Broadband measurements of the refractive indices of bulk Gallium Nitride

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Abstract: New measurements of the index of refraction for free-standing samples of Gallium Nitride are reported. A simple dispersive prism technique is used to obtain the birefringent indices from 500 to 5100 nm, covering most of the transparency range of this wide band gap semiconductor. Millimeter thick samples prepared by both ammonothermal growth and hydride vapor phase epitaxy are found to have nearly identical refractive indices. The observed dispersion fits well to a two-pole Sellmeier equation with an estimated overall accuracy of ± 0.002. Our results are found to be in good agreement with previous visible and near-IR measurements on thin-film GaN samples, however we observed significantly less dispersion in the mid-IR. Moderate heating of the samples also provided a new determination of *dn/dT*.

OCIS codes: (160.4760) Optical properties; (260.1440) Birefringence; (260.2030) Dispersion; (160.6000) Semiconductor materials.

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1. Introduction

Gallium nitride (GaN) is an emerging wide band gap III-V semiconductor, whose material properties make it an excellent choice for high power optical and optoelectronic devices. In the form of epitaxial films, this material has already led to innovations in visible light sources and high performance electronics [1]. As the crystal quality improves, it will no doubt find many new applications such as high power linear and nonlinear optical devices incorporating both bulk and waveguide forms of GaN. This paper reports precise refractive index measurements in support of these present and future applications.

The stable form of bulk GaN possesses a wurtzite crystalline structure with a space group of $P6_3mc$ [2]. With a 3.44 eV bandgap at room temperature, semi-insulating GaN is transparent from 360 nm to 7000 nm [3]. Its thermal conductivity is 2.6 W/cm-K, an order of magnitude higher than that of sapphire. GaN is hard and very chemically stable with a Vickers hardness of 10.8 GPa, comparable to the common laser crystal yttrium aluminum garnet ($Y_3Al_5O_{12}$) [4]. The highly polar Ga-N bonds lead to distinct Ga and N polar c-plane faces; (0 0 0 1) and (0 0 0 −1). While the N-polar faces can be slowly etched by a few basic solutions at room temperature, etching the Ga-polar faces of GaN requires a strong hot acid [5,6]. The polarized internal field also gives rise to a strong second-order nonlinearity, $\chi_{33} = -7.4$ V/pm, which is comparable to that of potassium titanyl phosphate ($KTiOPO_4$) [7].

Bulk GaN is produced commercially by at least two different techniques. The first and most common approach to growing bulk material is Hydride Vapor Phase Epitaxy (HVPE). In the HVPE process, crystals are grown on a large flat substrate under the flow of hot ammonia and GaCl vapor. This process typically produces well oriented GaN crystals with relatively low defect densities. Dopants can be added to yield *n*-type material with resistivity as low as 1E-3 Ohm-cm or *p*-type material with resistivity as low as 10 Ohm-cm. The resistivity of semi-insulating material can be as high as 1E + 12 Ohm-cm [8]. Typical wafers are available up to 50 mm diameter after the removal of the seeding substrate. The typical HVPE growth rates of 0.1-1 mm/hr make this process suitable for large scale production.

An important alternative to HVPE is ammonothermal growth. In this process, crystals are grown from a single crystal seed suspended in a hot, high pressure solution of ammonia and mineralizer. While somewhat slower than HVPE, ammonothermal growth produces significantly higher quality bulk crystals [9]. Centimeter-scale GaN crystals grown with this technique have exhibited dislocation defect densities below 5E + 3 cm^{-2} and x-ray rocking curve FWHM linewidths below 20 arc seconds. These crystals display a high degree of lattice flatness, with curvatures greater than 1000 m, indicating a very low level of internal strain.

Gallium nitride exhibits a positive uniaxial birefringence with the optical axis parallel to the c-axis. In this paper, we report new measurements of the two refractive indices in bulk samples prepared by both HVPE and ammonothermal growth techniques. A number of previous studies have characterized the chromatic dispersion in GaN [10–18]. These studies were limited to layers of micrometer-scale thickness grown hetero-epitaxially, principally on

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sapphire substrates. They employed a variety of measurement techniques such as reflectance ellipsometry, interferometric transmittance, prism-coupled waveguide mode analysis, and transmission electron microscopy, which are well suited for work with thin-films.

Most previous reports were limited to the visible and near-IR, where they found refraction indices differing by roughly 1%. The large variations were most likely due to the wide range of growth conditions, dopants, and epitaxial structures employed in the studies. The dispersion in the mid-wave infrared was reported in only one previous investigation of heteroepitaxial GaN films. While the present work confirms and refines the previously-reported dispersion relations for the visible to near-IR, its findings vary significantly from the earlier study of the mid-IR spectral range. We also provide the first precise broadband study of refraction in bulk GaN crystals. Since the refractive indices reported here cover most of the transparency range of GaN, they should significantly facilitate the design of future broadband optical devices.

2. Experimental approach

Measurements were performed on high quality commercial samples of GaN prepared by both HVPE and ammonothermal growth. The HVPE growth sample was an unintentionally doped, *n*-type, c-axis, Ga-polar wafer measuring 1x10x10 mm. The sample prepared by ammonothermal growth, also 1x10x10 mm, was fabricated with the m-axis (1 −1 0 0) normal to the largest face to within ± 0.2 degrees. This wafer was semi-insulating, with a resistivity exceeding 1E + 9 Ohm-cm. Both wafers were delivered with a commercial epi-quality polish on the top face.

Figure 1 illustrates the transparency range of the ammonothermal GaN sample. The spectrum was measured through the large m-plane face, using a Cary 5G spectrophotometer in combination with a Cary 670 FTIR. The absolute magnitude of the transmission was calibrated using a low power 1047 nm laser. The Fresnel losses shown in Fig. 1 (dashed curve) were calculated from the Sellmeier equations discussed in the next section. The absorption features in the visible are characteristic of the significant magnesium doping used to make the material semi-insulating.

Reliably measuring the refraction over the full transparency range of GaN presented some challenges. For many applications it is critical to know the absolute magnitude of the refractive index, while in others it is more important to know the precise shape of the dispersion. In order to obtain an accurate empirical fit to the dispersion, it is desirable to measure the refraction over many wavelengths spanning the visible through the mid-wave infrared. Furthermore, it is highly desirable for the instrument to cover the entire spectral range without changing components, so as to avoid systematic errors. Our approach was to build a continuously dispersive refractometer capable of covering the broadest possible spectral range, and then calibrating the data with a more accurate laser prism coupled instrument.

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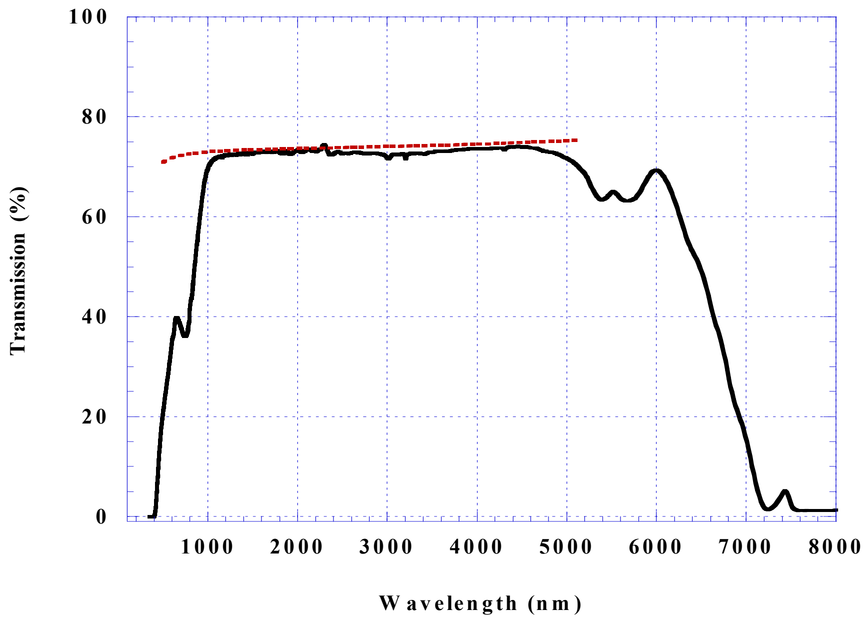

Fig. 1. Room temperature transmission of a semi-insulating GaN m-plane wafer 0.91 mm thick. Dotted line shows the calculated Fresnel losses based on the reported Sellmeier equations.

The dispersive refractometer as constructed is shown in Fig. 2. The refractometer combined an incandescent white light source, a GaN prism, and a liquid nitrogen cooled InSb detector. The response of the InSb detector limited measurements to the range from 500 to 5100 nm. The white light source was spatially filtered and collimated using a CaF_2 lens and several apertures that were laser bore-sighted. The beam was horizontally polarized by a stack of flat and parallel Cleartran (ceramic zinc sulfide) Brewster plates. The collimated 2 mm diameter beam then passed through a chopper wheel and was normally incident upon the GaN prism. Our experimental setup maintained the front surface (m-plane) normal to the incident beam. This insured that both polarizations co-propagated inside the GaN and arrived at the back surface at the same incident angle, α_W. After dispersion by the GaN, the beam propagated roughly 50 cm to the InSb detector. The detector was fitted with a narrow bandpass filter; one of a large set of commercial filters with nominal 80 nm FWHM transmission bands. Care was taken to ensure that the out-of-band blocking was adequate. The filtered InSb detector had a 0.1 mm diameter and was slowly translated across the horizontally dispersed beam. Signal averaging with the lock-in amplifier and chopper generated smooth reproducible beam profiles. Rotation of the Cleartran polarizer allowed independent measurements for the ordinary a-axis (−1 1 0 0) and the extraordinary c-axis (0 0 0 1). The recorded beam profiles were later analyzed to determine the deflected angle, θ_{bp}, corresponding to the bandpass filter centered at wavelength, λ_{bp}. After all bandpass filters were scanned, the GaN prism was removed to allow the undeflected beam to be scanned with the same detector. Profiles of the undeflected beams confirmed that the centroid of the detector's response was constant over the entire spectral response range.

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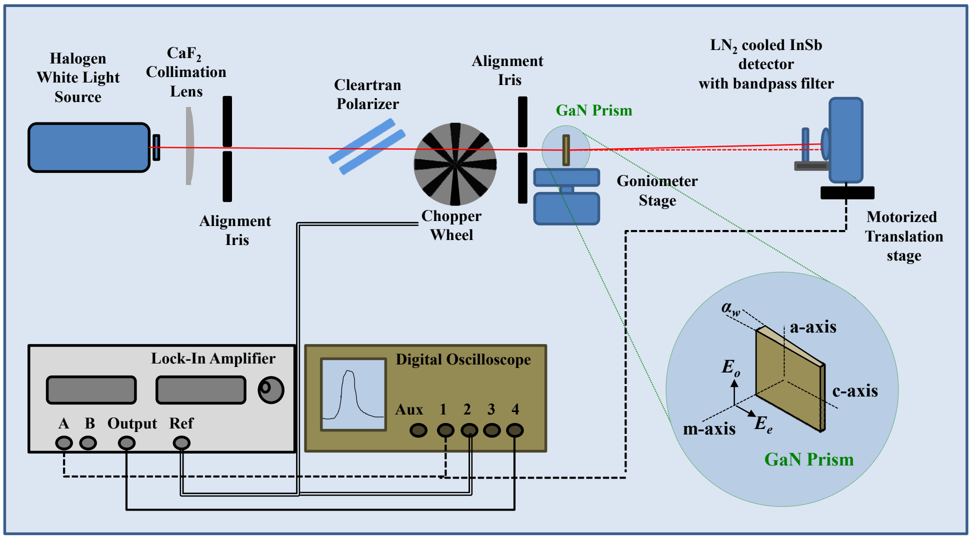

Fig. 2. Schematic of the experimental setup used to measure the chromatic dispersion of bulk GaN crystal. Inset shows orientation of GaN prism and directions of ordinary, E_o, and extraordinary, E_e, polarizations.

Knowing the wedge angle of the prism, α_w, the index of refraction can be computed from Snell's law applied to the prism's exit face:

$$n(\lambda_{bp}) = \frac{\sin\left(\alpha_W + \theta_{bp}\right)}{\sin(\alpha_W)}. \tag{1}$$

The dispersive prism was fabricated from the ammonothermal GaN wafer described earlier. The back surface, which was originally normal to the m-axis, was re-polished flat with a small angle about the a-axis, as shown in the inset of Fig. 2. With the incident beam normal to the m-plane of the front face, the beam was refracted into the m-c plane. The lower index ordinary ray of the GaN was polarized parallel to the a-axis, forming an S-wave with the back surface interface. The extraordinary ray was polarized parallel to the c-axis, forming a P-wave with the back surface.

Measurement errors were identified, and reduced wherever possible. Due to the nature of the refractive index, it was necessary to account for both random and systematic errors. Random errors that varied with each measured wavelength principally affected the shape of the dispersion curve, but not its magnitude. These errors were dominated by uncertainties in the location of the beam centroid as well as the bandwidth of the bandpass filters. Beam centroids were computed using a Gaussian fit of the full beam profiles. Uncertainties in the beam position were estimated from the centroid's variation with fits to the upper half of the beam profile. This led to a mean estimated error in the beam deflection angle of $\pm$ 0.07 mrad. The vertical error bars on the measured refractive indices displayed in Fig. 3 reflect these estimated uncertainties in the centroid position of the deflected beam. The horizontal error bars represent the measured FWHM of the spectral bandpass filters.

Systematic errors principally affected the magnitude of all the index measurements. The largest of these involved uncertainty of the prism wedge angle. This angle was measured with a Vernier-scaled goniometer to be $\alpha_W = 74.7 \pm 0.3\,\text{mrad}$. The precision of this measurement was limited by the resolution of the goniometer and flatness errors in the prism facet. This uncertainty in the wedge angle translates to a potential index error of $\Delta n = \pm 0.006$. Systematic errors in the sample-to-detector distance were estimated to be the second largest,

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contributing $\Delta n = \pm 0.0016$. To minimize these errors, the refraction measurements were repeated using independent alignments and different spots on the GaN prism. The standard deviation of the repeated indices was found to be 1.8E-4. This is roughly the same magnitude as the centroid error bars displayed in Fig. 3.

To improve the accuracy further, the refractive indices were also measured with a Metricon 2010/M Prism Coupler refractometer. This instrument can yield excellent accuracy when coupled to a laser source with high beam quality. In these measurements, the laser sources were at 0.6328 μm, 0.7800 μm, 1.057 μm, 1.310 μm, and 1.546 μm. The instrument used a standard Rutile prism whose index was calibrated at each wavelength with a reference Hi-Index glass sample provided from Metricon. The recorded index values were averaged over ten instrument scans. After calibration, test measurements on an undoped YAG plate were found to match literature values with a standard deviation of 1.6E-4. The m-plane face of the sample was measured and the polarizations aligned with the oriented wafer edges. The indices measured on the Metricon for the ammonothermal GaN wafer are plotted in Fig. 3.

The indices measured with the Metricon refractometer for the five laser lines were used to refine the value of the wedge angle of the GaN prism. As discussed above, this approach reduces the principal systematic uncertainty in the dispersive measurement and improves the absolute value of the refractive indices without modifying the shape of the dispersion. The angle correction was applied in an iterative process to best match the Sellmeier fits of the dispersive data to the Metricon calibration points. The standard deviations of the Sellmeier fit to the Metricon calibration points were calculated to be 1.6E-4 and 4.0E-4 for the ordinary and extraordinary waves, respectively. Details of the Sellmeier equations will be discussed in the next section. Figure 3 plots the corrected refractive index measurements and the fits.

The Metricon refractometer was also used to measure the free standing HVPE sample discussed earlier. Due to the cut of this wafer, only the ordinary ray could be measured. For the wavelengths tested, index for the HVPE sample was consistently 4.8E-4 higher than for the ammonothermal wafer. This small increase is close to our measurement uncertainty, but could also be a signature of residual strain in the HVPE material.

Finally, the temperature dependences of the indices were measured using the dispersion technique describe above. In this case, the sample was mounted on a temperature-controlled stage and the deflection was monitored for five temperatures ranging from 20 °C to 80 °C. For this experiment, the white light source was replaced with a low power cw laser that was deflected by the GaN prism. This provided more precise spectral and beam centroid data. The deflection was found to vary linearly with temperature over the range explored. The linear temperature coefficients for the refraction were found to be $dn_o/dT = +5.6 \pm 0.1 \cdot 10^{-5} K^{-1}$ and $dn_e/dT = +5.8 \pm 0.1 \cdot 10^{-5} K^{-1}$ at 532 nm. With a 1047 nm laser, the temperature coefficients were found to be $dn_o/dT = +3.2 \pm 0.1 \cdot 10^{-5} K^{-1}$ and $dn_e/dT = +5.4 \pm 0.1 \cdot 10^{-5} K^{-1}$.

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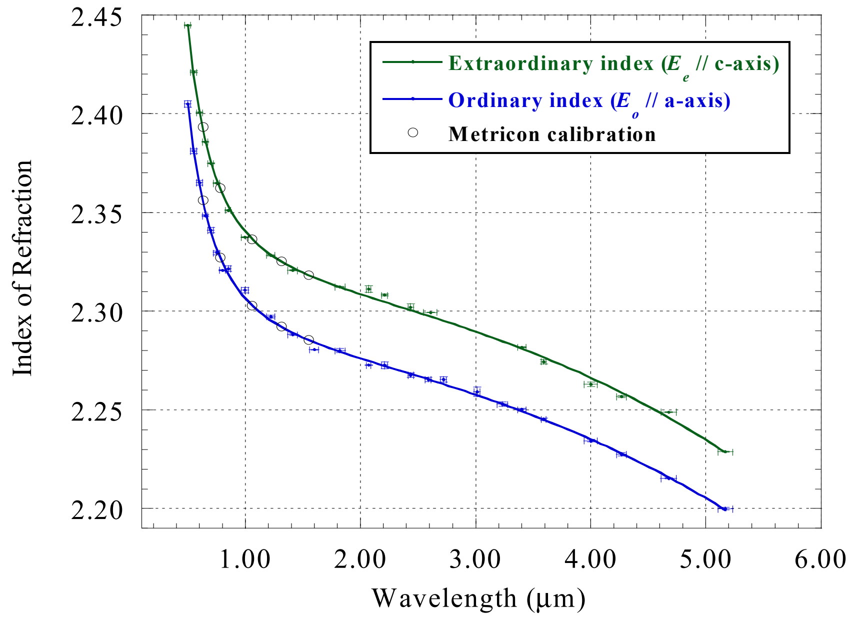

Fig. 3. Room temperature measurements of the refractive index of bulk GaN. Error bars and Metricon calibration points are discussed in the text. The solid curves are the best fit two-term Sellmeier Eqs. (2) and (3).

3. Results and discussion

The measured values of the refractive index are plotted in Fig. 3 with the estimated errors bars discussed in the previous section. The c-axis (n_e) and a-axis (n_o) data were fit to the standard two-pole Sellmeier equations:

$$n_e(\lambda) = \sqrt{1 + \left(\frac{4.347\lambda^2}{\lambda^2 - (0.1781)^2} \right) + \left(\frac{2.964\lambda^2}{\lambda^2 - (15.23)^2} \right)} \tag{2}$$

$$n_o(\lambda) = \sqrt{1 + \left(\frac{4.199\lambda^2}{\lambda^2 - (0.1753)^2} \right) + \left(\frac{3.625\lambda^2}{\lambda^2 - (17.05)^2} \right)} \tag{3}$$

where λ is the wavelength in microns. These equations fit the measured indices with overall standard deviations of 1.8E-3 and 1.7E-3, respectively. The fits should be more accurate in the calibrated spectral range from 633 to 1546 nm, as discussed in the previous section.

As mentioned above, several previous studies reported the refractive index dispersions in GaN [11–18]. Figures 4(a) and 4(b) compare fits by Chowdhury *et al.*, Sanford *et al.*, Pezzagna *et al.*, and Rigler *et al.* to the polarized Sellmeier equations over their reported ranges of validity in the visible and near IR for the extraordinary and ordinary polarizations, respectively. In this spectral range, the indices of the present work lie within the envelope of the values in the previous reports. In the near IR, the best agreement appears to be with the reports of References 13, 14, and the Ga-polar results of Reference 18. The more significant departures (as large as 1%) from the previously reported fits near the blue end of the spectral range may be attributed to modifications of the band edge by doping. Note that these departures are significantly larger than the error estimates discussed above.

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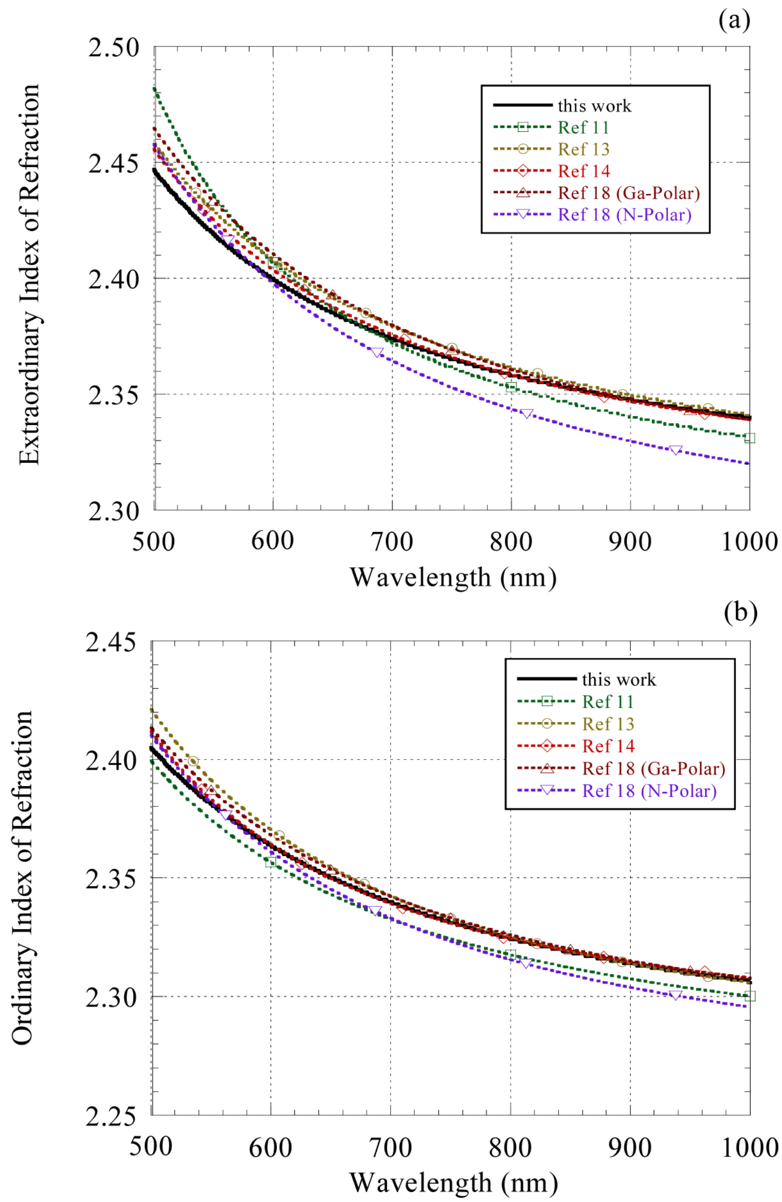

Fig. 4. Comparison of visible and near-IR Sellmeier fits of the extraordinary and ordinary refractive index of GaN.

Figures 5(a) and 5(b) show that dispersion in the mid-IR is very different in comparison with Reference 11, the only other report in this spectral range. This applies especially to the extraordinary ray, where the index departure is as large as 3%. While the index would be expected to display some dependence on the free- carrier density, it seems unlikely that such a

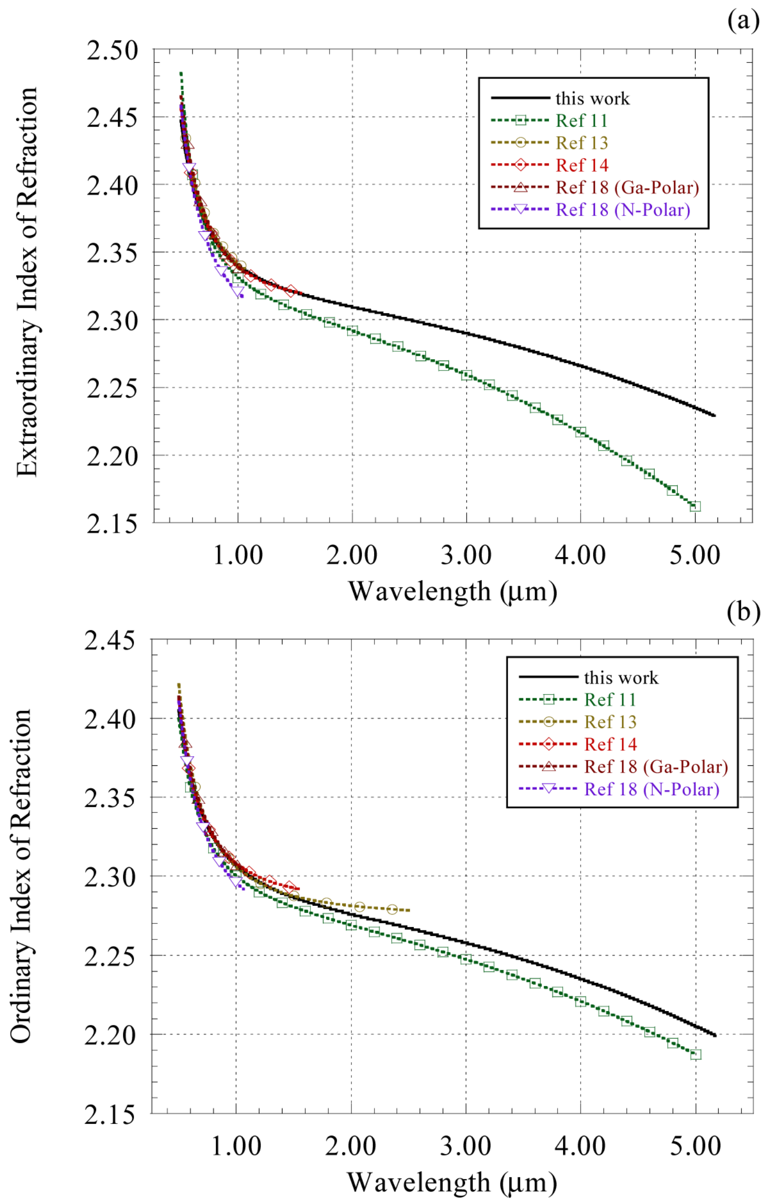

Fig. 5. Comparison of mid-IR Sellmeier fits of the extraordinary and ordinary refractive index of GaN.

large index modulation would occur in the absence of strong absorption features. Future studies should be performed to resolve this ambiguity in the mid-IR dispersion.

4. Summary

We have measured the extraordinary and ordinary refractive indices of bulk GaN grown by the ammonothermal technique. A dispersive refractometer was constructed to cover most of the broad transparency range of this wide-gap semiconductor. The results were calibrated in the visible to near-IR range with a standard prism-coupled instrument, and fit to a two-term Sellmeier equation. Standard deviations and error bars of both polarizations were approximately 2E-3. Controlled heating of the sample above room temperature produced

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$dn/dT \approx 5E\text{-}5\ K^{-1}$. Visible and near-IR tests on an *n*-type HVPE grown GaN wafer produced virtually the same refractive index as the ammonothermal crystal. The bulk refractive indices reported here are in reasonable agreement with previous reports of thin film measurements for the visible to near-IR range. However, we find significant differences in the mid-IR dispersion in comparison to the single previous report in this spectral range. Further refinement of the determination of refractive indices in this promising optical material is suggested.

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