Different optical absorption edges in AlN bulk crystals grown in \( m \)- and \( c \)-orientations

P. Lu,1 R. Collazo,1,a) R. F. Dalmau,2 G. Durkaya,3 N. Dietz,3 and Z. Sitar1

1Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695-7919, USA
2HexaTech, Inc., 991 Aviation Pkwy., Suite 800, Morrisville, North Carolina 27560, USA
3Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia 30303, USA

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AlN single crystals were grown on \( m \)-plane (10\( \bar{1} \)0) and \( c \)-plane (000\( \bar{1} \)) AlN seeds under identical growth conditions. The \( m \)-plane AlN crystals exhibited substantially lower oxygen incorporation, \( \sim 10^{18} \text{ cm}^{-3} \), than the \( c \)-plane crystals, \( \sim 10^{19} \text{ cm}^{-3} \). By investigating optical transmission spectra, \( m \)-plane AlN had absorption bands at 4.05 and 4.35 eV, while \( c \)-plane AlN had an absorption band edge at 4.85 eV. These below bandgap absorption bands strongly correlate with the reported transitions related to Al vacancy-impurity complexes, such as the complex of an Al vacancy and two oxygen atoms, \((V_{\text{Al}}-2\text{O})^{2-}\), and the complex of an Al vacancy and one oxygen atom, \((V_{\text{Al}}-\text{O})^{2-}\), becoming the major cause for the poor, below bandgap optical transparency \((\alpha > 200 \text{ cm}^{-1})\) of these crystals. © 2008 American Institute of Physics. [DOI: 10.1063/1.2996413]

Owing to its optical1 and high-temperature electronic properties,2 single crystal AlN is a promising substrate material for nitride-based optoelectronic devices exploiting the deep ultraviolet (UV) spectral range and for high-frequency electronics. Recent progress in bulk AlN crystal growth has been achieved in polar7 and nonpolar directions.8 Limited quantities of (0001) single crystalline AlN wafers are currently available for research9 and UV light emitting diodes,10 and laser diode structures have been grown on them.11 Nevertheless, below bandgap optical absorption bands in the blue/UV range are commonly observed in bulk AlN crystals,1,12 which are detrimental to the UV transparency and hinder the development of UV optoelectronic devices that depend on substrate transparency. Previous studies considered that the absorption bands in the midgap range \((3.5–4.5 \text{ eV})\) are caused by the presence of oxygen impurities, aluminum vacancies, and their complexes.13,14 However, the direct correlation between oxygen impurities and absorption bands still remains unclear. In this letter, by recognizing the difference in impurity incorporation between the AlN bulk crystals grown on \( m \)-plane (10\( \bar{1} \)0) and \( c \)-plane (000\( \bar{1} \)) seeds, we compare their corresponding optical transmission spectra, identifying three different absorption edges and the point defects causing them.

To obtain the bulk single crystals, seeded growth of AlN on \( m \)-plane and \( c \)-plane (000\( \bar{1} \)) seeds was performed by physical vapor transport (PVT) using tungsten crucibles in an inductively heated reactor.15 Sintered AlN powder was held at the bottom of the crucible as the source material, while the seed crystals were attached at the top of the crucible. Single crystal \( m \)- and \( c \)-plane AlN seeds were obtained by cutting wafers out of freestanding AlN single crystals. The cuts were made parallel to the desired orientation. Seeds were characterized by x-ray diffraction to confirm the crystallographic orientation and crystal quality. The \( m \)-plane and \( c \)-plane (000\( \bar{1} \)) seeded growths were carried out using identical process conditions. Prior to growth, the reactor chamber was evacuated to a background pressure of \( 1 \times 10^{-5} \text{ Torr} \), and then filled with \( \text{N}_2 \) to 500 Torr. During growth, the source temperature was controlled at \( 2260–2280 ^\circ \text{C} \), and the seed was maintained at \( 60–80 ^\circ \text{C} \) lower temperature. Freestanding crystal boules, 6–7 mm in diameter, 5 mm long, were obtained in about 25 h of growth along either direction, indicating that the crystal growth rate was controlled mainly by the designed thermal profile within the growth crucible rather than by differences due to their crystalline orientation.

In order to study the optical properties of the AlN bulk crystals, \( m \)- and \( c \)-plane wafers were cut from the corresponding AlN boules perpendicular to the growth direction and polished on both sides to a final thickness of 175 \( \mu \text{m} \). Figure 1 shows the Raman spectra for the \( m \)- and \( c \)-plane AlN wafers. The spectra were taken at room temperature in the backscattering geometry \( z(xx)\bar{z} \) using an excitation energy of 2.33 eV. The observed phonon modes in the Raman spectra of \( c \)- and \( m \)-plane AlN wafers obey the \( C_{6v} \) group symmetry rules for the corresponding scattering configuration. The \( E_2(\text{low}) \), \( E_2(\text{high}) \), and \( A_1(\text{LO}) \) modes were observed in the \( c \)-plane wafer. The full width at half maximum (FWHM) of the peak for the \( E_2(\text{high}) \) mode was 3.9 cm\(^{-1}\). Raman scattering in the \( z(xx)\bar{z} \) configuration in an \( m \)-plane wafer translates into scattering in the \( x(yy)\bar{z} \) configuration for a wurtzite structure. The \( A_1(\text{TO}) \), and \( E_2(\text{high}) \), and \( E_2(\text{low}) \) modes were observed in the \( m \)-plane wafer. The FWHM of the peak for the \( A_1(\text{TO}) \) mode was 6.4 cm\(^{-1}\). The observed Raman spectra of \( c \)- and \( m \)-plane AlN wafers are in agreement with the expected modes for the given crystal orientations.16

The impurity incorporation in the \( m \)- and \( c \)-plane AlN crystals was characterized by secondary ion mass spectroscopy (SIMS). SIMS depth profiling was performed using a CAMECA IMS-6f with a 50 nA Cs\(^+\) beam over a 180 \( \times \) 180 \( \mu \text{m}^2 \) area. Three major impurities, silicon, carbon, and...
surface coverage is estimated to be around 1 eV/atom lower for a (0001) surface than that for a (0001) surface for the corresponding expected reconstructions during growth. Differences in the impurity incorporation between different facets are expected to occur during growth of bulk AlN, although they have not been directly measured. In addition, orientation dependent effects have been observed in impurity dopant incorporation of III-V semiconductors grown by metal-organic vapor phase epitaxy. The m- and c-plane grown AlN exhibited the same amount of silicon, $2 \times 10^{19}$ cm$^{-3}$, indicating that the formation energy of the silicon impurity is either similar on m- and c-planes of AlN, or it is very low, so that the silicon incorporation is controlled by mass transport and not by different surface chemistries. The m-plane AlN had twice the amount of carbon ($2 \times 10^{19}$ cm$^{-3}$) as compared to the c-plane AlN ($1 \times 10^{19}$ cm$^{-3}$).

Optical transmission measurements of the crystals were recorded between 0.8 and 5.3 eV (1550 and 235 nm), allowing the investigation of the impurity-related transition bands in the near infrared, visible, and UV range, as shown in Fig. 3. The m-plane AlN has a transmission cutoff between 4.0 and 4.1 eV, whereas the c-plane AlN has a transmission cutoff between 4.8 and 4.9 eV. Both wafers have a significant reduction in the transmission below the bandgap (6.1 eV).

Figure 3 also shows the uncorrected (spectral reflectance data is not available) absorption coefficient $\alpha$ for the two different wafers. It is important to establish that the expected absorption coefficient at the AlN fundamental absorption edge is on the order of $10^5$ cm$^{-1}$ or several orders of magnitude higher than the absorption coefficients from Fig. 3. Assuming a transition between an acceptorlike defect level and the empty conduction band, the absorption coefficient should be proportional to the product of the defect density, $N_d$, and the conduction band density of states at the transition energy, $\alpha h\omega \sim n_d h\omega (e_g - \Delta e_g)$, where $e_g$ is the energy band gap and $\Delta e_g$ is the acceptor ionization energy. Figure 4 shows a plot of the square of the product of the absorption coefficient and the photon energy as a function of photon energy in order to determine the energy of different absorption edges for both m- and c-plane AlN. Straight lines can be fitted through the measured data, and their intersections with the abscissa yield the energy position of the absorption band edges. In c-plane AlN, one sharp absorption band edge is observed at 4.85 eV, while in m-plane AlN, two absorption band edges are observed at 4.05 and 4.35 eV.

FIG. 1. (Color online) Raman spectra for the m- and c-plane AlN wafers taken at room temperature in the $z(xx)z$ geometry. The dashed lines represent the positions of the different AlN Raman peaks.

FIG. 2. (Color online) SIMS depth profile of c-plane and m-plane AlN for oxygen, carbon, and silicon.

FIG. 3. (Color online) Optical transmission spectra and uncorrected absorption coefficient $\alpha$ for the m-plane and c-plane grown AlN crystals recorded between 0.8 and 5.3 eV.

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Absorption bands below the bandgap in GaN, AlGaN, and AlN have been attributed to impurity electronic transitions related to the presence of deep acceptors. In AlN, the deep acceptors can be an isolated Al vacancy with three negative charges ($V_{\text{Al}}^{3-}$) or the Al vacancy complex with two negative charges or one negative charge ($V_{\text{Al}}^{2-}$ complex)–$^2$ and ($V_{\text{Al}}^{1-}$ complex)$^2$. The absorption band edge at 4.85 eV closely matches the energy (4.7 eV) of the transition associated with the complex of an Al vacancy and two oxygen atoms ($V_{\text{Al}}^{1-}$–2O$_2^-$), and the shallow donor or conduction band. Similarly, the absorption band at 4.05 eV is consistent with the transition (4.0 eV) associated with the complex of an Al vacancy and one oxygen atom ($V_{\text{Al}}^{1-}$–O$_2^-$), and the shallow donor or conduction band. In addition, the calculated difference in binding energy between ($V_{\text{Al}}^{1-}$–2O$_2^-$) and ($V_{\text{Al}}^{1-}$–O$_2^-$) is about 0.7 eV, which agrees well with our experimental result of 0.8 eV. Therefore, in c-plane AlN, the presence of a larger amount of oxygen, $1 \times 10^{19}$ cm$^{-3}$, the stable deep acceptor defect is the complex ($V_{\text{Al}}^{1-}$–2O$_2^-$), while in m-plane AlN, where the oxygen concentration is much lower, $2 \times 10^{18}$ cm$^{-3}$, one of the stable deep acceptor defects is the complex ($V_{\text{Al}}^{1-}$–O$_2^-$). Moreover, in m-plane AlN, another absorption band edge is observed at 4.35 eV that is clearly not related to the pure Al vacancy ($V_{\text{Al}}^{1-}$), which has a much lower transition energy of 3.4 eV. The observed absorption band is probably caused by the complex of excess ($V_{\text{Al}}^{1-}$) with some other impurity. Since the crystals contain a fair amount of Si, one could suspect a ($V_{\text{Al}}^{1-}$–Si$_{\text{Al}}^{2-}$) complex, however, this would imply interaction between second nearest neighbors, with a corresponding small binding energy. A luminescence peak corresponding to a transition at 4.4 eV has been observed for carbon doped AlN thin films, suggesting that this transition is due to carbon related defects.

In summary, we have investigated the optical transmission of m- and c-plane AlN single crystals and related the observed absorption band edges to specific point defects. At the reported particular process conditions, m-plane AlN exhibited a lower oxygen concentration, 10$^{18}$ cm$^{-3}$, than c-plane AlN, 10$^{19}$ cm$^{-3}$. However, both orientations incorporated a similar concentration of Si impurities, 10$^{19}$ cm$^{-3}$. m-plane and c-plane AlN crystals showed different absorption band edges below bandgap, which are related to the oxygen concentration in the crystals. The energies of the absorption bands, 4.05 eV in m-plane and 4.85 eV in c-plane AlN, coincide with the energy of the transitions already identified with complexes of Al vacancies and oxygen ($V_{\text{Al}}^{1-}$–O$_2^-$) and ($V_{\text{Al}}^{1-}$–2O$_2^-$), respectively. In addition, an unidentified absorption band at 4.35 eV in m-plane AlN remains unidentified and is likely caused by a complex of Al vacancy and an impurity other than silicon.

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