a thick film seeded on a 6H-SiC(0001) substrate, and (c) a bare 6H-SiC(0001) substrate. [Raman lines common to spectra (b) and (c) clearly originate from the substrate.]

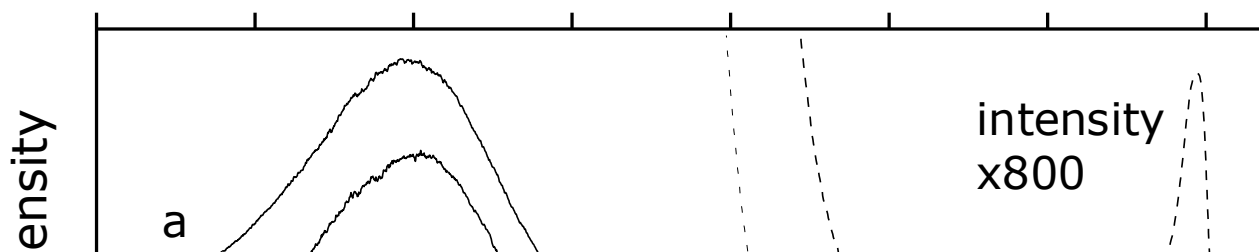


Figure 3. Cathodoluminescence spectra from AlN (a) a freely-nucleated AlN crystal, and (b) a thick film seeded on a 6H-SiC substrate.

between the freely-nucleated crystals and the thick films, and are also broadened less in comparison to the other modes. The E_2 modes are thus apparently less sensitive to the imperfections that cause the peak shift and broadening in the thick films. Our narrowest $E_2(654\text{ cm}^{-1})$ FWHM was 12 cm^{-1} , compared to value of 7.0 cm^{-1} reported by Balkas *et al* [3] for AlN/6H-SiC, and 2.2 cm^{-1} reported by McNeil and French for a bulk crystal [5].

Two overlapping near-band-edge CL peaks were observed in the freely nucleated samples: a higher energy peak located at 5.92 eV to 5.96 eV (FWHM 0.07 eV to 0.10 eV) and a lower energy peak at 5.84 eV to 5.90 eV (FWHM 0.14 eV to 0.18 eV) (Figure 3(a)). We tentatively attribute these peaks to excitons bound to impurities or point defects. A much more intense CL peak is located at 3.5 eV, with a full width of 0.7 eV. Previous researchers have proposed that the broad 3.5 eV peak is due to a combination of oxygen, nitrogen vacancies, interstitial aluminum, and point defects. The AlN/6H-SiC film does not show the exciton peak, only the peak at 3.5 eV (Figure 3(b)).

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