

Refractive indices of ZnSiN₂ on *r*-plane sapphire

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II–IV–N₂ wide band gap semiconductors such as ZnSiN₂, ZnGeN₂, and ZnSiGeN₂ have potential uses for nonlinear materials and as lattice matching compounds for the growth of SiC and GaN devices. In this study, the dispersion of the TE and TM indices of refraction has been measured systematically using the prism coupling technique for an orthorhombic ZnSiN₂ epitaxial layer grown on *r*-plane sapphire. The resulting index dispersion is extracted from the measured optical modes using a layered biaxial waveguide analysis, which shows that although the ZnSiN₂ crystal is orthorhombic, for practical purposes it can be treated as a uniaxial material.

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Recently, wide band gap II–IV–N₂ semiconductors such as ZnSiN₂, and ZnGeN₂ and ZnSiGeN₂ have been synthesized, but very little is known about their band structure, optical properties, or electronic properties.^{1–5} Bulk crystals are hard to synthesize because high temperatures and pressures are required. The crystal phase of these compounds has been observed to be orthorhombic, wurtzite, or monoclinic depending on the method of growth, preparation, and analysis.² In the report of ZnGeN₂ in the monoclinic phase, the angle β was reported to be 118°53', which is very close to the wurtzite structure value $\beta=120^\circ$. Band gaps ranging from about 2.6 to 4.3 eV can be expected depending on crystal structure and composition.⁵ Moreover, the atomic arrangement of the (001) surface in an orthorhombic crystal structure with space group *Pna*2₁ is hexagonal. This leads to the attractive possibility that the II–IV–N₂ compounds could be lattice matched to other wide band gap semiconductor lattice constants. Simulation indicates that by varying the alloy composition the lattice constants can be varied with the following ranges: 3.052–3.213 Å for the *a* axis and 4.976–5.147 Å for the *c* axis. Potentially this matches well with lattice constants of GaN where *a*=3.189 Å, *c*=5.185 Å, and 4H SiC where *a*=3.073 Å and *c*=10.53 Å. In the case of GaN, where at present there is no native substrate available, these materials may offer additional flexibility in device design and growth.⁶ Other potential applications include use as a dilute magnetic semiconductor.⁷

In this investigation we report the visible wavelength index dispersion of a ZnSiN₂ film, grown by metalorganic

chemical vapor deposition, in order to ascertain the suitability of films to act as waveguides. The ratio of Zn to Si in ZnSiN₂ can be varied under growth conditions. In the film studied the Zn and Si atoms were present in equal amounts and were verified by SIMS analysis to be constant ratio throughout the film. The film studied was deposited on a <50-nm-thick *a*-plane GaN buffer layer grown on *r*-plane sapphire. The film was visually transparent, had a very smooth morphology, and was thick enough (~1 μm) to support multiple modes. At room temperature, the absorption edge of the film was not sharp and photoluminescence was not observed following excitation by either a HeCd laser at 325 nm or a more powerful, multiline Ar⁺ laser at 275–305 nm. This is consistent with the ZnSiN₂ having an indirect band gap as predicted theoretically.^{4,8}

Prism coupling experiments using a birefringent rutile TiO₂ prism were carried out using a modification of the custom-built apparatus previously described.^{9,8,10} The study of orthorhombic ZnSiN₂ films on *r*-plane sapphire is much more complicated than previous studies of wurtzitic AlGaIn on *c*-plane sapphire because the film is potentially biaxial in nature and the orientation of the uniaxial substrate could be expected to have an effect. Therefore, the experimental apparatus was modified so that the sample could be rotated azimuthally with respect to the incident plane of light. Care was taken to maintain the same spot on the film to avoid errors in thickness. As shown in Fig. 1, for a given wavelength and incident TE polarization, the effective index changes periodically with the azimuthal angle between TE_{min} and TE_{max}. By contrast, the effective index for incident TM polarization (not shown) is nearly equal to the TE_{min} value but does not change with azimuthal angle. The data in Fig. 1 can be considered raw experimental data since they neglect

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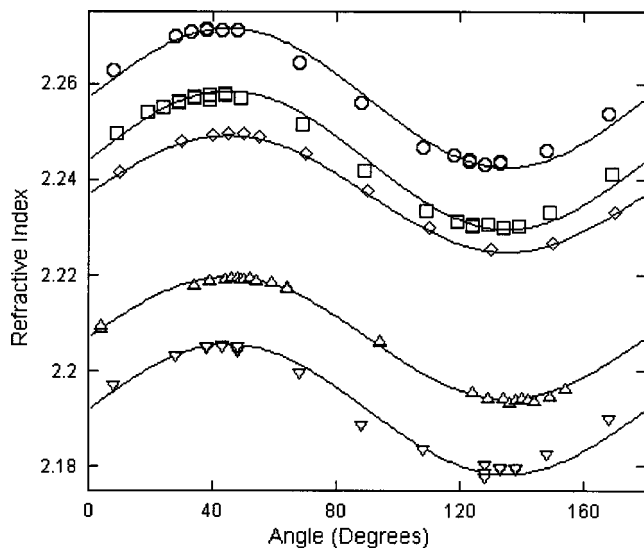


FIG. 1. Initial modal refractive index data as a function of film orientation for TE polarized light. Each curve is for prism coupling at a different wavelength of light. TM modal indices were not observed to change significantly as a function of angle and are not plotted.

the effect of the birefringent substrate and the biaxial nature of the film. To extract the refractive indices, the influence of the birefringent substrate must be estimated, and the crystal orientation of the film must be found.

As depicted in Fig. 2, the optical axis (crystallographic z' axis) of r -plane sapphire is oriented 57.6° from the normal, and the crystallographic x' axis is parallel to the substrate. The crystal orientation of the film was assumed to be that measured by x ray performed in reference films grown in the same reactor.⁴ The y axis of the ZnSiN_2 film is normal to the substrate, the x axis is parallel to the x' axis of the substrate, and the z axis is parallel to the projection of the z' axis of the substrate on the film plane. Fortunately, the refractive index of the waveguide biaxial film is high enough to minimize penetration of the modal field into the negative uniaxial substrate cut at an angle with respect to the optical axis. Thus the guided TE modes were polarized mainly along the x and z axes, while the TM modes were mainly along the y axis. The sapphire could then be treated as an isotropic material

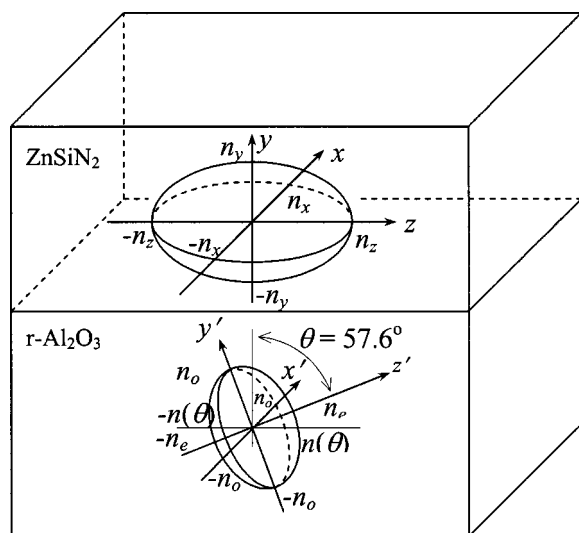


FIG. 2. The relative crystallographic orientation of ZnSiN_2 with respect to the r -plane sapphire it was grown on.

with index of refraction calculated using the sapphire's ellipsoid indices under the assumption that the electric flux density vector was polarized along the x , z , and y directions, respectively. We refer to these indices as n_{sx} , n_{sz} , and n_{sy} . The n_{sx} index is equal to the ordinary index of sapphire, while n_{sz} and n_{sy} are defined by both ordinary and extraordinary indices and by the angle θ . The sapphire's ordinary and extraordinary indices at wavelengths of interest were calculated using handbook data.¹¹

For a given mutual orientation of crystallographic axis of the film and the substrate, the contribution of substrates' birefringence to the modal indices will reduce the index of TE modes polarized in z direction. This may reduce or increase the observed birefringence of the modal indices TE_{max} and TE_{min} depending on whether the TE_{max} indices correspond to modes polarized along z or x axis, respectively. This uncertainty was resolved by running the fitting algorithm to extract the principal film indices and assuming both possibilities: $n_z > n_x$ and $n_z < n_x$. The fitting error for the case $n_z > n_x$ was consistently smaller by about 25%–40%, compared to the case $n_z < n_x$. Thus we concluded that the birefringence of the film is slightly compensated by the birefringence of the substrate.

As mentioned previously, the film samples under study contained a thin, ~ 40 nm a -plane GaN buffer. For accurate determination of the ZnSiN_2 indices based on the measured modal indices, the buffer layer has to be explicitly included into the model. The buffer's index n_b of refraction¹² was calculated for all wavelengths of interest, while the buffer thickness was one of the independent variables in the analysis.

Taking into account the simplified consideration of the above-noted uniaxial substrate, the dispersion formula for TE modes polarized along one of the principal axes follows a conventional formula for a two-layer isotropic waveguide.¹³

The known parameters are the refractive indices of substrate and buffer calculated as described above and the measured modal indices. The unknown variables are the film index n_f and the buffer thickness d . The thickness of the film is constant for all modes, wavelengths, and polarizations. By minimizing root mean square deviation of the difference between the thickness of the individual modes (for specific wavelengths and polarization) and the average thickness obtained from all modes, the best values of n_f and d to match a given set of measured modal indices n_N can be found. In the case of TM modes, the formulas for isotropic films cannot be used because the TM modes always have an electric field component parallel to the plane of the film. Thus, the birefringence of the film has to be explicitly taken into account.

Using the above-mentioned procedures, modal indices were obtained for each wavelength and polarization. From these the principal film indices were extracted and provided in Table I. The TM indices represent the averaged value of TM_{max} and TM_{min} , which are always within ± 0.0004 of the averaged value. Of all the above-discussed uncertainties, the most unknown is the possibility that measurements at different wavelength or polarization probed slightly different locations on the sample, resulting in tiny spot-to-spot variations in sample thickness. When the analysis was allowed to consider ZnSiN_2 layer thickness variations, the analysis returned nearly identical thicknesses for all indices extracted at a given wavelength and polarization. When the polarization was changed for a given wavelength, the TM mode indicated

TABLE I. Principal refractive indices for each wavelength.

Wavelength (nm)	TE _{max}	TE _{min}	TM
457.9	2.271	2.243	2.243
488.0	2.257	2.230	2.228
514.5	2.249	2.225	2.219
632.8	2.219	2.225	2.194
676.4	2.205	2.179	2.180

a thickness that was 86 ± 13 nm thicker than the TE mode, probably due to differing waveguide confinement of the two modes. Smaller thickness variations were observed when the wavelength was changed, although it appears that the 632.8 nm data probed a thinner portion (average thickness 948 ± 40 nm) of the sample than the other wavelengths (average thickness 1048 ± 44 nm). The inclusion of the effects of the buffer layer gave better consistency of data, but the values of the layer index extracted from the experimental data changed only slightly if the buffer layer was removed from the analysis.

A recent estimate of $\epsilon_{\infty XX} = 5.0$ obtained from best fits to Fabry–Perot oscillations in IR reflectance spectra is consistent with the index values reported here.⁴ Despite its biaxial, orthorhombic crystalline structure, the most striking observation is that the TE_{min} and TM indices are nearly identical. This is consistent with the earlier observation that ZnSiN₂ is only slightly orthorhombic and therefore nearly wurtzitic with uniaxial optical properties. For the similar orthorhombic material ZnGeN₂, first-principles calculations also predict nearly uniaxial optical characteristics across the transparency region.¹ In general, the symmetry of optical indices can be higher than the crystal symmetry due to coincidental (near-)degeneracy of the optical polarizability tensor. Other orthorhombic minerals have been observed with uniaxial or even isotropic optical behavior.¹⁴ Most important, the effective birefringence in ZnSiN₂ is similar in magnitude (0.03) and wavelength dispersion to that observed in GaN, whose

nominal index value in the visible is approximately 0.2 larger.¹⁰ Thus, good optical confinement within GaN films on a ZnSiN₂ substrate can be expected at all visible wavelengths and polarizations, rendering it an excellent substrate candidate for optical as well as crystallographic reasons.

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