SHG SPECTROSCOPY OF GALLIUM NITRIDE THIN FILMS ON SAPPHIRE
WITH ULTRASHORT PULSES

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ABSTRACT

SHG SPECTROSCOPY OF GALLIUM NITRIDE THIN FILMS ON SAPPHIRE WITH ULTRASHORT PULSES

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We present results of ultrafast second-harmonic generation spectroscopy of GaN/Al₂O₃ samples. We develop a formalism to calculate the nonlinear response of thin nonlinear films excited by an ultrashort laser source (Ti:Al₂O₃). and we use this formalism to extract $\chi^{(2)}_{zzz}(\omega = 2\omega_0)$ and $\chi^{(2)}_{zzz}(\omega = 2\omega_0)$ from our SHG measurements over a two photon energy range of 2.6-3.4 eV. By comparing spectra from several samples, we find a weak sub-band gap enhancement of $\chi^{(2)}_{zzz}(\omega = 2\omega_0)$ at a two photon energy of 2.80 eV that is not present in $\chi^{(2)}_{zzz}(\omega = 2\omega_0)$. This enhancement is independent of the carrier concentration, intentional doping, and presence of the "yellow luminescence band" defects. This feature may result from a three photon process involving a midgap defect state. We analyze three photon processes that include a defect state with group theory and demonstrate that several processes contribute to $\chi^{(2)}_{zzz}(\omega = 2\omega_0)$ but not to $\chi^{(2)}_{zzz}(\omega = 2\omega_0)$. In addition, we determined sample orientational miscuts by rotational SHG, and we found that these miscuts do not generate strain induced interface states. We determined a Sellmeier dispersion relationship for the index of refraction of GaN by a novel light transmission method.
and we report on photoluminescence of our GaN/Al₂O₃ samples.

In a second project we have designed and built a nonlinear optical microscope. We have used the new tool to perform preliminary investigations of the nonlinear optical properties of carbon nanoropes. We suggest that nonlinear optical microscopy is a potentially useful technique for analyzing carbon nanotube symmetry, as well as in studies of other heterogeneities. Finally, we place an upper limit on the dominant second order hyperpolarizability, $\alpha^{(2)}$, of carbon nanotubes based on our nonlinear optical microscopy measurements.
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Chapter 1

Introduction

Nonlinear optical spectroscopy has a rich history as a probe of condensed matter systems. Our understanding of factors that influence the nonlinear optical properties of materials has continued to evolve in studies of bulk materials, surfaces, and solid and liquid interfaces. One of the first experiments to address these areas was performed by Chang, Duncan, and Bloembergen. They measured second-harmonic generation from several zincblende semiconductors and determined the dispersion of the second-order susceptibility of these semiconductors [1]. Their investigations demonstrated a correlation between the second-order nonlinear susceptibility and semiconductor band structure.

More recently, nonlinear optical spectroscopy has focused on three areas: the observation of the electronic and optical properties of solid/solid interfaces [2, 3, 4, 5], the determination of symmetry of condensed matter structures [6, 7, 8, 9], and the detection of defect states [10, 11, 12]. The application of nonlinear optical spectro-
scopies as a probe of these features stems from its high sensitivity to symmetry. The symmetry of a material determines its unique nonzero second-order susceptibility elements, whose amplitude and transformation properties in turn determine the sample second-harmonic emission properties.

In this thesis, we are concerned with the optical properties of solid/solid interfaces, the determination of material symmetry, the observation of defect states, and bulk nonlinear optical spectroscopy. Experimentally, we have performed ultrafast nonlinear optical spectroscopy of GaN, and we have constructed a nonlinear optical microscope. The ultrafast nonlinear optical spectroscopy represents the majority of our effort and has produced a thorough investigation of the linear and nonlinear optical properties of GaN. In addition, we have designed and constructed a nonlinear optical microscope to examine the nonlinear optical properties of a variety of systems including carbon nanotubes. The latter area is an ongoing experiment that may lead to the comparison of carbon nanotube second-order susceptibility elements and the examination of nanotube symmetry. We briefly summarize each project.

Our nonlinear optical experiments of GaN were motivated by the recent investigations of the optical, electrical, structural, and defect properties of GaN [13, 14, 15, 16, 17]. These investigations stem from GaN's attractiveness as a material for electro-optic devices [18, 19]. Previous measurements of the nonlinear optical properties of GaN have been limited to a single fundamental wavelength of 1064 nm [20, 21, 22, 23]
and to nonlinear optical spectroscopy with a two photon energy greater than the band gap energy [24]. However, none of these measurements have probed the second-order susceptibility as a function of wavelength at energies less than the direct band gap. Here, defect states, such as those associated with yellow band luminescence, may contribute to the nonlinear optical properties of GaN. In addition, interface states may result from the unique structural and electronic properties of the GaN/Al$_2$O$_3$ interface, and are more easily detected against the spectrally flat bulk response at energies below the band gap.

Our ultrafast nonlinear optical investigations of GaN required a series of linear optical experiments and the development of a theory of ultrafast nonlinear pulse propagation for spectroscopic purposes. We determined a Sellmeier dispersion relationship for the index of refraction of GaN by measuring the index of refraction over 22 wavelengths from 370 to 900 nm. We incorporated the Sellmeier equation into our theory of the nonlinear optical response of GaN. In addition, we measured the photoluminescence properties of GaN. Our nonlinear spectra were independent of photoluminescent features, and were compared with theory [25].

Nonlinear optical microscopy was first developed by Robert Hellwarth and Paul Christensen in 1974 [26, 27], but has remained a relatively unexplored field. Our interest in nonlinear optical microscopy stems from its ability to spatially resolve the nonlinear optical response of materials. This is potentially valuable when conven-
tional linear microscopy is unable to resolve structural inhomogeneities. For example, linear microscopy has serious limitations in samples such as polycrystalline films that have a uniform index of refraction. In contrast, nonlinear optical processes are highly sensitive to material symmetry, and therefore a greater variety of spatial inhomogeneities. Nonlinear optical microscopy is also well suited to discriminate between nonlinear and linear materials. We are attempting to exploit this sensitivity in order to probe the nonlinear optical properties of carbon nanotubes on glass.

The synthesis of carbon nanotubes by Iijima [28] in 1991 has nurtured an exciting field of research. One of the most interesting properties of carbon nanotubes is their unique structure. Carbon nanotubes are fullerene related structures that consist of a graphene cylinder closed at each end with a cap. A (10,10) nanotube has a diameter of 1.4 nm and may have a length of a few microns. The nanotubes are packaged together to form carbon nanoropes, and the raw synthesized material consists of tangled carbon nanoropes and other carbonaceous materials. Typically, the tubes and ropes are produced by a current discharge between carbon electrodes [29]. While intensive experimental effort has been directed toward the growth of nanotubes and the characterization of the structural and electrical properties of carbon nanotubes, the linear and nonlinear optical properties of carbon nanotubes have been largely unexplored.

Our nonlinear optical microscopy of carbon nanotubes was motivated to under-
stand not only the nonlinear optical properties of carbon nanotubes, but also to distinguish nanotube symmetry. Several nanotube symmetries and morphologies have been postulated [30, 31, 32]. Nanotubes may be characterized by examining the allowed second-order susceptibility elements. The nonlinear optical microscope has high spatial sensitivity and can, in principle, examine the nonlinear optical properties of a single nanorope. In contrast, isolation of a single second-order nonlinear susceptibility from a collection of randomly oriented tubes is impossible. Our efforts so far have been directed toward the detection of carbon nanotubes, the imaging of carbon nanoropes, and the eventual symmetry characterization of a single carbon nanotube.

This thesis is organized as follows. Chapter 2 describes the theoretical basis for nonlinear optical spectroscopy. We review the physical origin of nonlinear optics and the relationship of the second-order susceptibility to symmetry. We also develop a theory of the propagation of ultrafast second-harmonic fields through a nonlinear medium. Because our fundamental light generating source, the Ti:Al₂O₃ laser, produces ~100 fs pulses, this theory is essential to describe the propagation of SH light through our quartz normalization slab and through the samples themselves. In contrast to the traditional monochromatic theory of nonlinear field propagation, our theory includes the group velocity of the nonlinear fields. We show that nonlinear optical interference is damped by group velocity mismatch between the bound and free waves. Finally, we suggest and show how the suppression of nonlinear optical
interference by group velocity mismatch may be used to easily measure ultrafast laser pulse durations.

Chapter 3 describes our experimental apparatus for nonlinear optical investigations of GaN. We highlight the characteristics of the Ti:Al₂O₃ laser and describe techniques for its operation.

Chapter 4 investigates the linear optical properties of GaN. The propagation of second-harmonic light is highly dependent on linear optical properties. We discuss techniques for measuring thin film thicknesses of GaN films deposited on a transparent sapphire substrates. A dispersion relationship for the index of refraction of GaN is determined by a novel transmission method. Finally, we distinguish our GaN samples by photoluminescence measurements. Our samples are characterized by the presence or absence of a yellow luminescence band at 2.2 eV.

The properties of GaN are described in Chapter 5. Emphasis is placed on the electronic and optical properties of GaN. We also discuss the defect structure of GaN. In addition, we introduce group theory techniques to determine optical selection rules. We use these techniques to calculate contributions to the three unique second-order susceptibility elements of GaN, \( \chi_{zzz}^{(2)} \), \( \chi_{zxx}^{(2)} \), and \( \chi_{zxy}^{(2)} \), that are resonantly enhanced when the second-harmonic photon energy is approximately equal to the band gap energy of GaN.

Chapter 6 presents our nonlinear optical experiments in GaN. We demonstrate
that SHG is highly sensitive to the miscut angle between the GaN z-axis and the normal to the GaN/Al₂O₃ surface. We calculate the SHG light transmitted through GaN/Al₂O₃. This theory includes ultrafast techniques described in Chapter 2. Second-harmonic generation of GaN in the s-in/p-out polarization reveals a slight resonant enhancement in \( \chi^{(2)}_{zzz} \) at a two photon energy of 2.80 eV. In contrast, SHG from GaN in the p-in/p-out polarization reveals that this feature is absent in \( \chi^{(2)}_{zzz} \). The feature at a two photon energy of 2.80 eV is independent of yellow band defects, and may result from an intrinsic midgap defect state. We also estimate the magnitude of the second-order hyperpolarizability and density of this defect. Using the group theory methods introduced in Chapter 5, we show that several three photon processes exist that contribute to \( \chi^{(2)}_{zzz} \) but not to \( \chi^{(2)}_{zzz} \). Finally, we perform a series of rotational SHG measurements to measure the effect of the GaN miscut on interface states. No interface states were observed in our measurements.

In Chapter 7 we discuss our ongoing nonlinear optical microscopy experiments of carbon nanotubes. The nonlinear optical microscope and techniques of nonlinear optical microscopy are described. In addition, we present our calculations of the SHG signal from carbon nanotubes.
Chapter 2

Introduction to Nonlinear Optics: Applications to Ultrafast
Second-Harmonic Generation

In 1961, P. Franken et al. demonstrated second-harmonic generation of a ruby laser pulse in a quartz crystal [33]. This marked the birth of nonlinear optics as a new field of study. This chapter serves as an introduction to nonlinear optical phenomena with an emphasis on factors that affect second-harmonic generation as a probe of condensed matter systems. These factors include origin of nonlinearities, properties of the second-order susceptibility, the relationship between symmetry and the second-order susceptibility tensor, and the propagation of nonlinear optical fields through linear and nonlinear media.
2.1 Origin of the Second-Order-Nonlinear Susceptibility

In conventional linear optics, the polarization of a medium, $P_i(k, \omega)$, induced by a light field, $E_j(k, \omega)$ are related as

$$P_i(k, \omega) = \chi^{(1)}_{ij}(k, \omega)E_j(k, \omega).$$  \hspace{1cm} (2.1)

In equation (2.1), $k$ is the wavevector of light, $\omega$ is the angular frequency of light, and $\chi^{(1)}_{ij}(k, \omega)$, called the linear susceptibility, is a second rank tensor that describes that material's response to the light field. This equation describes a local response between $P_i$ and $E_j$, i.e. $P_i$ is a function of $E_j$ and not derivatives of $E_j$. Unless otherwise indicated, we assume that the all susceptibilities are independent of $k$. Physically, the susceptibility's independence of $k$ means the media is homogeneous. The susceptibility is related to the dielectric constant, $\epsilon(k, \omega)$, and the index of refraction, $n(k, \omega)$ as

$$\epsilon_{ij}(k, \omega) = n_i^2(k, \omega) = 1 + 4\pi \chi_{ij}(k, \omega).$$ \hspace{1cm} (2.2)

We use cgs units to express equation (2.2) and all other equations in this thesis. The linear relationship expressed in equation (2.1) is invalid in the weak perturbation limit. In other words, it is valid when the applied field is much weaker than the atomic electric fields.

When a material is exposed to a strong pulsed laser source, equation (2.1) is no longer valid. Instead, the induced polarization may be expressed as a power series in
the electric fields as

\[ P_i(\omega) = \chi_{ij}^{(1)}(\omega)E_j(\omega) + \chi_{ijk}^{(2)}(\omega = \omega_1 + \omega_2)E_j(\omega_1)E_k(\omega_2) + \]
\[ \chi_{ijk}^{(2)}(\omega = \omega_1 - \omega_2)E_j(\omega_1)E_k^*(\omega_2) + \]
\[ \chi_{ijk}^{(2)}(\omega = -\omega_1 + \omega_2)E_j^*(\omega_1)E_k(\omega_2) + \]
\[ \chi_{ijk}^{(2)}(\omega = -\omega_1 - \omega_2)E_j^*(\omega_1)E_k^*(\omega_2) + \]
\[ \chi_{ijkl}^{(3)}(\omega = \omega_1 + \omega_2 + \omega_3)E_j(\omega_1)E_k(\omega_2)E_l(\omega_3) + \ldots. \] (2.3)

In this thesis, we are concerned principally with second-harmonic generation (SHG), which is mediated by the second term in equation (2.3) with \( \omega = 2\omega_0 \), i.e.

\[ P_i^{(2)}(\omega) = \chi_{ijk}^{(2)}(\omega = 2\omega_0)E_j(\omega_0)E_k(\omega_0). \] (2.4)

Since dipole allowed nonlinearities occur in GaN, the local field approximation is valid.

Once the second-order nonlinear polarization is determined from the second-order susceptibility and the incident fields, the nonlinear fields generated within the medium are determined from boundary conditions and the nonlinear wave equation

\[ \nabla \times \nabla \times E(\omega) + \frac{\epsilon(\omega)}{c^2} \frac{\partial^2}{\partial t^2} E(\omega) = -\frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} P^{(2)}(\omega). \] (2.5)

Solutions to equation (2.5) must also satisfy

\[ \nabla \cdot D(\omega) = 0 \] (2.6)
for materials with no free charge. This implies

\[ \nabla \cdot \mathbf{E}(\omega) = -\frac{4\pi \nabla \cdot \mathbf{P}^{(2)}(\omega)}{\varepsilon(\omega)}. \]  

(2.7)

2.2 Properties of \( \chi_{ijk}^{(2)}(\omega = 2\omega_0) \)

A full expression for the second-order susceptibility element that describes second-harmonic generation is

\[
\chi_{ijk}^{(2)}(\omega = 2\omega_0) = -2N\frac{e^3}{\hbar^2} \sum_{mnl} \rho_{il}^{(0)} \left( \frac{\langle \langle l | r_i | n | r_i | m \rangle \langle m | r_i | l \rangle \rangle}{[(\omega - \omega_{nl}) + i\gamma_{nl}][(\omega - \omega_{ml}) + i\gamma_{ml}]} \right.
\]

\[ + \frac{\langle \langle l | r_i | n | r_i | m \rangle \langle m | r_i | l \rangle \rangle}{[(\omega - \omega_{nm}) + i\gamma_{nm}][(\omega + \omega_{nl}) + i\gamma_{nl}]} \]

\[ + \frac{\langle \langle l | r_i | n | r_i | m \rangle \langle m | r_i | l \rangle \rangle}{[(\omega + \omega_{mn}) - i\gamma_{nm}][(\omega - \omega_{ml}) + i\gamma_{ml}]} \]

\[ + \frac{\langle \langle l | r_i | n | r_i | m \rangle \langle m | r_i | l \rangle \rangle}{[(\omega + \omega_{ml}) - i\gamma_{ml}][(\omega + \omega_{nl}) + i\gamma_{nl}]} \). \]  

(2.8)

Equation (2.8) can be derived from first principles using quantum statistical mechanics with the proper choice of the interaction Hamiltonian [34]. In equation (2.8) \(|l\rangle, |m\rangle, \text{and} |n\rangle\) are quantum mechanical states of the system; \(\rho_{il}^{(0)}\) is the unperturbed density of the state \(|l\rangle\), i.e. \(\rho^{(0)}\) is the equilibrium population distribution: \(-er_i\) is the dipole moment operator along direction \(i\); \(\hbar\omega_{nm}\) is the energy difference between states \(|n\rangle\) and \(|m\rangle\); and \(\gamma_{nm}\) is a dephasing term. The different terms in equation (2.8) correspond to different time ordering of the photons. This is discussed further in section 5.4.1.

There are a few salient features of equation (2.8) that bear discussion. First.
SHG is a virtual process, i.e. there is no population transfer, even for lossy materials. Population transfer occurs under a variety of circumstances including two common mechanisms: one photon absorption and two photon absorption. In one photon absorption, the absorption of a single photon excites a material. This process is mediated by the imaginary part of the linear susceptibility, $\chi^{(1)}$. Two photon absorption is a process in which a material absorbs two photons simultaneously. This process is mediated through the imaginary part of the third-order nonlinear susceptibility, $\chi^{(3)}$. The existence of one and two photon channels in a material does not alter the form of equation (2.8), but influences the propagation of the fundamental and SHG fields.

Second, $\chi^{(2)}_{ijk}(\omega = 2\omega_0)$ is nonzero only if the initial state $|l\rangle$ is occupied. This restriction has been exploited by J. Qi et al. to distinguish between nonlinear optical process that originate from a midgap state as opposed to the valence band [10].

Third, the second-order susceptibility is enhanced when the energy of the incident or second-harmonic photons, $\hbar\omega_0$ and $2\hbar\omega_0$ respectively, match an energy difference between two states in the medium. This phenomena forms the basis for nonlinear spectroscopy: an increase in measured SHG signal can be correlated with an electronic or vibrational excitation in the material. Often one uses SHG to probe systems that are inaccessible when using conventional linear optics or competing spectroscopic techniques. The measurement of electronic states at the interface between two materials...
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is an example of such an experiment.

Fourth, the process is symmetric in the last two indices, i.e. $\chi_{ij}^{(2)}(\omega = 2\omega_0) = \chi_{ik}^{(2)}(\omega = 2\omega_0)$. This is true for SHG but is not true in general for other second-order nonlinear processes, such as sum frequency generation (SFG) and difference frequency generation (DFG).

Fifth, $\chi_{ijk}^{(2)}(\omega = 2\omega_0)$ is zero for any media with inversion symmetry. This is obvious if one considers the following simple argument [35]. Assume a field $E(\omega_0)$ induces a nonlinear polarization, $P^{(2)}(2\omega_0)$, in a medium with inversion symmetry. Due to inversion symmetry, an applied field $-E(\omega_0)$ induces a polarization $-P^{(2)}(2\omega_0)$. However, since the nonlinear polarization results from a quadratic field, $E(\omega_0)$ and $-E(\omega_0)$ must induce the same polarization. Therefore, $P^{(2)}(2\omega_0)$ and $\chi_{ijk}^{(2)}(\omega = 2\omega_0)$ are zero for any media with inversion symmetry. The effect that the symmetry of the medium has on $\chi_{ijk}^{(2)}(\omega = 2\omega_0)$ is discussed further in the following section.

The magnitude of $\chi_{ijk}^{(2)}(\omega = 2\omega_0)$ depends on the energy of the incident laser pulse (an experimentally controllable parameter), and the dipole moments between states, which can be controlled to some extent by light polarization. Thus, although a nonlinear interaction may be enhanced by judicious choices of the laser energy and polarization, the matrix elements in equation (2.8) will limit the magnitude of the signal for fixed input energy.
2.3 $\chi_{ijk}^{(2)}$ and Symmetry

In general $\chi_{ijk}^{(2)}(\omega = 2\omega_c)$ has 18 unique elements. Group theory can be used to reduce this complexity further by determining relationships among the nonzero elements.

The present discussion focuses on the nonlinear susceptibility elements of GaN, but the general application of group theory to determine relationships among the elements of a general response function follows similarly.

The strength of group theory for determination of the relationships among the susceptibility elements arises from Neumann's principle. Neumann's principle states that any macroscopic physical property has at least the symmetry of the point group of the space group of that medium [36]. By applying the symmetry operators of the appropriate point group to $\chi_{ijk}^{(2)}$, which transforms as a three component Cartesian tensor, relationships among the symmetry elements are determined.

GaN has $C_{6v}$ or 6mm symmetry, which is the symmetry of a regular hexagon. The generators of this group are

$$C_{6v} = \{E, C_2, 2C_3, 2C_6, 3\sigma_v, 3\sigma_d\}.$$  \hspace{1cm} (2.9)

Definitions of these symbols are found in reference [36]. Note, $C_{6v}$ contains only symmetry operators in a plane. Therefore for GaN [0001], which is the cut of our samples, the surface and interface have the same nonzero nonlinear susceptibility elements as the GaN bulk. Because far fewer atoms participate in a nonlinear process
Figure 2.1: Symmetry and generators of $C_{6v}$. $\sigma_{v1}$ is a mirror plane that bisects the vertices of the regular hexagon. $\sigma_{d1}$ is a mirror plane that bisects the line segments of the regular hexagon. Additional mirror planes and rotation operators define the full symmetry of the hexagon.

that originates from the surface or interface as compared with bulk, bulk nonlinearities dominate second-harmonic generation spectroscopy of GaN.

Fig. 2.9 shows $C_{6v}$ and two generators of this group. Under the operator $\sigma_{v1}$ the coordinates transform as

$$
\begin{align*}
x & \rightarrow +x \\
y & \rightarrow -y \\
z & \rightarrow +z.
\end{align*}
$$

Similarly, $\sigma_{d1}$ transforms the coordinates as

$$
\begin{align*}
x & \rightarrow -x
\end{align*}
$$
Table 2.1: Nonzero second-order susceptibility elements for GaN

\[
\chi^{(2)}_{zzz} = \chi^{(2)}_{yyy} = \chi^{(2)}_{zzz} = \chi^{(2)}_{yyz} = \chi^{(2)}_{yyz}
\]

Since the second-order susceptibility transforms as the product of three vectors, it is clear that under the application of \( \sigma_{v1} \)

\[
\chi^{(2)}_{zzz} \rightarrow -\chi^{(2)}_{zzz}.
\] (2.12)

However, Neumann's principle requires that any macroscopic property must be invariant under the application of a generator of a point group. Therefore, \( \chi^{(2)}_{zzz} = 0 \). By similar application of the other generators of \( C_{6v} \) one can calculate the relationships shown in Table 2.1. Once the nonzero susceptibility elements are determined, the second-harmonic generated intensity as a function of crystal orientation and second-harmonic and linear light polarizations can be determined. Experimental data and calculations for GaN are presented in section 6.2.
2.4 Interference in Nonlinear Optical Measurements: The Maker Fringe Problem

In section 2.4.1 we develop techniques to analyze nonlinear optical signals from a model system. In particular we consider the second-harmonic light generated by a monochromatic laser beam propagating through a quartz slab at normal incidence. This analysis introduces the concepts of interference in nonlinear optical measurements, which can have a rather significant effect on the measured intensity. We then generalize this problem to include the second-harmonic response of a quartz wedge excited by the ultrafast light pulses used in all of our experiments. The section also introduces the nomenclature that is used throughout this thesis to describe second-harmonic signals.

2.4.1 Excitation with a Monochromatic Light Source

In 1962 P. D. Maker and coworkers experimentally demonstrated phase matching of SHG in a quartz plate [37]. In this phenomena, now called Maker fringes, the measured intensity of SHG light oscillates strongly as a function of the orientation of the quartz plate with respect to the incident beam propagation direction. The observed alternating maxima and minima in the transmitted intensity of SHG light is strongly dependent on the wavelength of the fundamental light, the index of refraction of quartz, and the thickness of the quartz slab. In order to accurately measure
$\chi^{(2)}_{ijk}(\omega = 2\omega_o)$ of our GaN samples, a full understanding of interference in these samples is required.

M. S. Yeganeh [38] developed techniques to analyze nonlinear interference in stacks of thin slabs using some of the early work of Bloembergen and Pershan [39]. Here we review the theory for the second-harmonic generated signal transmitted through a quartz slab at normal incidence.

Fig. 2.2 schematically displays the geometry of second-harmonic generation from a quartz slab and labels all of the nonlinear fields. The geometry consists of two semi-infinite linear media, labeled 0 and 2, separated by a nonlinear slab, labeled 1. The linear field propagates from the vacuum to the nonlinear quartz crystal, at $y = 0$, where it generates a second-harmonic field. This field propagates through the crystal to the second crystal/vacuum interface at $y = -d$. A second-harmonic field is transmitted through this interface and has a magnitude that depends on the boundary conditions. Generally the simple Maker fringe model assumes that multiple reflections of the second-harmonic waves and fundamental waves in the quartz crystal are unimportant. Even without incorporating these effects in the calculation, the model captures the oscillation in the SHG intensity from a nonlinear slab. In our model, we include the effects of a reflected free wave from the quartz/vacuum interface.

We used $y$-cut quartz as a normalization material in our experiments (for more detail see section 3.5). In this geometry, the fundamental field couples to the dominant
Figure 2.2: Schematic of second-harmonic fields generated in a quartz slab. The fields are labeled as in the text. The dashed line corresponds to the fundamental field. Note all fields, except the incident linear field, have an angular frequency of $2\omega$. 
nonlinear element of quartz, $\chi_{xxx}^{(2)}(\omega = 2\omega_o) = 2.2 \times 10^{-9}$ esu [40]. There are two solutions to the nonlinear wave equation (equation (2.5)): a homogeneous solution and a particular solution. We refer to the particular solution as the "bound wave" solution; the bound wave solution exists only in the nonlinear optical crystal. This field is bound to the linear field and propagates with a wavevector twice that of the linear field. This field may be written as

$$E_{b1} = \hat{x} E_{b1} e^{i(k_{b1} \cdot r - 2\omega_o t)}. \quad (2.13)$$

The subscript $b$ designates a bound wave solution. The bound wavevector, $k_{b1}$, is

$$k_{b1} = \frac{2n(\omega_o) \omega_o}{c}. \quad (2.14)$$

The magnitude of this field is calculated directly from equation (2.5) and has a value of

$$E_{b1} = \frac{4\pi P_{x}^{(2)}}{\epsilon_{b1} - \epsilon_{f1}}. \quad (2.15)$$

Note, $\epsilon_{b1} \equiv \epsilon(\omega_o)$, $\epsilon_{f1} \equiv \epsilon(2\omega_o)$ and

$$P_{x}^{(2)} = t_{01}^2(\omega_o) \chi_{xxx}^{(2)} E_x(\omega_o) E_x(\omega_o), \quad (2.16)$$

where $t_{01}(\omega_o)$ is the Fresnel transmission coefficient for light with angular frequency $\omega_o$ which propagates from vacuum into quartz. The homogeneous solution to the wave equation is

$$E_{f1} = \hat{x} E_{f1} e^{i(k_{f1} \cdot r - 2\omega_o t)}. \quad (2.17)$$
The free wavevector, \( k_{f1} \), is determined from the homogeneous solution to the non-linear wave equation and has a value of

\[
k_{f1} = \frac{2n(2\omega_o)\omega_o}{c}.
\]  

(2.18)

The magnitude of this wave is determined by continuity of the tangential components of the electric and magnetic fields, \( E_{\tan} \) and \( H_{\tan} \) respectively, at both interfaces. These boundary conditions (at \( y = 0 \) and \( y = -d \)) imply the following equations:

\[
E_{fr0} = E_{f1} + E_{b1}
\]  

(2.19)

\[
k_{fr0}E_{fr0} = k_{fr1}E_{fr1} + k_{b1}E_{b1}.
\]

\[
E_{f1}e^{ik_{f1} \cdot d} + E_{fr1}e^{ik_{fr1} \cdot d} + E_{b1}e^{ik_{b1} \cdot d} = E_{f2}e^{ik_{f2} \cdot d}
\]

\[
k_{fr1}E_{f1}e^{ik_{f1} \cdot d} + k_{fr1}E_{fr1}e^{ik_{fr1} \cdot d} + k_{b1}E_{b1}e^{ik_{b1} \cdot d} = k_{f2}E_{f2}e^{ik_{f2} \cdot d}.
\]

These boundary conditions ignore multiple reflections of the nonlinear and linear fields. Multiple reflections of the nonlinear (linear) fields modify the transmitted SHG intensity by approximately 4% (0.2%). This is a minor effect when compared to Maker fringes, for which the transmitted intensity is modified by 100%.

In equation (2.19), \( k_{b1} = k_{b1} \cos \theta \). Since our system is vacuum/quartz/vacuum, \( k_{f0} = k_{f2} \). Also note \( k_{ai} = k_{a1} \), where \( \alpha = b \) or \( f \) and \( i = 0, 1, \) or \( 2 \), since the beams propagate at normal incidence to the quartz crystal. This more general notation is introduced for consistency with the calculations of the second-harmonic fields generated from GaN/Al\(_2\)O\(_3\) films. The solution to equation (2.19) yields the magnitude of
the transmitted wave, $E_{T}^{2\omega_{0}}$,

$$E_{T}^{2\omega_{0}} \equiv E_{f2} = \left( \frac{-2k_{f1}(k_{f0} + k_{b1})}{(k_{f1} + k_{f0})^2} e^{id(k_{f1} - k_{f0})} + \frac{k_{b1} + k_{f1}}{k_{f0} + k_{f1}} e^{i\Delta(k_{b1} - k_{f0})} \right) E_{b1}. \quad (2.20)$$

The measured signal, $I_{T}^{2\omega_{0}}$ is

$$I_{T}^{2\omega_{0}} = C_{1}^2 + C_{2}^2 + 2C_{1}C_{2} \cos ((k_{b1} - k_{f1})d) \quad (2.21)$$

where

$$C_{1} = \frac{-2k_{f1}(k_{f0} + k_{b1})}{(k_{f1} + k_{f0})^2} E_{b1} \quad \text{and} \quad C_{2} = \frac{k_{b1} + k_{f1}}{k_{f0} + k_{f1}} E_{b1}. \quad (2.22)$$

We observed Maker fringes by measuring the SHG intensity from a quartz wedge excited by a Nd:YAG pumped dye laser. By translating the quartz wedge through the dye laser light, the phase difference between the bound and free waves changes as the quartz thickness changes. Fig. 2.3 demonstrates the simplified experimental geometry used to observe Maker fringes [41]. Fig. 2.4 displays the Maker fringe data and a fit to the data using equation (2.21). The salient feature of this fitting function is that the intensity oscillates as a function of the phase velocity mismatch, $(k_{b1} - k_{f1})$, times the crystal thickness, $d$.

### 2.4.2 Excitation with a Ultrafast Light Source

In linear optics, propagation of ultrafast laser pulses in dispersive media depends in part on group velocity dispersion (GVD). In this phenomena, an ultrafast laser pulse is broadened as it traverses a dispersive media. The pulse broadens more rapidly when
Figure 2.3: Experimental set up for observing Maker fringes with a monochromatic light source. The quartz wedge is mounted on a translation stage that has a direction of travel perpendicular to the laser light. The inset shows the miscut angle of the quartz wedge, $\alpha = 1.0^\circ$. 
Figure 2.4: Maker fringe data for a monochromatic light source. The figure and data are adapted from reference [41].
the medium dispersion increases and/or when the initial temporal width of the pulse
decreases. This phenomena occurs because the higher frequency spectral components
of the pulse have smaller group velocities than the lower frequency spectral compo­
nents. In most frequency ranges, materials are normally dispersive and have an index
of refraction that increases with increasing spectral frequency. This accounts for the
decrease in group velocity that occurs as the spectral frequency is increased. After
propagating through the medium, the lower frequency spectral components arise at
the beginning of the pulse and the higher frequency spectral components arise at the
rear of the pulse.

Ultrafast nonlinear pulse propagation in a dispersive media is also dependent on
GVD. The phenomena that dramatically alters the propagation of ultrafast nonlinear
fields is called group velocity mismatch. In section 2.4.1, we observed that the Maker
fringes in the SHG intensity from a quartz slab depend on the interference of the
free and bound waves (wavevector mismatch). In this section, we calculate the SHG
intensity from a quartz slab excited by a ultrafast laser pulse. We demonstrate that
the intensity depends on both wavevector mismatch and group velocity mismatch
between the free and bound waves. This difference in group velocity produces an
incomplete overlap of the free and bound waves, and hence an incomplete interference
between the waves. The interference of the bound and free waves for a monochromatic
and an ultrafast source is displayed schematically in Figs. 2.5 and 2.6.
Figure 2.5: Interference of the bound and free waves excited by a monochromatic light source. The real component of the bound (free) wave is represented by the thick (thin) line. At the end of the crystal, a phase difference exists between the two waves because of the dispersion of the crystal.
Figure 2.6: Interference of the bound and free waves excited by an ultrafast light source. The real component of the bound (free) wave is represented by the thick (thin) line. At the end of the crystal, a phase difference exists between the two waves because of the dispersion of the crystal. In addition, the free wave lags behind the bound wave because its group velocity is lower.
The bound wave, which propagates as a pulse with twice the wavevector of the fundamental pulse, \( k_b = 2\omega_o n(\omega_o)/c \), propagates through the crystal and arrives at the crystal/quartz interface before the free wave, which propagates with a wavevector \( k_f = 2\omega_o n(2\omega_o)/c \).

There have been several theoretical investigations of ultrafast nonlinear pulse propagation [42, 43, 44, 45]. The focus of these papers is to calculate conversion efficiencies for nonlinear optical crystals. In general, the papers include the effects of group velocity mismatch and GVD. Comly and Garmire [43] solve the problem of ultrafast nonlinear pulse propagation by summing over a series of discrete plane wave modes. We develop our theory from first principles to calculate the nonlinear pulse propagation for any geometry. Our goal is to develop a theory that accurately predicts the response of nonlinear materials to an ultrafast excitation in the low conversion limit. This theory is useful for interpretation of our nonlinear optical spectroscopic data.

The remainder of this section is organized as follows. First we calculate the nonlinear polarization induced by an ultrafast fundamental field. Next, we calculate the bound wave field from the nonlinear polarization. The free wave field generated from an ultrafast fundamental pulse is then calculated. Finally, the transmitted second harmonic field is calculated.
2.4.3 Determination of $P^{(2)}(\omega)$

We calculate the nonlinear polarization induced in a material by an ultrafast laser source. We again use quartz as our model. We assume without a loss of generality that the fundamental beam propagates in the $y$ direction normal to the quartz surface ($\theta = 0$). We also assume the incident fundamental field is $x$ polarized and couples to $\chi^{(2)}_{xxx}$. This theory is generalized for other geometries in section 6.3.

For bookkeeping purposes, we assume that our fundamental fields are labeled 1 and 2. This notation is used to explicitly exhibit the mixing of different frequency components of the same pulse in the SHG process. The form of the fundamental fields in frequency space is

$$E_1(\mathbf{r}, \omega_1) = \frac{\hat{x}}{2\pi} E e^{i k_1(\omega_1) y} \exp\left(-\frac{4(\omega_1 - \omega_o)^2}{\Delta \omega^2}\right)$$  \hspace{1cm} (2.23)

and

$$E_2(\mathbf{r}, \omega_2) = \frac{\hat{x}}{2\pi} E e^{i k_2(\omega_2) y} \exp\left(-\frac{4(\omega_2 - \omega_o)^2}{\Delta \omega^2}\right).$$  \hspace{1cm} (2.24)

The coefficient of the field strength is represented by $E$. The form of the spectral envelope function was determined experimentally by measuring the wavelength distribution of the modelocked pulse from our Ti:Al$_2$O$_3$ laser. The measured spectral intensity was Gaussian, i.e.

$$I(\lambda) = I_o \exp\left(-\frac{8(\lambda - \lambda_o)^2}{\Delta \lambda^2}\right),$$  \hspace{1cm} (2.25)

where $\lambda_o$ is the center wavelength and $\Delta \lambda$ is the full width at which the intensity is
1/e² its maximum value. This distribution can be converted to the angular frequency distribution

\[ I(\omega) = I_0 \exp\left(\frac{-8(\omega - \omega_0)^2}{\Delta \omega^2}\right) \]  

through the vacuum dispersion relationship \( \omega = kc = 2\pi c/\lambda \). The angular frequency bandwidth varied as the pulse duration changed. Typically, \( \Delta \omega \) ranged from 0.021 to 0.053 fs⁻¹ over the spectral range of the Ti:Al₂O₃ laser.

Also note, the wavevectors are expressed explicitly as a function of the angular frequency, \( k(\omega_1) \), in order to exhibit the dispersive nature of the medium. We can simplify equations (2.23) and (2.24) and facilitate the calculation of the nonlinear polarization induced by an ultrafast fundamental source by expanding the wavevector \( k(\omega_1) \) to first-order as a power series in \( (\omega_1 - \omega_o) \), i.e.

\[ k(\omega_1) = \frac{n(\omega_0)\omega_o}{c} + \frac{\partial k}{\partial \omega_1}(\omega_1 - \omega_o). \]  

In Appendix A, the expansion up to first-order is rigorously justified for the systems of interest. The second-order expansion term accounts for the broadening of the fundamental pulse. We calculate that for our quartz sample thicknesses, the pulse is broadened less than 0.3%. For the GaN samples, the broadening is even less. Hence, a first-order expansion is valid. The symbols in equation (2.27) have their usual meanings: \( n(\omega_0) \) is the index of refraction at frequency \( \omega_0 \) and \( c \) is the speed of light.
We further simplify the notation so that

$$k(\omega_1) = k_1^0 + \frac{\omega_1 - \omega_0}{v_{g1}}$$  \hspace{1cm} (2.28)

with

$$k_1^0 = \frac{n(\omega_0)\omega_0}{c} \quad \text{and} \quad \frac{1}{v_{g1}} = \left. \frac{\partial k}{\partial \omega_1} \right|_{\omega_0}.$$  \hspace{1cm} (2.29)

Physically, $v_{g1}$ is the group velocity of the pulse with angular frequency $\omega_1$. This is the speed at which the pulse propagates through the dispersive medium (quartz or GaN).

With this simplification, the nonlinear polarization is calculated from the fundamental fields through the relationship

$$P_i^{(2)}(\omega) = 4\pi^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi_{ijk}^{(2)}(\omega = \omega_1 + \omega_2)E_j(\omega_1)E_k(\omega_2)\delta(\omega - (\omega_1 + \omega_2))d\omega_1d\omega_2.$$  \hspace{1cm} (2.30)

Equation (2.30) is the frequency space representation of second-order nonlinear response function. This equation is derived in Appendix B. Performing the first integration over $\omega_1$, we generate an expression for $P_x^{(2)}(r, \omega)$, i.e.

$$P_x^{(2)}(r, \omega) = C \int_{-\infty}^{\infty} e^{i\left(\frac{\omega - \omega_0 + \omega_1}{\nu_b}\right)y} e^{i\left(\frac{\omega - \omega_0}{\nu_b}\right)y} \exp\left(-\frac{4\left((\omega - (\omega_2 + \omega_0))^2 + (\omega_2 - \omega_0)^2\right)}{\Delta \omega^2}\right)d\omega_2.$$  \hspace{1cm} (2.31)

with

$$C = e^{i2k_1^0y}E^2\chi_{xxx}^{(2)}(\omega = 2\omega_0).$$  \hspace{1cm} (2.32)
Here, $\chi^{(2)}_{zzz}(\omega = 2\omega_o)$ is a constant for quartz over a wide range of frequencies. $\chi^{(2)}_{zzz}(\omega = 2\omega_o)$ for quartz varies by less than 0.4% over the bandwidth of the Ti:Al$_2$O$_3$ laser.

Integration over $\omega_2$ yields

$$P_z^{(2)}(r, \omega) = P_0 e^{ik_b(\omega)y} \exp \left( \frac{-2(\omega - 2\omega_o)^2}{\Delta \omega^2} \right).$$

(2.33)

with

$$P_0 = \frac{\sqrt{\pi}}{2\sqrt{2}} \Delta \omega E^2 \chi^{(2)}_{zzz}(\omega = 2\omega_o)$$

(2.34)

Note the use of the symbol $k_b(\omega)$ in the phase $P_z^{(2)}$. This symbol denotes that $k_b(\omega)$ is the bound wavevector. This is clear from the functional form of $k_b(\omega)$, i.e.

$$k_b(\omega) = 2k^o + \frac{(\omega - 2\omega_o)}{v_b},$$

(2.35)

which is simply twice the wavevector of the fundamental field (equation (2.28)). This is the same result as for the the monochromatic case: the nonlinear polarization is coupled or bound to the fundamental wave and propagates with a wavevector twice that of the fundamental wave. As a final note, the subscripts 1 and 2 are no longer necessary because we integrated over the angular frequency spectrum of the fundamental fields. Notation used henceforth is absent of these subscripts. To summarize this section, we have calculated the nonlinear polarization generated from an ultrafast, or broadband, fundamental light source using a first-order expansion in the wavevectors of the fundamental fields.
2.4.4 Calculation of the Bound Wave From the Nonlinear Wave Equation

Once the nonlinear polarization is determined from the fundamental fields, the nonlinear waves may calculated from the nonlinear wave equation and boundary conditions. This section outlines the calculation of the nonlinear bound wave from the wave equation and the nonlinear polarization.

The nonlinear wave equation in frequency space is

\[ \nabla \times (\nabla \times E(\mathbf{r}, \omega)) - \frac{\varepsilon(\omega)\omega^2}{c^2} E(\mathbf{r}, \omega) = \frac{4\pi\omega^2}{c^2} \mathbf{P}^{(2)}(\mathbf{r}, \omega). \]  

The particular solution to the nonlinear wave equation must oscillate with the same phase as the nonlinear polarization (equation (2.33)), i.e. \( e^{ik_b \omega y} \). Since, \( k_b \) is the bound wavevector, we subscript the particular solution of the wave equation with "b" to denote it is the bound wave field. This solution has the form

\[ E_b(\mathbf{r}, \omega) = \mathcal{A} E_{bx}(\mathbf{r}, \omega) = \mathcal{A} \zeta_b(\omega) e^{ik_b \omega y}. \]  

Thus, the wave equation for \( E_{bx} \) is

\[ \left[ k_b^2(\omega) - \frac{\varepsilon(\omega)\omega^2}{c^2} \right] E_{bx}(\mathbf{r}, \omega) = \frac{4\pi\omega^2}{c^2} \mathbf{P}_x^{(2)}(\mathbf{r}, \omega). \]  

We further simplify this expression by making a zeroth-order approximation for the coefficients in equation (2.38). We assume that \( \omega = 2\omega_0 \). In other words, we assume that the angular frequency is identically equal to the center frequency of the Gaussian for the coefficients in equation (2.38). This approximation leads to the following
simplifications

\[
\kappa_b^2(\omega) = \left(\frac{2n(\omega_0)\omega_0}{c} + \frac{\omega - 2\omega_0}{v_b}\right)^2 \rightarrow \left(\frac{2n(\omega_0)\omega_0}{c}\right)^2 = \frac{4\epsilon_b\omega_0^2}{c^2} \tag{2.39}
\]

and

\[
\frac{\epsilon(\omega)\omega^2}{c^2} \rightarrow \frac{4\epsilon_f\omega_0^2}{c^2} \tag{2.40}
\]

with \(\epsilon_b \equiv \epsilon(\omega_0)\) and \(\epsilon_f \equiv \epsilon(2\omega_0)\). Therefore, equation (2.38) reduces to

\[
E_{bx}(\omega) = \frac{4\pi P_{2s}^{(2)}(\omega)}{\epsilon_b - \epsilon_f} \tag{2.41}
\]

We calculated the effect of this substitution on the measured intensity for GaN and quartz (see Appendix C). Note, \(E_{bx}\) has exactly the same functional form as the bound wave generated from a monochromatic light source (equation (2.15)). We found this approximation leads to at most a 0.2\% (0.04\%) error in the magnitude of the measured SHG intensity from GaN (quartz).

2.4.5 Calculation of the Free Wave from Boundary Conditions

To review, we have calculated the bound wave field from the nonlinear wave equation and the incident field. Although \(E_b(r, \omega)\) satisfies the nonlinear wave equation (equation (2.36)), the addition of a homogeneous solution of the nonlinear wave equation is required to satisfy boundary conditions. This homogeneous solution is of the form

\[
E_{f1}(r, \omega) = \hat{\zeta}_{f1}(\omega)e^{ik_{f1}(\omega)y}. \tag{2.42}
\]
Solution of the homogeneous wave equation determines $k_{f1}$ as

$$k_{f1}^2 = \frac{\epsilon_{1}(\omega)\omega^2}{c^2}. \quad (2.43)$$

Note, we use the same notation for this calculation as we did for the monochromatic case: nonlinear fields reflected off of the front surface of the quartz are subscripted with 0, nonlinear fields in the quartz are subscripted with 1, and nonlinear fields transmitted through the quartz are subscripted with 2.

The model for SHG generated by an ultrafast fundamental source and transmitted through a quartz slab is the same for the SHG generated by a monochromatic source. The fundamental field is transmitted through the quartz slab without reflection. This field generates a bound wave, $E_b(r, \omega)$, and free wave, $E_{f1}(r, \omega)$, that propagate through the crystal and a free wave that is reflected off of the front surface of the quartz, $E_{f0}(r, \omega)$. A free wave, $E_{fr1}(r, \omega)$, is also reflected from the second quartz/air interface. The reflected waves have functional forms similar to $E_{f1}(r, \omega)$ except they propagate in the opposite direction, i.e.

$$E_{fr1}(r, \omega) = \hat{x}\zeta_{fr1}(\omega)e^{-ik_{f1}(\omega)y}. \quad (2.44)$$

and

$$E_{f0}(r, \omega) = \hat{x}\zeta_{f0}(\omega)e^{-ik_{f0}(\omega)y}. \quad (2.45)$$

The transmitted free wave is denoted $E_{f2}(r, \omega)$. See Fig. 2.2 for a schematic of the
nonlinear waves. This model assumes no multiple reflections of the free waves. Multiple reflections affect the transmitted intensity by 4%, and are therefore insignificant.

We apply the continuity of $E_{\tan}$ and $H_{\tan}$ at both quartz/air interfaces ($y = 0$ and $y = -d$) to determine the free wave fields (see section 2.4.1). Here we repeat this calculation to determine the angular frequency envelopes of the free waves, $\zeta(\omega)$, and hence the free waves. Ultimately, we want to calculate the intensity of the transmitted second-harmonic field, $E_{f2}(r, t)$, and compare this with the SH intensity generated from a monochromatic source.

Matching boundary conditions for an ultrafast pulse is complicated by the spread in frequencies, and hence wavevectors. This dilemma is solved by selecting a specific $\omega$, which forces the vacuum $k$ to be $\omega/c$. In other words, the boundary conditions hold for each angular frequency of the pulse. With this in mind, the continuity equations at $y = 0$ are

\begin{align}
\zeta_{f1}(\omega) + \zeta_{b1}(\omega) &= \zeta_{f0}(\omega) \\
k_{f1}(\omega)\zeta_{f1}(\omega) + k_{b1}(\omega)\zeta_{b1}(\omega) &= -k_{f0}(\omega)\zeta_{f0}(\omega).
\end{align}

Propagating the fields to $y = -d$ and applying the continuity of the tangential components of the fields yields

\begin{align}
\zeta_{f1}(\omega)e^{ik_{f1}(\omega)d} + \zeta_{b1}(\omega)e^{ik_{b1}(\omega)d} + \zeta_{f2}(\omega)e^{-ik_{f1}(\omega)d} = \zeta_{f2}(\omega)e^{ik_{f0}(\omega)d}
\end{align}
and
\[ k_f(\omega) \zeta_f(\omega) e^{ik_f(\omega)d} + k_{b1}(\omega) \zeta_{b1}(\omega) e^{ik_{b1}(\omega)d} = k_f(\omega) \zeta_{f1}(\omega) e^{-ik_f(\omega)d} = k_{f0}(\omega) \zeta_{f2}(\omega) e^{ik_{f0}(\omega)d}. \] (2.49)

This leads to the following solution for the envelope function of the transmitted field
\[ \zeta_f(\omega) = \frac{\zeta_{b1}(\omega)}{k_f(\omega) + k_{f0}(\omega)} \left[ -2k_f(\omega) \left( \frac{k_{b1}(\omega) + k_{f0}(\omega)}{k_f(\omega) + k_{f0}(\omega)} \right) e^{i(k_f(\omega)-k_{f0}(\omega)d} \right. \\
\left. + (k_{b1}(\omega) + k_f(\omega)) e^{i(k_{b1}(\omega)-k_{f0}(\omega)d}. \right] \] (2.50)

In a zeroth-order approximation, the relationships between the coefficients \( k \) and \( \omega \) are
\[ k_f(\omega) = \frac{n_f 2\omega}{c} \quad \text{and} \quad k_{b1}(\omega) = \frac{n_{b1} 2\omega}{c}. \] (2.51)

with
\[ n_{f1} \equiv n(2\omega) \quad \text{and} \quad n_{b1} \equiv n(\omega). \] (2.52)

Equation (2.50) can be rewritten as
\[ \zeta_f(\omega) = \alpha \zeta_{b1}(\omega) e^{i(k_f(\omega)-k_{f0}(\omega)d} + \beta \zeta_{b1}(\omega) e^{i(k_{b1}(\omega)-k_{f0}(\omega)d} \] (2.53)

with
\[ \alpha = \frac{-2n_f (n_{b1} + 1)}{(n_{f1} + 1)^2} \quad \text{and} \quad \beta = \frac{n_{b1} + n_{f1}}{n_{f1} + 1}. \] (2.54)

Note that \( \alpha \) and \( \beta \) do not depend on \( \omega \). This determines the angular frequency representation of the transmitted SHG field. \( \mathbf{E}_{f2}(r, t) \) is determined by applying the
Fourier transform to $E_{f2}(r, \omega)$ as

$$E_{f2}(r, t) = \int_{-\infty}^{\infty} E_{f2}(r, \omega)e^{-i\omega t}d\omega = \tilde{E} \int_{-\infty}^{\infty} \zeta_{f2}(\omega)e^{i(k_{f2}(\omega)y-\omega t)}d\omega.$$  \hspace{1cm} (2.55)

When $k_f$ is used as a coefficient, (2.51) is the appropriate equation. A first-order expansion,

$$k_{f1}(\omega) = n_{f1} \frac{2\omega_o}{c} + \left| \frac{\partial k}{\partial \omega} \right|_{(2\omega_o)} (\omega - 2\omega_o)$$  \hspace{1cm} (2.56)

is required for any $k_f$ which appears in a phase. The second term in equation (2.56) contains an expression for the free wave group velocity in the quartz crystal.

$$\left| \frac{\partial k}{\partial \omega} \right|_{2\omega_o} = \frac{1}{\upsilon_{f1}}.$$  \hspace{1cm} (2.57)

The functional form of $\zeta_{b1}(\omega)$ is determined by the calculations in section 2.4.4 as

$$\zeta_{b1}(\omega) = \frac{4\pi P_o}{\epsilon_b - \epsilon_f} \exp\left(\frac{-2(\omega - 2\omega_o)^2}{\Delta \omega^2}\right).$$  \hspace{1cm} (2.58)

with $P_o$ is defined by equation (2.34). Using equations (2.27), (2.50), (2.54), (2.55), (2.56), and (2.58), the $\alpha$ part of the frequency space representation of the transmitted nonlinear field can be Fourier transformed to the time domain in the following steps.

The $\alpha$ integral can be expressed as

$$e^{i2\omega_o(n_{f1} - 1)}d e^{i\frac{2\pi}{c} \frac{4\pi P_o}{\epsilon_b - \epsilon_f} \int_{-\infty}^{\infty} \alpha \exp\left(\frac{-2(\omega - 2\omega_o)^2}{\Delta \omega^2}\right) e^{i\frac{\upsilon_{f1}}{\upsilon_f} \omega t} d\omega.}.$$  \hspace{1cm} (2.59)

Integration of equation (2.59) with respect to $\omega$ yields

$$e^{-i2\omega_o t} \Phi_1 \alpha \exp\left(\frac{-\Delta \omega^2}{8}\left(t - \frac{d}{\upsilon_f}\right)^2\right).$$  \hspace{1cm} (2.60)
The transmitted field is

$$E_{f_2}(r, \omega) = \mathcal{E} e^{-i2\omega t} \left( \Phi_1 \alpha \exp \left( \frac{-\Delta \omega^2}{8} \left( t - \frac{d}{v_f} \right)^2 \right) + \Phi_2 \beta \exp \left( \frac{-\Delta \omega^2}{8} \left( t - \frac{d}{v_b} \right)^2 \right) \right)$$  \hspace{1cm} (2.62)

with $\Phi_2$ defined as $\Phi_1$ with $n_b$ replacing $n_f$. Finally, the intensity can be expressed in notation similar to equation (2.21) as

$$I_{f_2}(t) = C_1^2 + C_2^2 + 2C_1C_2 \cos \left( \frac{2\omega_o}{c} (n_{f_1} - n_{b_1})d \right)$$  \hspace{1cm} (2.63)

with

$$C_1 = \frac{\Delta \omega^2 \pi^2}{\sqrt{2}(\varepsilon_b - \varepsilon_f)} E^2 \chi^{(2)}_{xxx}(\omega = 2\omega_o) \alpha \exp \left( \frac{-\Delta \omega^2}{8} \left( t - \frac{d}{v_f} \right)^2 \right)$$  \hspace{1cm} (2.64)

and

$$C_2 = \frac{\Delta \omega^2 \pi^2}{\sqrt{2}(\varepsilon_b - \varepsilon_f)} E^2 \chi^{(2)}_{xxx}(\omega = 2\omega_o) \beta \exp \left( \frac{-\Delta \omega^2}{8} \left( t - \frac{d}{v_b} \right)^2 \right).$$  \hspace{1cm} (2.65)

Experimentally, the Gaussian shape of the laser pulse is not observed because it occurs on a time scale which is much shorter than the response time of the detector electronics. Therefore, the detector effectively integrates equation (2.63) as

$$I_{\text{detected}} = \int_{-\infty}^{\infty} \left( C_1^2 + C_2^2 + 2C_1C_2 \cos \left( \frac{2\omega_o}{c} (n_{f_1} - n_{b_1})d \right) \right) dt.$$  \hspace{1cm} (2.66)

We attempted to measure Maker fringes using the Ti:Al$_2$O$_3$ laser and lock-in detection with an optical set up as in Fig. 2.3. Fig. 2.7 displays the SHG intensity from a quartz wedge. The fit to the data is equation (2.66) with a quartz thickness of
3 mm and with the parameters displayed in Table 2.2. Remarkably, the data is free of Maker fringes that characterize excitation of a quartz wedge with a monochromatic light source (see Fig. 2.4.) In addition, equation (2.66) is plotted in Fig. 2.8 as a function of crystal length. After \( \sim 200 \, \mu \text{m} \), the oscillations are damped to half of their value for the thin film, i.e. a film in which the bound and free waves are temporally overlapped.

Physically, the fundamental light pulse generates both a free and a bound wave pulse at the first vacuum/quartz interface. The bound wave is coupled to the free wave and propagates through the quartz wedge with a group velocity characteristic of the fundamental pulse, \( v_b \). In contrast, the free wave propagates through the quartz wedge with a group velocity characteristic of a pulse of twice the frequency of the fundamental pulse, \( v_f \). If the quartz wedge is thick enough, the bound wave arrives before the free wave at the second vacuum/quartz interface, and interference does not occur.

In section section 2.4.1, we discussed the phenomena of Maker fringes generated from a monochromatic laser source, which are directly related to the phase velocity mismatch of the nonlinear bound and free wave fields in the crystal. In contrast, excitation of a dispersive medium with an ultrafast laser source produces a nonlinear signal that depends on both phase and group velocity mismatches. The effect of group velocity becomes more significant as the interaction length of SHG increases.
Figure 2.7: Maker fringe data for a broad band, ultrashort light source. The quartz wedge was translated perpendicularly to the Ti:Al$_2$O$_3$ beam. The experimental apparatus for measuring the Maker fringe data from a quartz wedge excited by an ultrafast Ti:Al$_2$O$_3$ laser is similar to the apparatus displayed in Fig. 2.3. The free and bound waves do not interfere to produce oscillations.
Figure 2.8: Calculated Maker fringes with a broadband source as a function of quartz thickness. The light generating source is a Ti:Al₂O₃ laser. The Maker fringes damp out as the quartz slab gets thicker.

the material becomes more dispersive, or the pulse duration of the laser decreases.

i.e. the bandwidth increases.

Note. the index of refraction and the group velocity were derived from the Laurent expression for the ordinary index of refraction of quartz

\[ n^2 = B_1 + B_2 \lambda^2 + \frac{B_3}{\lambda^2} + \frac{C_1}{\lambda^4} + \frac{C_2}{\lambda^6} + \frac{C_3}{\lambda^8}. \]  

(2.67)

The parameters for equation (2.67) are displayed in Table 2.3.
<table>
<thead>
<tr>
<th>parameter</th>
<th>symbol</th>
<th>value</th>
</tr>
</thead>
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<tr>
<td>speed of light</td>
<td>$c$</td>
<td>$0.3 , \mu m/\text{fs}$</td>
</tr>
<tr>
<td>wavelength of light</td>
<td>$\lambda$</td>
<td>$0.800 , \mu m$</td>
</tr>
<tr>
<td>angular frequency of fundamental light</td>
<td>$\omega_o$</td>
<td>$2.35 , \text{fs}^{-1}$</td>
</tr>
<tr>
<td>angular frequency bandwidth of fundamental light</td>
<td>$\Delta \omega$</td>
<td>$0.053 , \text{fs}^{-1}$</td>
</tr>
<tr>
<td>pulse width</td>
<td>$\tau$</td>
<td>$80 , \text{fs}$</td>
</tr>
<tr>
<td>index of refraction for fundamental light</td>
<td>$n_b$</td>
<td>$1.5384$</td>
</tr>
<tr>
<td>index of refraction for second-harmonic light</td>
<td>$n_f$</td>
<td>$1.5577$</td>
</tr>
<tr>
<td>group velocity for fundamental light</td>
<td>$v_b$</td>
<td>$0.19300 , \mu m/\text{fs}$</td>
</tr>
<tr>
<td>group velocity for second-harmonic light</td>
<td>$v_f$</td>
<td>$0.18089 , \mu m/\text{fs}$</td>
</tr>
</tbody>
</table>

Table 2.2: Parameters used for ultrafast Maker fringe calculation. Note the use of “ultrafast units.”
Table 2.3: Laurent series parameters for the ordinary index of quartz [47].

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
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<tr>
<td>$B_1$</td>
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</tr>
<tr>
<td>$B_2$</td>
<td>-0.01170000 $\mu m^{-2}$</td>
</tr>
<tr>
<td>$B_3$</td>
<td>0.01054000 $\mu m^2$</td>
</tr>
<tr>
<td>$C_1$</td>
<td>$1.34143 \times 10^{-4} \mu m^4$</td>
</tr>
<tr>
<td>$C_2$</td>
<td>$-4.45368 \times 10^{-7} \mu m^6$</td>
</tr>
<tr>
<td>$C_3$</td>
<td>$5.92362 \times 10^{-8} \mu m^8$</td>
</tr>
</tbody>
</table>

2.5 Novel Technique and Apparatus to Measure Ultrafast Pulses

The analysis in the previous section suggests a technique to measure the spectral bandwidth of ultrafast laser pulses. Typically pulse lengths are measured by an autocorrelation technique (see section 3.4.) The autocorrelator method measures the pulse duration by a nonlinear interferometric technique [48]. The disadvantage of this technique is that it requires the interfering light pulses to be overlapped in both time and space, which is somewhat difficult to achieve in practice. If instead one measured the SHG response of a $\sim 300 \mu m$ quartz wedge excited by a Ti:Al$_2$O$_3$ ultrafast laser pulse, the damped Maker fringes could be observed. A "damping factor" may be
defined as
\[
\eta = \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}} \tag{2.68}
\]
where \(I_{\text{max}}\) is the SHG intensity from a Maker fringe peak and \(I_{\text{min}}\) is the SHG intensity from a Maker fringe valley. This ratio is defined in terms of the ultrafast coefficients (equations (2.64) and (2.65)) as
\[
\eta = \frac{\int_{-\infty}^{\infty} 2C_1 C_2 dt}{\int_{-\infty}^{\infty} (C_1^2 + C_2^2) dt}. \tag{2.69}
\]

By comparing the calculated \(\eta\) with the experimentally observed \(\eta\), one can determine \(\Delta \omega\) of the pulse. This comparison proceeds as follows. First, the thickness of the quartz wedge, typically 250 \(\mu m\) at the thinnest edge, and the angle of the quartz wedge, typically 1°, are determined. Note that the wedge angle is directed along the x axis of the crystal. Second, the wedge is positioned at normal incidence to the Ti:Al\(_2\)O\(_3\) beam. The Ti:Al\(_2\)O\(_3\) beam is focussed on the quartz wedge to a beam size of less than 100 \(\mu m\). If the beam has a large spatial extent, i.e. greater than 1 mm, each section of the beam travels a different path length, and the transmitted intensity from each section of the beam is different. This latter effect also suppresses Maker fringes [38]. Therefore, a small beam diameter is required to ensure that the damped Maker fringes result from ultrafast effects and not from finite beam effects. Third, the quartz wedge is translated perpendicularly across the Ti:Al\(_2\)O\(_3\) pulse. Note that the direction of translation is such that the beam traverses a different quartz thickness during the translation. The second-harmonic intensity from the quartz wedge
is measured as a function of translation distance. For a quartz wedge with a 1° angle excited by an 800 nm Ti:Al₂O₃ pulse, the damped Maker fringe has a period of 2.4 mm. In other words, translating the quartz wedge by 2.4 mm results in one Maker fringe. Fourth, a value for $\Delta \omega$ is assumed and the Maker fringe damping parameter, $\eta$, is calculated from the measured SHG intensity as a function of position, the quartz thickness, the wavelength of the incident light, and the quartz wedge angle. Fifth, the measured $\eta$ is compared with the calculated $\eta$. If the measured $\eta$ is greater than the calculated $\eta$, then $\eta$ is recalculated assuming a smaller $\Delta \omega$. Conversely, if the measured $\eta$ is smaller than the calculated $\eta$, then $\eta$ is recalculated assuming a larger $\Delta \omega$. This procedure is repeated until the calculated $\eta$ equals the measured $\eta$. This procedure determines $\Delta \omega$.

We define $\Delta \omega$ as full width at which the intensity of the pulse falls to $1/e^2$ of its maximum value. Assuming the pulse is Fourier transform limited, the angular frequency bandwidth is related to the time width of the pulse as

$$\tau_{FW} = \frac{8}{\Delta \omega_{FW}}. \quad (2.70)$$

Conventionally, pulse widths are reported in terms of the full width at half maximum, $\tau_{FWHM}$ rather than $\tau_{FW}$. These quantities are related as

$$\tau_{FWHM} = \frac{\ln 2}{2} \tau_{FW}. \quad (2.71)$$

We discuss typical values of $\tau_{FWHM}$ and $\Delta \omega$ for our Ti:Al₂O₃ laser system in section 3.9.
Table 2.4: Comparison of ultrafast pulse measurement techniques. Higher order correlations, e.g. non-collinear four wave mixing, provide additional information including asymmetry in the pulse. These measurements are correspondingly more difficult to align.

Table 2.4 compares the damped Maker fringe and autocorrelation techniques for measuring ultrafast laser pulse duration. One could construct a stand alone device to measure ultrafast pulse durations by damped Maker fringes. A schematic of this device is displayed in Fig. 2.10. This device would operate in a manner described by the flow chart displayed in Fig. 2.9.

<table>
<thead>
<tr>
<th></th>
<th>Maker fringe</th>
<th>autocorrelation</th>
</tr>
</thead>
<tbody>
<tr>
<td>technique</td>
<td>single beam SHG</td>
<td>non-collinear two beam SHG</td>
</tr>
<tr>
<td>advantages</td>
<td>ease of use</td>
<td>observe tails of pulse</td>
</tr>
<tr>
<td></td>
<td>portability</td>
<td></td>
</tr>
<tr>
<td>disadvantages</td>
<td>no direct information regarding</td>
<td>difficult to align</td>
</tr>
<tr>
<td></td>
<td>temporal pulse shape</td>
<td>(no frequency information)</td>
</tr>
<tr>
<td>use</td>
<td>commercial Ti:Al₂O₃ laser systems</td>
<td>homemade laser systems</td>
</tr>
<tr>
<td></td>
<td></td>
<td>regenerative amplifiers</td>
</tr>
</tbody>
</table>
Figure 2.9: Flow chart for measuring pulse lengths with damped Maker fringe technique.
Figure 2.10: Device for measuring ultrafast pulse using damped Maker fringe technique.
2.6 Conclusion

In this brief section we relate the theoretical results derived in this chapter to the nonlinear optical properties of GaN, which are presented in the subsequent chapters.

In section 2.2, we discuss the properties of the second-order nonlinear susceptibility, $\chi^{(2)}_{ij}(\omega = 2\omega_0)$. We suggest which states lead to a resonant enhancement of $\chi^{(2)}_{ijk}(\omega = 2\omega_0)$ for both GaN bulk and defect states in sections 5.4.1 and 6.5, respectively. The determination of the states that contribute to the nonlinear optical response follows directly from the application of group theory to equation 2.8.

In section 2.3 we discuss the relationship between material symmetry and second-order susceptibility elements. Using symmetry, we determined the unique nonzero susceptibility elements for GaN. These elements, combined with experimental geometry, influence nonlinear optical transmittance spectra of GaN (see chapter 6).

Finally, the majority of this introductory nonlinear optics chapter is concerned with a detailed investigation of nonlinear optical interference, i.e. Maker fringes. We contrast nonlinear optical interference for monochromatic and ultrafast laser sources. We demonstrated that nonlinear optical interference, which is due to wavevector mismatch, is damped by group velocity mismatch. We apply this ultrafast analysis to determine the second-order susceptibility elements from the nonlinear optical spectra of GaN in sections 6.3 and 6.4.
Chapter 3

Experimental Ultrafast Nonlinear Optical Spectroscopy

In this chapter we discuss the nonlinear optical spectroscopy experimental setup. A further discussion of our spectra normalization and the effects of an ultrafast laser pulse on our measured second-harmonic generation signals (see also section 2.4.2) is given. In addition, the characteristics of the fundamental light generating source, the Ti:Al$_2$O$_3$ laser, are discussed at length.

3.1 Optical Setup

Fig. 3.1 displays a schematic of the nonlinear optical setup. This setup is somewhat similar to the one used by M. S. Yeganeh and J. Qi [49, 41], but with a different fundamental light source. The fundamental light source with frequency \( \omega \) was a Ti:Al$_2$O$_3$ laser, the details of which will be more thoroughly discussed in section 3.3. Briefly, the Ti:Al$_2$O$_3$ laser produces ultrashort near IR laser pulses (\( \sim 700-1000 \) nm) at rate of 76 MHz. The individual ultrashort pulses have sufficiently high peak powers (\( \sim 50 \) kW) to produce measurable nonlinear optical effects. Polarization of both
Figure 3.1: Set-up for nonlinear spectroscopy measurements
the fundamental and second-harmonic beams constrains the second-order susceptibility elements probed. The fundamental output from a Ti:Al₂O₃ laser is p-polarized (horizontally polarized). We used a simple combination of prisms [38] to rotate the p-polarized beam by 90° for the fundamental s-polarized measurements. As indicated by Fig. 3.2, the prism pair lowered the height of the fundamental beam. The original beam height was restored using a combination of gold coated mirrors. Although this optical setup is not the most elegant solution for converting a p-polarized beam into an s-polarized beam, it avoided the problem associated with using a half wave plate over a broad spectral range. In the latter case, for wavelengths far from the central operating wavelength of the half wave plate, the waveplate is unable to introduce a relative phase shift of \( \pi \) between polarization components of the wave, and is therefore unable to rotate one linear polarization into another.
After polarization, the beam was amplitude modulated with a standard optical chopper (1 kHz) and a sequence of optics were used to direct the beam to a beam splitter which transmitted ~90% of the fundamental light to the sample. The remaining 10% of the Ti:Al₂O₃ pulse was reflected and propagated along an identical optical line containing a quartz wedge. This line was used to normalize the nonlinear optical signal, which will be described in greater detail in a following paragraphs. The sample was placed at the focal point of an f/4.0 achromatic lens which focused the 4 mm beam to 100 μm spot. The achromatic lens has a Rayleigh range of 4 mm which ensured that the spot size of the beam did not vary significantly as the wavelength of the fundamental beam was scanned. Any second-harmonic signal generated along the beam path prior to the sample was removed with a low pass optical filter.

Interaction of the ultrafast Ti:Al₂O₃ laser pulse with the sample or quartz produced a second-harmonic generation pulse with angular frequency 2ω. The SHG pulse was separated from the fundamental pulse by high pass filters and a Jarrel Ash Monospec 18 monochrometer with entrance and exit slit widths of 2 mm. This slit configuration has a top hat transmission function with a full width wavelength bandwidth of Δλ = 10 nm. The monochrometer grating was blazed at 500 nm to maximize sensitivity to near IR frequency doubled light. In addition, the SHG signal was polarized to probe various second-order susceptibility elements. The SHG signal was detected by a Hamamatsu R943-02 photomultiplier tube. The R943-02 is a high
gain, low noise, head-on photomultiplier tube. The photocathode is made of GaAs, which has a quantum efficiency of $\sim 14\%$ over the range of our SHG spectroscopic measurements $^1$.

### 3.2 Data Acquisition

The signals from the sample and reference photomultiplier tubes were sent directly to a pair of Stanford Research Systems SR530 lock-in amplifiers. The data from the lock-in amplifiers were transferred through a GPIB cable to a National Instruments AT-GPIB/TNT GPIB board in a 100 MHz Dell computer with a Pentium processor. I wrote a Quick Basic 4.5 program to graphically display, analyze, and store the data. All experiments in this thesis, with the exception of the photoluminescence experiment, acquire data in the same manner as the nonlinear spectroscopy data acquisition scheme.

Prior to measuring the signals from the sample and quartz, a background measurement from both the sample and reference lines was made with the laser blocked. The appropriate background measurements were subtracted from the sample and reference signals, and a normalized signal was reported as the ratio of the sample to reference signals. In a typical nonlinear spectroscopic measurement, the lock-in amplifiers were set to a 300 ms time constant and data was acquired every second for

$^1$The R943-02 has a quantum efficiency of $\sim 15\%$ at 350 nm which monotonically decreases to $\sim 13\%$ at 500 nm.
1-25 seconds depending on the magnitude of the signal. For a 200 mW p-polarized fundamental beam, a typical measured SHG signal from the GaN/Al₂O₃ sample was $2 \times 10^5$ photons/s.

### 3.3 Ti:Al₂O₃ Laser

The fundamental light generating source in our experiments is a Coherent Ti:Al₂O₃ laser model Mira 900B. A Coherent Innova 310 Ar ion laser pumps the Ti:Al₂O₃ in a multiline configuration with 8 W. A schematic of the laser is displayed in Fig. 3.3. Table 3.1 displays some of the properties of our Ti:Al₂O₃ laser.
<table>
<thead>
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<th>characteristic</th>
<th>value</th>
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<tr>
<td>pump source</td>
<td>8W Ar ion laser</td>
</tr>
<tr>
<td>wavelength range</td>
<td>700-1000 nm</td>
</tr>
<tr>
<td>peak power (cw)</td>
<td>1.5 W at 800 nm</td>
</tr>
<tr>
<td>peak power (modelocked)</td>
<td>800 mW at 800 nm</td>
</tr>
<tr>
<td>typical pulse length</td>
<td>80-150 fs</td>
</tr>
<tr>
<td>pulse peak power</td>
<td>50 kW</td>
</tr>
<tr>
<td>repetition rate</td>
<td>76 MHz</td>
</tr>
<tr>
<td>bandwidth of modelocked pulse</td>
<td>10 meV</td>
</tr>
</tbody>
</table>

Table 3.1: Characteristics of Ti:Al$_2$O$_3$ Laser
Figure 3.4: Energy band diagram for Ti:Al₂O₃. Straight lines correspond to optical transitions. The crystal relaxes by emission of phonons (wavy lines). This process is the crystalline analog of the Franck-Condon principle [50].

There are two essential characteristics of the fundamental light generating source for a nonlinear spectroscopy experiment: tunability of the fundamental wavelength and generation of high peak power laser pulses. The tunability of the Ti:Al₂O₃ laser is directly related to the coupling of the active medium (Ti ion) to the host crystal (Al₂O₃). This coupling is represented in Fig. 3.4. A birefringent filter is used to select the wavelength of the laser. Fig. 3.5 displays the experimentally determined tuning curve for birefringent filter.
Figure 3.5: Ti:Al$_2$O$_3$ wavelength as a function of birefringent filter position. Data is for the mid wavelength (MW) optics set.
The production of ultrafast, high peak power pulses in the Ti:Al₂O₃ laser occurs through a passive modelocking process called Kerr-lens modelocking. The cw laser light in the laser cavity is composed of a spectrum of frequencies. The width of this spectrum is determined by the active medium and the optics in the laser cavity. These frequencies, or longitudinal modes, are discrete as a result of the boundary conditions at the high reflector and output coupler mirrors. The modes are separated by a frequency $\pi c/L$, where $L$ is the length of the cavity. When the laser is operating in cw mode, the phases between the modes are random. We can add a mechanism to the laser cavity that favors the propagation of a pulsed laser source as opposed to a cw source. The cw laser source will evolve to a pulsed laser source due to the gain differential between the two modes. This transformation from cw to pulsed mode occurs by fixing or locking the phase relationships between the modes to non-random values. In other words, by defining phase relationships, the longitudinal modes can add together to form a high intensity laser pulse.

For the Ti:Al₂O₃ laser, the laser crystal not only functions as the active medium, but also as a Kerr lens, i.e. the active medium has an intensity dependent index of refraction that is exploited to produce ultrafast pulses. By placing a partially closed shutter in front of the output coupler, a loss is added to the cavity. If a noise spike, i.e. an intense pulse of light, is introduced into the cavity, the higher intensity of the spike will activate the Kerr lens modelocking and the light associated with the noise spike
Figure 3.6: Shutter configuration in the Ti:Al₂O₃ laser. The high intensity of the pulsed laser activates the Kerr lensing action of the Ti:Al₂O₃ crystal. This focuses the modelocked laser pulse (thick lines) through the shutter without loss. In contrast, the cw beam (thin lines) is not focused through the slit. The shutter mechanism is very similar to the saturable absorber method used to modelock dye lasers.

will be focused through the slit without attenuation (see Fig. 3.6). Thus, the noise spike proceeds through the cavity unattenuated and is amplified at the expense of the cw beam until it forms a femtosecond laser pulse with negligible cw background. Noise is introduced into the cavity through the starter galvo which rapidly oscillates with a small amplitude to slightly alter the cavity alignment. Modelocking was optimized by observing the laser signal with a fast silicon photodiode terminated by a 50 Ω resistor on an oscilloscope. Fig. 3.7 displays a typical modelocked power spectrum for the Ti:Al₂O₃ laser. Once the modelocking of the laser was optimized by adjusting the shutter position and width, the stater galvo was turned off. Typically, we modelocked the laser at the peak of its tuning curve, ~800 nm. It is advisable to modelock the laser at the peak of its tuning curve and then tune the birefringent filter to the desired wavelength rather than attempt to modelock the laser at the desired wavelength.
Figure 3.7: Modelocked power spectra of Ti:Al₂O₃ laser. Data is for the mid wavelength (MW) optics set.
Figure 3.8: Pulse propagation through Brewster prisms. The red and blue components of the ultrafast pulse are not overlapped due to group velocity dispersion. This is compensated by the prism pairs shown. The red frequency components traverse more glass through the second Brewster prism than the blue frequency components. This overlaps the red and blue frequency components by negative group velocity dispersion. This figure is adapted from [51].

We observed that the duration of the femtosecond pulse is strongly influenced by the position of the Brewster prism pair. The Brewster prisms counteract the tendency of the ultrafast pulse to spread out as it propagates through the cavity (see Fig. 3.8). This phenomena, known as group velocity dispersion, occurs because the ultrafast pulse is composed of a band of frequencies that have different group velocities. The cw power of the laser is relatively insensitive to the positions of the prisms, but the stability of the modelocking is highly sensitive to their positions. I found through trial and error that optimal modelocking stability is achieved when the Ti:Al₂O₃ laser pulse is ~2-3 mm from the front edge of BP1 and ~5-8 mm from the front edge of BP2. BP2 is mounted on a micrometer stage to allow adjustment during spectroscopic
measurements. Typically, I increased (decreased) the BP2 monochrometer setting by ~2 mm for every 40 nm decrease (increase) in the wavelength of the laser.

3.3.1 Techniques for Optimizing the Performance of the Ti:Al2O3 Laser

We conclude this section by listing some techniques for alignment of the Ti:Al2O3 laser. Aligning the Ti:Al2O3 laser to lase is fairly easy, but aligning the Ti:Al2O3 to modelock and produce femtosecond pulse over a wide frequency range is somewhat difficult. The mode quality of the Argon pump laser is critical for optimal operation of the Ti:Al2O3. The transverse mode of the Argon laser must be Gaussian. Higher order spatial modes, e.g. TEM_{01} and TEM_{10}, may be eliminated from the Argon beam by reducing the aperture setting of the laser. The smaller diameter of the aperture attenuates the higher order modes more than the Gaussian modes, and hence reduces the higher order modes relative to the Gaussian mode. (Normally the aperture is set to 8, but I have occasionally pumped the Ti:Al2O3 with an aperture setting of 6 or 7).

Another common problem with the Argon laser is contamination of the Brewster window. The Brewster window is a quartz window that seals the Argon laser tube. The normal to the window is 45° from vertical. This window frequently picks up dust, which is almost immediately burned onto the window. The power and mode quality of the Argon laser diminishes significantly once the window has been contaminated. The contaminant may be observed by inspecting the Brewster window during laser
operation while wearing a pair of alignment goggles. Note that a beam is reflected off of the Brewster window. It is necessary to identify and avoid this beam prior to observing the Brewster window. Once the contaminant is identified, the window should be cleaned with HPLC grade methanol. I have found that cleaning a contaminated Brewster window with methanol occasionally does not remove the contaminant. The contaminant may be removed by etching the window with Ammonium Bifloride (ABF). The ABF cleaning procedure may be obtained from Coherent Laser Group.

Another potential problem is the spatial mode of the pump beam, which may also be distorted by dust on the pump beam optics. These optics are extremely susceptible to picking up dust, and must be cleaned frequently (once a week). An additional technique to optimize the performance of the Ti:Al₂O₃ laser is to “walk” the Ti:Al₂O₃ beam to the center of every mirror in the laser cavity. This procedure, which is outlined in the manual, maximizes the overlap of the Ti:Al₂O₃ beam with the pump beam, and hence maximizes the Ti:Al₂O₃ power. In my experience, this procedure often produces an increase in power necessary for modelocked operation.

It is equally important to center the Argon pump laser on the pump optics while simultaneously centering the pump beam on the Ti:Al₂O₃ crystal. The procedure for centering the beam on the crystal is not in the laser manual, but I have observed the Coherent field service engineers employ this method to increase the power of the Ti:Al₂O₃ laser. The reader is referred to the laser manual to identify the optics.
described below. Note that laser alignment goggles should be worn during this procedure. The procedure is as follows.

1. Reduce the power of the Argon laser to its lowest level.

2. Remove the lens that focuses the Argon beam on the crystal from the Ti:Al$_2$O$_3$ laser cavity.

3. Adjust the pump beam steering optics to their center position.

4. Center the Argon beam on the first pump optic mirror (P1) by slightly adjusting the pump beam steering optics.

5. Adjust the set screw that holds P1 in place and adjust the position of P1 to center the Argon beam on optic P2. Tighten the set screw.

6. Adjust P2 to center the beam on P3 using a procedure similar to step 5.

7. Adjust P3 to center the beam on P4 using a procedure similar to step 5.

8. When the beam is centered on P4, loosen the set screw that holds P4 in place and center the Argon beam on the Ti:Al$_2$O$_3$ crystal by adjusting the position of P4. Tighten the set screw.

9. Replace the lens that focuses the Argon beam on the Ti:Al$_2$O$_3$ crystal. The pump beam should remain centered on the crystal.

10. Adjust the pump steering controls to maximize the power of the Ti:Al$_2$O$_3$ laser. This should be a minor adjustment.
3.4 Autocorrelation

Unlike a dye pumped Nd:YAG laser, the pulse length of the Ti:Al₂O₃ laser changes as a function of wavelength and the laser cavity alignment. In order to fully characterize the Ti:Al₂O₃ pulse and optimize laser operation, we built an autocorrelator to measure the sub-picosecond laser pulse.

Fig. 3.9 displays the optical setup of the autocorrelator. The autocorrelator is es-
sentially a nonlinear optical interferometer, which functions as follows. The Ti:Al₂O₃ pulse enters the autocorrelator and is split by a 50/50 beam splitter. The beams are reflected from pairs of mirrors mounted on a speaker and a translation stage. The beams are separated by ~1 cm when they reach a lens with a 100 mm focal length, which focuses the beams to a point inside a nonlinear crystal. We used a 0.4 mm thick KDP crystal cut for type I phase matching, i.e. both of the non-collinear fundamental beams have the same polarization, at 800 nm. The two beams are coupled in the KDP crystal to produce an SHG signal whose magnitude is proportional to the temporal overlap of the fundamental beams. Note, the geometry of this optical setup, non-collinear phase matching, is ideally suited for separating the SHG signal from the overlapped fundamental pulses from the SHG from the individual pulses.

In “ultrafast units”, the speed of light has a value of 0.3 μm/fs. Therefore, increasing the path length of one of the interference arms by 50 μm drastically changes the temporal overlap of the Ti:Al₂O₃ pulses in the KDP crystal. We can exploit this experimentally to measure the duration of the Ti:Al₂O₃ pulse by oscillating the speaker mirrors at 60 Hz and detecting and analyzing the SHG signal intensity from the overlap of the ultrafast pulses with a PMT and an oscilloscope.

The measurement of the pulse duration is as follows. First, with the time constant of the oscilloscope set to 5 ms, the pulse width is measured. The pulse corresponds to the envelope function of the temporal overlap of the individual pulses. Second,
the translation stage with the reflecting mirrors is moved \( \sim 50 \mu m \). This changes the round trip distance for the translation stage arm by 100 \( \mu m \), corresponding to 300 fs.

and shifts the position of the envelope function on the oscilloscope by a few ms. Thus, a relationship is established between the 300 fs round trip time change and the change in the position of the envelope pulse. The width of the Ti:Al\(_2\)O\(_3\) pulse is

\[
\Delta t_{\text{Ti:Al}\_2\text{O}_3} = \frac{2L \Delta t_{\text{width}}}{c \Delta t_{\text{position}}}
\]

(3.1)

where \( L \) is the mirror translation distance, \( \Delta t_{\text{position}} \) is the time shift of the envelope pulse, and \( \Delta t_{\text{width}} \) is the width of the envelope pulse. A typical autocorrelation measurement of the Ti:Al\(_2\)O\(_3\) pulse length as a function of wavelength is displayed in Fig. 3.10. This figure also displays the inverse bandwidth of the pulse, i.e. \( 1/\Delta \omega \), which roughly follows the pulse width. This parameter is essential to determine the damping of the Maker fringes.

The autocorrelator is somewhat difficult to align because the fundamental beams must be overlapped both spatially and temporally. I briefly describe some techniques to align the device. During a spectroscopic measurement, a small fraction of light (less than 5%) is reflected into the autocorrelator from a glass slide. However, during alignment I place a mirror directly behind and in contact with the glass slide. This reflects the entire beam into the autocorrelator, which produces an SHG signal much greater than the one generated when only the glass slide is used. During the alignment, I overlap the two beam from the different arms of the interferometer slightly
Figure 3.10: Measured pulse length of the Ti:Al$_2$O$_3$ pulse as a function of wavelength. ◇ (□) is the data for the pulse length (inverse bandwidth). The discontinuity in the data results from adjusting BP2, which altered the GVD of the laser cavity, and hence altered the pulse duration. Data is for the mid wavelength (MW) optics.
before their focal point. This facilitates overlapping of the beams. The nonlinear crystal is centered on the overlap of the two beams. I rotate the crystal about the normal to its face to maximize the SHG from each individual beam. This procedure aligns the beams' polarizations in the proper plane for type I phase matching. I adjust the angle of incidence between the fundamental beams and the crystal normal to produce an equal amount of SHG from each of the fundamental beams; this can be verified visually. This ensures maximum SHG from the overlap of the beams. Finally, I place the PMT directly between the SHG from the fundamental beams. Phase matching ensures that the SHG from the overlap of the fundamental beams will propagate in this direction. The fundamental beams may be approximately temporally overlapped by constructing the arms of the interferometer to have equal distances. The overlap of the fundamental pulses is detected by observing the signal from the PMT on an oscilloscope while the speaker is on.

3.5 Normalization

There are three components required of any properly normalized spectral measurement: elimination of the effects of the temporal fluctuations of the source, compensation for the spectral variations of the source, and compensation or elimination of the inherent spectral response of the detection system. This section discusses the experimental techniques that address these issues.
Unlike the linear spectroscopic measurements presented in chapter 4, nonlinear optical spectra are highly sensitive to a number of factors including:

- pulse duration
- beam polarization
- beam spot size or diameter
- beam spatial profile
- pulse energy

During a spectral scan, the pulse duration may vary from 80-150 fs and the cw power may vary from 500-800 mW due to the position of the Brewster prisms and shutter and the frequency dependence of the Ti:Al₂O₃ crystal. The influence of the uncertainties and variations in these parameters on the nonlinear response of our samples is eliminated by simultaneously measuring the nonlinear response of a y-cut quartz slab. Quartz has well-measured linear optical properties as well as a second-order susceptibility, \( \chi_{xxx}(2\omega = \omega_0) \), that is spectrally flat [52]. We chose y-cut quartz because it is free of optical activity [41], which would confuse the interpretation of a polarized measurement.

While comparison of the nonlinear response of quartz to that of a sample eliminates the signal's dependence on the characteristics of the Ti:Al₂O₃ pulse and any temporal fluctuations of the source, it does not eliminate any discrepancy in the spectral response of the detection apparatus. We minimized this discrepancy by us-
ing identical optical components in the sample and reference arms. The potentially greatest cause of discrepancy is the beam splitter. Our beam splitter was optically engineered to reflect 10% of a $p$-polarized incident beam at an angle of incidence of $45^\circ$. I tested the relative spectral responses of the two arms by measuring the SHG signal with $y$-cut quartz in both the sample and reference arm. For both the $p$-polarized and $s$-polarized input Ti:Al$_2$O$_3$ pulses, the relative response of the sample arm to the reference arm varied *repeatedly and predictably* by less than 15%.

In order to fully eliminate both effects of the Ti:Al$_2$O$_3$ pulse’s characteristics and the inherent spectral response of the detection system, nonlinear signals of GaN/Al$_2$O$_3$ are reported as

$$I_{\text{GaN}}^{\text{reported}}(\omega = 2\omega_0) = \frac{I_{\text{sample}}^{\text{GaN}}(\omega = 2\omega_0)}{I_{\text{reference}}^{\text{quartz}}(\omega = 2\omega_0)}.$$

(3.2)

Note that $I_{\text{GaN}}^{\text{sample}}(\omega = 2\omega_0)$ refers to the measured second-harmonic intensity of GaN in the sample arm. The first measurement in equation (3.2),

$$\frac{I_{\text{sample}}^{\text{GaN}}(\omega = 2\omega_0)}{I_{\text{reference}}^{\text{quartz}}(\omega = 2\omega_0)},$$

(3.3)

measures a relative value of the signal from GaN that is free of the spectral characteristics of the laser source and fluctuations in the laser power. The second measurement, 

$$\frac{I_{\text{sample}}^{\text{quartz}}(\omega = 2\omega_0)}{I_{\text{reference}}^{\text{quartz}}(\omega = 2\omega_0)},$$

(3.4)

is also free of the spectral characteristics of the laser and fluctuations in laser power. In addition, this measurement determines the response of the detection system. There-
fore, the ratio of these two quantities, equation (3.3) to equation (3.4), is an absolute measurement of the SHG signal from GaN referenced to the nonlinear response of quartz and is totally free of systematic errors in the detection scheme or any characteristics or temporal fluctuations of the fundamental source. An additional benefit of reporting our measurements in this manner is that an absolute value for the nonlinear susceptibility of GaN may be determined if the linear optical properties of GaN and quartz are known.
Chapter 4

Linear Optical Measurements

Investigation of the optical properties of a material naturally begins with a measurement of its dielectric constants. The dielectric constants, \(\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)\), determine the transmission, reflection, and absorption coefficients of light from matter. Along with the thickness of the medium, these coefficients precisely specify the propagation of light through a medium. Since the second-harmonic fields generated in our nonlinear materials are strongly dependent on the linear optical properties of the media, precise knowledge of linear optical properties is required to extract \(\chi^{(2)}_{ijk}(\omega = 2\omega_0)\) from our nonlinear optical spectroscopic data.

Previous measurements of GaN had not measured the dielectric constant near the band gap [22, 13, 53]. In order to fully characterize the linear optical properties of our GaN/Al\(_2\)O\(_3\) films, we performed a series of linear spectroscopic measurements, which are described in the following sections.

We have described the sample preparation in section 5.5. Briefly, a 0.050 \(\mu\)m layer
of AlN is deposited on the Al₂O₃ substrate prior to deposition of GaN. The AlN film serves as a buffer layer and facilitates nucleation of GaN on the substrate. All of our calculations of linear and nonlinear optical transmission and reflection approximate the GaN/AlN/Al₂O₃ sample as a GaN/Al₂O₃ sample. Using the reported values for the index of refraction of AlN [54] and the nonlinear susceptibility of AlN [55], we calculated that this simplified two film model introduces an error of less than 1.4% (6%) in the linear (nonlinear) transmission measurements as compared with the three slab model. Therefore, we are justified in ignoring the contribution of the thin AlN buffer layer in our calculations, and adopt the simpler model.

4.1 Linear Measurement of Film Thicknesses

Because linear spectroscopic measurements inherently encompass multiple interference, knowledge of the thin film thickness is required to determine the optical constants. In this section, I describe the theory and experimental techniques we used to determine the thickness of thin films grown on transparent substrates.

4.1.1 Experimental Techniques

The experimental apparatus used to measure thin film thickness is displayed in Fig. 4.1. The experiment consisted of measuring the reflection coefficient as a function of the angle between the GaN/Al₂O₃ surface normal and the incident beam. The
sample was mounted on a goniometer, which had an accuracy of 0.01° in the angle of incidence. A laser beam was aligned with the center of the goniometer, optically chopped at 2kHz, and p-polarized with a Newport Glan-Thompson calcite polarizer model 10GT04AR. The reflected light was detected by a Thor Labs silicon photodiode model FDS100 and measured by a Stanford Research Systems lock-in amplifier model 530. The absolute reflection coefficient was determined by measuring the light transmitted through the optical system without the sample, mounting the sample on the goniometer, measuring the light reflected from the sample as a function of angle, and calculating the ratio of the reflected light to transmitted light. Note, the effect of temporal fluctuations on the intensity of reflected light was removed by measuring a fraction of the incident beam and the light reflected from the sample simultaneously. The angular spectrum was then renormalized to remove temporal fluctuations.

There are two experimental difficulties in measuring the thickness of a ~1 μm GaN film grown on a sapphire substrate. First, the effective film thickness, \( n \) where \( n \) is the index of refraction and \( d \) is the film thickness, is several times the incident wavelength. In theory, a reflection measurement can unambiguously determine a film thickness only if the effective thickness is less than the wavelength of incident light. The measured intensity is produced by the interference of a wave that is reflected off of the front surface and a wave that is transmitted into the thin film where it undergoes a series of reflections and is partially transmitted out of the film. If the effective
Figure 4.1: Linear reflection experimental setup
thickness of the film is greater than the wavelength of light, the phase difference, \( \phi \), between the wave reflected from the surface and the wave reflected off of back surface of the film is

\[
\phi = 2\pi m + \phi_0,
\]

where \( 0 \leq \phi_0 < 2\pi \) and \( m \) is an integer. Since the interference of these waves depends only on \( \phi_0 \), a fit to the reflection data yields a series of thicknesses if the effective thickness is greater than the wavelength of light (\( m > 0 \)). We removed this uncertainty in the reflection measurement by performing film thickness measurements with a HeNe laser (\( \lambda = 632.8 \) nm) and the 488 nm line of an Ar laser. Fits to both sets of reflection data produced two sets of possible film thicknesses. The film thickness that appeared in both sets of data was the correct thickness.

A second experimental difficulty is the transparent sapphire substrate. Reflection from the back surface of the substrate can contribute to the measured signal. We suppressed this contribution by putting a thin layer of index matching fluid between the back surface of the sapphire substrate and a glass slide. The other surface of the glass slide was sand blasted to suppress specular reflections. Although the indices of the index fluid and glass slide (\( n \sim 1.5 \)) do not match that of sapphire (\( n \sim 1.76 \)), this technique effectively suppressed nearly all of the reflected light from the sapphire back surface. This was experimentally verified by accurately fitting the reflected light from a sapphire slab/index fluid/glass slide with a semi-infinite slab theory.
Figure 4.2: Schematic of the GaN sample with index matching fluid and glass slab. This experimental setup suppressed reflected light from the back sapphire surface.

The reflection data from the GaN/sapphire/index fluid/glass slab matched the calculated reflection from a GaN film on a semi-infinite slab of sapphire more closely than theoretically predicted. We define the average normalized error introduced by the glass substrate as

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=0}^{N} \left( \frac{I_i^\text{sapphire} - I_i^\text{glass}}{I_i^\text{sapphire}} \right)^2}$$  \hspace{1cm} (4.2)$$

where $I_i^\text{sapphire}$ represents the theoretically predicted reflection coefficient at an angle of incidence of $i$ degrees from a GaN film on a sapphire semi-infinite substrate. $I_i^\text{glass}$ represents the reflection from GaN grown on sapphire followed by a semi-infinite glass slab. $N$ is the total number of points at which $\sigma$ was evaluated, i.e. $N = 15$. We calculated $\sigma = .094$ but measured $\sigma = .016$. Possible explanations for this discrepancy include a nonuniform thickness of the sapphire substrate and the finite divergence of the HeNe beam. Both of these effects damp the oscillations from the interference of the light multiply reflected from the GaN film and the sapphire substrate.
Table 4.1: Constants for sapphire Sellmeier equation

<table>
<thead>
<tr>
<th>i</th>
<th>$A_i$</th>
<th>$\lambda_i^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.023798</td>
<td>0.00377588 $\mu m^2$</td>
</tr>
<tr>
<td>2</td>
<td>1.058264</td>
<td>0.01222544 $\mu m^2$</td>
</tr>
<tr>
<td>3</td>
<td>5.280792</td>
<td>321.3616 $\mu m^2$</td>
</tr>
</tbody>
</table>

4.1.2 Theory and Analysis

We developed a simple theory to analyze the reflected light from a thin dielectric film on a semi-infinite slab. We used the standard Sellmeier equation for the ordinary index of refraction for sapphire [56]

$$n_o = \sqrt{1 + \sum_{i=1}^{3} \frac{A_i \lambda^2}{\lambda^2 - \lambda_i^2}}.$$  \hspace{1cm} (4.3)

The parameters for the Sellmeier equation are displayed in Table 4.1. The extraordinary index of refraction, tabulated in [57], is $\sim 0.01$ less than the ordinary index of refraction. Since the sapphire index of refraction only affects Fresnel coefficients and not phases, our assumption of an isotropic index of refraction is valid. We initially assumed the value for the index of refraction of GaN found in the literature [58] in order to determine a first guess about the film thickness. The film thickness and index of refraction for GaN were then determined iteratively.

Fig. 4.3 displays reflected and transmitted fields in the GaN thin film. The re-
Figure 4.3: Coordinate system for linear reflectivity. A single reflection in the GaN film is displayed. The phase difference between the wave reflected from the surface and the wave that is transmitted from the GaN film is $\delta$.

The reflected electric field, $E_r$, is expressed in terms of the incident electric field, $E_i$, as

$$\frac{E_r}{E_i} = r_{01} + t_{01}t_{10}r_{12}e^{i\delta} + t_{01}t_{10}^2r_{12}^2e^{2i\delta} + \ldots. \quad (4.4)$$

In equation (4.4), $r_{ij}$ refers to the Fresnel reflection coefficient for p-polarized light incident from medium i and reflected from medium j, $t_{ij}$ is the Fresnel transmission coefficient for p-polarized light incident from medium i and transmitted through medium j, and $\delta$ is the phase difference between the beams that are reflected from the front and back surfaces of the medium 1 and can be expressed as

$$\delta = \frac{4\pi\cos\theta_1 n_1 d}{\lambda}. \quad (4.5)$$
Figure 4.4: Linear reflectivity of GaN/Al₂O₃ as a function of angle. The measurements were made at 488 nm (□) and 632.8 nm (○). The fit to the 488 nm data yields a GaN film thickness of 1.022 μm and the fit to 632 nm data yields 1.018 μm.

Equation (4.4) may be written in a simplified form as

$$\frac{E_r}{E_i} = r_{01} + \frac{r_{12}t_{10}e^{i\delta}}{1 - r_{12}t_{10}e^{i\delta}}.$$  \hspace{1cm} (4.6)

Fig. 4.4 displays the normalized reflection data and best fits for the HeNe and Ar ion measurements. The data were fitted by a $\chi^2$ fit to the theoretical and experimental data with the film thickness as the only free parameter.
4.2 Measurement of Indices of Refraction and Absorption Coefficient

We measured the index of refraction and absorption coefficient for GaN over an energy range from the UV to the IR. These measurements are essential for an accurate determination of $\chi_{ijk}^{(2)}(\omega = 2\omega_0)$.

4.2.1 Experimental Techniques

We measured the real and imaginary parts of the dielectric function with the apparatus shown in Fig. 4.5. The light source was an Oriel 450 W Xe lamp with an f/1.0 UV enhanced lens. The spectral range of this lamp is 200-2500 nm. The wavelength was selected by a Jarrel Ash Monospec 25 monochrometer with a 1200 grooves/mm grating. The wavelength of the monochrometer was selected by a computer controlled stepper motor. The light from the monochrometer was p-polarized and a fraction was used to remove temporal fluctuations as in section 4.1.1. The sample was rotated by a stepper motor to change the angle of incidence. By measuring transmitted light intensity as a function of the angle of incidence, the dielectric constant can be accurately determined.

4.2.2 Calculations of Dielectric Constants

We formulate a description of the transmission of light through a multilayer film by matrix methods [56, 59]. The technique relates the tangential electric and magnetic...
Figure 4.5: Experimental set-up for transmission measurements
fields at the $j^{th}$ interface to the known tangential electric and magnetic fields at the adjacent $(j-1)^{th}$ interface. In general, optical properties are described by a complex index of refraction, $\tilde{n} = n + i\kappa$. However, our GaN thin films are characterized by a real index of refraction over the spectral range probed in our experiments. Thus, we derive our transmission theory assuming a real index of refraction of GaN. The more general transmission theory with complex indices of refraction, which describes transmission and reflection including effects of absorption, is discussed in Appendix D.

We first describe the method for the transmission of $p$-polarized light through a single layer. We then generalize the theory to multiple layers and apply it to our case of light transmission through the GaN/Al$_2$O$_3$ sample.

Fig. 4.6 displays the geometry of light incident on a single thin film. By applying boundary conditions at each interface, a relationship is developed between the tangential components of the fields on each side of the interface. In addition, fields at different locations within the same layer are related to one another via a phase factor. From these relationships, the transmission coefficient of the thin film is calculated.

In the following analysis, we use bold faced letters, e.g. $\mathbf{E}$, to denote total fields, and script letters, e.g. $\mathcal{E}$, to denote tangential fields.

A single thin film consists of three layers: the incident layer, the thin film layer, and the substrate layer. In layer 1, the electric field consists of a positive and negative
Figure 4.6: Coordinate system for linear transmission through a single slab.
traveling wave, i.e.

\[ E_1 = E_1^+ e^{i(k_1^+ r - \omega t)} + E_1^- e^{i(k_1^- r - \omega t)} \] \hspace{1cm} (4.7)

where the wavevectors are

\[ k_1^+ = k_i (\cos \theta_1 \hat{z} + \sin \theta_1 \hat{x}) \quad \text{and} \quad k_1^- = k_i (\cos \theta_1 \hat{z} + \sin \theta_1 \hat{x}). \hspace{1cm} (4.8) \]

The subscript labels the layer in which the variables are defined. Angles in other layers are derived from Snell’s law. Henceforth, we omit the \( \omega \) dependence of the wave. Note that equation (4.7) is the general solution to Maxwell’s equations in each layer assuming a plane wave incident on the film stack with a well defined wavevector.

The formulation of the transmission coefficient is somewhat complicated because the boundary conditions are expressed in terms of the total tangential field, e.g. \( E_1 \), while the propagation of the field from one boundary to another in the same layer is expressed in terms of the positive and negative going tangential fields, e.g. \( E_1^+ \) and \( E_1^- \). The calculation may be summarized in six steps as follows. First, the tangential fields across boundary \( b \) are related to one another by boundary conditions. Second, the boundary conditions at interface \( b \) are expressed in terms of the positive and negative going tangential fields in layer 1. Third, the positive and negative going fields at boundary \( b \) are related to the positive and negative going fields in layer 1 at boundary \( a \). Fourth, the positive and negative going waves at boundary \( a \) are expressed in terms of the total tangential fields, and boundary conditions are applied.
at this interface. Note that "total tangential fields at boundary a" refers to the tangential fields in both layer 0 and layer 1 at boundary a, i.e. boundary conditions require the equality of the tangential fields on both sides of the interface. Fifth, the reflection coefficient of the thin slab is determined from the tangential fields at boundary a. Sixth, the transmission coefficient of the thin film is determined from the reflection coefficient of the slab.

Step 1 - Apply boundary conditions at boundary b.

Our calculation determines the transmission of p-polarized light through a single thin film. Therefore, the tangential electric field is related to the total electric field as

\[ \mathcal{E}_i = \hat{x} (\hat{x} \cdot \mathbf{E}_i), \] (4.9)

where \( i = 0, 1, \text{ or } 2 \), which denotes the incident region, the thin film, and the substrate, respectively. For p-polarized light the tangential component of the magnetic field is identically equal to the total magnetic field, i.e.

\[ \mathcal{H}_i = \mathbf{H}_i. \] (4.10)

Therefore, boundary conditions at boundary b imply

\[ \mathcal{E}_{1b} = \mathcal{E}_{2b} \] (4.11)

and

\[ \mathcal{H}_{1b} = \mathcal{H}_{2b}. \] (4.12)
Note that the additional subscript, $b$, denotes that the tangential fields are defined at boundary $b$.

**Step 2** - Rewrite the boundary conditions at boundary $b$ in terms of the positive and negative going tangential fields.

In the substrate region, i.e. layer 2, only a positive going wave exists. Also note that boundary $b$ is defined at $z = 0$. Therefore, the boundary conditions at boundary $b$ may be rewritten as

$$\mathcal{E}^+_{2b} = \mathcal{E}^+_{1b} + \mathcal{E}^-_{1b} \quad (4.13)$$

and

$$\mathcal{H}^+_{2b} = \mathcal{H}^+_{1b} + \mathcal{H}^-_{1b}. \quad (4.14)$$

From $\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{H}}{\partial t}$ we can write equation (4.14) as

$$\eta_2 (\hat{z}_1 \times \mathcal{E}^+_{2b}) = \eta_1 (\hat{z} \times \mathcal{E}^+_{1b} - \hat{z} \times \mathcal{E}^-_{1b}), \quad (4.15)$$

where $\eta_i = \frac{n_i}{\cos \theta_i}$. Equation (4.15) is derived in Appendix D.

**Step 3** - Determine the positive and negative going waves at boundary $a$ from the positive and negative going waves at boundary $b$ in the same layer (layer 1).

Boundary $a$ is located at $z = -d$. Following equation (4.7), the positive and negative going tangential fields at boundary $a$ are defined in terms of the positive and negative going waves at boundary $b$ as

$$\mathcal{E}^+_{1a} = \mathcal{E}^+_{ib} e^{i\delta_i}, \quad \mathcal{E}^-_{1a} = \mathcal{E}^-_{ib} e^{-i\delta_i}, \quad \mathcal{H}^+_{1a} = \mathcal{H}^+_{ib} e^{i\delta_i}, \quad \text{and} \quad \mathcal{H}^-_{1a} = \mathcal{H}^-_{ib} e^{-i\delta_i}. \quad (4.16)$$
where $\delta_1 = \frac{-2\pi n_1 \cos \theta \cdot d}{\lambda}$. 

**Step 4 -** Express the tangential positive $(\mathcal{E}_{1a}^+)$ and negative $(\mathcal{E}_{1a}^-)$ going fields at boundary $a$ in layer 1 in terms of the total tangential fields $(\mathcal{E}_{1a})$ at boundary $a$. 

From equations (4.13), (4.14), and (4.16), the equations that define the tangential fields at boundary $a$ are

\[
\mathcal{E}_{1a}^- = \mathcal{E}_{1a}^+ + \mathcal{E}_{1a}^-, \quad (4.17)
\]
\[
\mathcal{E}_{1a}^+ = \mathcal{E}_{1b}^+ e^{i\delta_1} + \mathcal{E}_{1b}^- e^{-i\delta_1}, \quad (4.18)
\]
\[
(\hat{z} \times \mathcal{E}_{1a}) = (\hat{z} \times \mathcal{E}_{1b}^+) e^{i\delta_1} + (\hat{z} \times \mathcal{E}_{1b}^-) e^{-i\delta_1}, \quad (4.19)
\]
and
\[
\mathcal{H}_{1a}^+ = \mathcal{H}_{1b}^+ e^{i\delta_1} + \mathcal{H}_{1b}^- e^{-i\delta_1}. \quad (4.20)
\]

Note that equations (4.17), (4.18), and (4.19) express the continuity of the tangential electric field at boundary $a$, while equation (4.20) expresses the continuity of the tangential magnetic field at boundary $a$. Using equations (4.14) and (4.15), the positive and negative going tangential fields are expressed in terms of the total tangential fields (on either side of the interface) as

\[
(\hat{z} \times \mathcal{E}_{1b}^+) = \frac{1}{2} \left( \frac{\mathcal{H}_b}{\eta_1} + (\hat{z} \times \mathcal{E}_b) \right)
\]
\[
(\hat{z} \times \mathcal{E}_{1b}^-) = \frac{1}{2} \left( -\frac{\mathcal{H}_b}{\eta_1} + (\hat{z} \times \mathcal{E}_b) \right)
\]
\[
\mathcal{H}_{1b}^+ = -\frac{1}{2} (\mathcal{H}_b + \eta_1 (\hat{z} \times \mathcal{E}_b))
\]
\[
\mathcal{H}_{1b}^- = -\frac{1}{2} (-\mathcal{H}_b + \eta_1 (\hat{z} \times \mathcal{E}_b)). \quad (4.21)
\]

Equation (4.21) is derived in Appendix D. Note that the total tangential fields, e.g.
$\mathcal{E}_b$, are defined only at the interface, e.g. $b$, and not by the layer, e.g. 1 or 2. By definition, the tangential fields at the interface are continuous, e.g. $\mathcal{E}_b = \mathcal{E}_{1b} = \mathcal{E}_{2b}$, and thus the layer subscript is unnecessary. Combining equations (4.19) and (4.20) with equation (4.21) yields

$$ (\hat{z} \times \mathcal{E}_a) = (\hat{z} \times \mathcal{E}_b) \frac{e^{i\delta_1} + e^{-i\delta_1}}{2} + \frac{1}{\eta_1} \mathcal{H}_b \frac{e^{i\delta_1} - e^{-i\delta_1}}{2} $$

(4.22)

and

$$ \mathcal{H}_a = \eta_1 (\hat{z} \times \mathcal{E}_b) \frac{e^{i\delta_1} - e^{-i\delta_1}}{2} + \mathcal{H}_b \frac{e^{i\delta_1} - e^{-i\delta_1}}{2}. $$

(4.23)

Equations (4.22) and (4.23) may be written in a matrix form as

$$ \begin{pmatrix} (\hat{z} \times \mathcal{E}_a) \\ \mathcal{H}_a \end{pmatrix} = M_1 \begin{pmatrix} (\hat{z} \times \mathcal{E}_b) \\ \mathcal{H}_b \end{pmatrix} $$

(4.24)

with

$$ M_1 = \begin{pmatrix} \cos \delta_1 & \frac{1}{\eta_1} \sin \delta_1 \\ i\eta_1 \sin \delta_1 & \cos \delta_1 \end{pmatrix}. $$

(4.25)

A useful form of equation (4.24) is obtained by normalizing the field $(\hat{z} \times \mathcal{E}_b)$ at the output interface (interface $b$). In this case we obtain

$$ \begin{pmatrix} B \\ C \end{pmatrix} = M_1 \begin{pmatrix} 1 \\ \eta_2 \end{pmatrix} $$

(4.26)

with

$$ B = \frac{(\hat{z} \times \mathcal{E}_a)}{(\hat{z} \times \mathcal{E}_b)} $$

(4.27)
and

\[ C = \frac{\mathcal{H}_a}{(\hat{z} \times \mathcal{E}_b)}. \] (4.28)

Note that equation (4.26) follows from

\[ \eta_2 = \frac{n_2}{\cos \theta_2} = \frac{\mathcal{H}_b}{(\hat{z} \times \mathcal{E}_b)}. \] (4.29)

**Step 5 - Determine the reflection coefficient at boundary a.**

Steps 1 - 4 determine the tangential fields at boundary a in terms of the tangential fields at boundary b. We can write the transmission coefficient, \( T \), in terms of the reflection coefficient, \( R \). \( R \) is calculated from the boundary conditions at interface a, which are

\[ (\hat{z} \times \mathcal{E}_{0a}^+) + (\hat{z} \times \mathcal{E}_{0a}^-) = (\hat{z} \times \mathcal{E}_{1a}^+) + (\hat{z} \times \mathcal{E}_{1a}^-) \] (4.30)

and

\[ \mathcal{H}_{0a}^+ + \mathcal{H}_{0a}^- = \mathcal{H}_{1a}^+ + \mathcal{H}_{1a}^- . \] (4.31)

Equation (4.31) may be rewritten as

\[ \eta_0 ((\hat{z} \times \mathcal{E}_{0a}^+) - (\hat{z} \times \mathcal{E}_{0a}^-)) = \mathcal{H}_{1a}^+ + \mathcal{H}_{1a}^- . \] (4.32)

We solve equations (4.30) and (4.32) to determine \( \mathcal{E}_{0a}^- \), setting \( \mathcal{E}_{2b}^+ = \mathcal{E}_2 \). It is thus assumed that only a positive going wave exists in the substrate region, and therefore the tangential electric field defined at boundary b, i.e. \( \mathcal{E}_2 = \mathcal{E}_{2b}^+ \) is explicitly related to the reflection coefficient.
Equations (4.30) and (4.32) are combined with equations (4.27) and (4.28) to determine the reflection amplitude as

$$r = \frac{(\hat{z} \times \vec{E}_{0a}^-)}{(\hat{z} \times \vec{E}_{0a}^+)} = \frac{E_0^-}{E_0^+} = \frac{\eta_0 B - C}{\eta_0 B + C}. \quad (4.33)$$

Equation (4.33) is derived in Appendix D. The reflection coefficient is

$$R = rr^*. \quad (4.34)$$

**Step 6 - Calculate the transmission coefficient.**

The transmission coefficient of the thin film is calculated from the reflection coefficient as

$$T = 1 - R. \quad (4.35)$$

Equation (4.35) assumes that the layers have real indices of refraction, i.e. the layers do not absorb light. From equations (4.33) and (4.35), we express the transmission coefficient as

$$T = \frac{2\eta_0 (BC^* + B^*C)}{(\eta_0 B + C)(\eta_0 B + C)^*}. \quad (4.36)$$

The real part of the product $BC^*$ is easily determined by performing the matrix multiplication in equation (4.26) and using the fact that $M_1$ (equation (4.25)) has a determinant equal to 1, and noting that $\eta_1$ is real (this is true only for a real index of refraction). The derivation of the transmission coefficient for a complex $\eta_1$, i.e. a
complex index of refraction, is presented is Appendix D. For a real index of refraction, the expression for the real part of $BC^*$ is

$$\text{Real}(BC^*) = \eta_2.$$ (4.37)

Thus, combining equations (4.36) and (4.37) determines $T$ as

$$T = \frac{\eta_2}{\eta_0} tt^*$$ (4.38)

where

$$t = \frac{2\eta_0}{\eta_0 B + C}.$$ (4.39)

For an $l$ layer stack, the equations (4.26) and (4.38) are modified as

$$\begin{pmatrix} B \\ C \end{pmatrix} = M_1 M_2 \ldots M_l \begin{pmatrix} 1 \\ \eta_{l+1} \end{pmatrix}$$ (4.40)

and

$$T = \frac{\eta_{l+1}}{\eta_0} tt^*,$$ (4.41)

where $M_i$ is defined as equation (4.25) with its characteristic thickness, $d_i$, and angle of incidence of the fields, $\theta_i$. Note, the layers are labeled from 1, which is the layer adjacent to the incident medium, to $l$, which is the layer adjacent to the substrate material.

In contrast to the HeNe and Ar ion lasers used in the thin film thickness measurements, the Xe lamp has a non-negligible bandwidth that must be accounted for in
the calculation of the transmitted intensity. The spectral characteristics of our light source may be approximated by a function of the form

$$I(\omega) = I_0 e^{[-\frac{\Delta \lambda - \lambda_0^2}{\Delta \lambda^2}]}.$$

(4.42)

where $\Delta \lambda = 4$ nm is the light source wavelength bandwidth and $\lambda_0$ is the central wavelength. In practice, the interference of light with a broadband spectral intensity distribution of equation (4.42) exhibits dramatically different behavior in thin and thick films. Thin films are characterized by a thickness $d$ that satisfies $d << \frac{2\lambda^2}{n\Delta \lambda}$, where $n$ for GaN ranges from 2.32 to 2.68 over our measurement. The transmission of light through a thin film is highly sensitive to the film's index of refraction and thickness due to the interference of multiply reflected waves in the film. Conversely, in thick films, where $d >> \frac{2\lambda^2}{n\Delta \lambda}$, both constructive and destructive interference of the multiply reflected light occur in the film. Thus, the light transmitted through the thick film is relatively insensitive to the film thickness and is only mildly sensitive to the index of refraction due to Fresnel coefficients. For our system, GaN is a thin film ($\frac{dn\Delta \lambda}{\lambda^2} < 0.2$), while sapphire is a thick film ($\frac{dn\Delta \lambda}{\lambda^2} \sim 10$). This is the ideal combination for measuring the index of refraction of GaN because the transmitted intensity is highly sensitive to the index of refraction of GaN but is relatively insensitive to the optical properties of sapphire.

Calculations of the transmission coefficient incorporated the finite bandwidth effects by summing over a series of monochromatic transmission coefficients weighted
Table 4.2: Empirical constant for GaN Sellmeier equation. The $\lambda_i$ parameters are expressed in $\mu$m.

by a normalized Gaussian frequency distribution, i.e. equation (4.42). We performed a least squares fit to the data with the index of refraction as the only free parameter. Appendix F discusses our optimization methods. This method is used for all data fitting in this thesis.

Fig. 4.7 displays transmission data and calculations for a 1.020 $\mu$m GaN film on Al$_2$O$_3$. This measurement was repeated in $\sim$0.1 eV increments from $\lambda = 370$-900 nm. We fitted the observed dispersion in the GaN index of refraction with a two term Sellmeier equation

$$n(\lambda) = \sqrt{1 + \frac{A_1 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{A_2 \lambda^2}{\lambda^2 - \lambda_2^2}}.$$  \hspace{1cm} (4.43)

The empirically determined constants for the Sellmeier equation are displayed in Table 4.2. This dispersion relationship holds for all of our GaN samples.

GaN, like sapphire, is a birefringent material. However, all calculations of the
Figure 4.7: Optical transmission data for GaN/Al₂O₃ with a film thickness of 1.021 μm. Transmission spectra are for λ = 777 nm (○) and λ = 549 nm (□). The solid (dashed) line is the best fit to the λ = 777 (549) nm data.
linear and nonlinear properties in this thesis assume that GaN is isotropic. The justification of this assumption follows. All samples investigated in this work are grown with the c axis, or the extraordinary axis, normal to the surface. The extraordinary index is related to the ordinary index by $n_e - n_o \approx 0.02$ [58]. Assuming the incident wave is polarized in the plane containing the extraordinary axis, the index of refraction for light propagating with an angle $\theta$ to the in the extraordinary axis is [60]

$$n_e(\theta) = n_o \sqrt{\frac{1 + \tan^2 \theta}{1 + (n_\text{ex}/n_e)^2 \tan^2 \theta}}. \quad (4.44)$$

In all of our linear and nonlinear experiments, the angle of between the incident beam and the surface normal is less than $75^\circ$. The light transmitted into the GaN sample refracts such that the angle between extraordinary axis and the direction of propagation is reduced to less than $24^\circ$. Using equation (4.44), we estimated that our optical experiments always probe an effective index of refraction that is within 0.15% of the ordinary index. This correction alters the phase of light traversing a GaN film by at most $2^\circ$.

Using the transmission measurement, we also determined the absorption constant for GaN in the vicinity of the band gap ($\sim 3.4 \text{ eV}$). Absorption can be included in the matrix-transmission theory by multiplying the transmission coefficient, $T$, in equation (4.6) by $e^{-\alpha d}$. The coefficient $\alpha$ is related to the imaginary part of the index
of refraction, $\kappa$, as

$$\alpha(\lambda) = \frac{4\pi}{\lambda} \kappa(\lambda).$$  \hspace{1cm} (4.45)

Fig. 4.8 displays the absorption data. This experiment measured a larger value for $\alpha$ than the Zhang et al. measurement [13]. Finally, the fitted Sellmeier parameters accurately reproduce the linear spectral behavior of the GaN/Al$_2$O$_3$ film (see Fig. 4.9).
Figure 4.9: Transmission coefficient of GaN/Al\textsubscript{2}O\textsubscript{3}. The solid line is the data from a normal incident transmission data. The dashed line is a fit to the data using the two slab matrix model with the Sellmeier equation and the measured absorption coefficient as parameters.
4.3 Photoluminescence of GaN

To characterize the defect structure of GaN we measured the photoluminescence spectra of several GaN samples. The optical layout for the photoluminescence measurement is displayed in Fig. 4.10. A 10 mW 356 nm beam from a Spectra-Physics model 2025-11 CW Krypton-Ion laser optically excited electrons from the GaN valence band to the conduction band. The photoluminescent light from the GaN sample was collected using a lens and then focused on the entrance slit of a ISA model HR320 single pass monochrometer with a 1200 grooves/mm grating. The light was detected with a Hamamatsu PMT and measured with a lock-in amplifier. The monochrometer slits were set to 0.25 mm to resolve the spectrum to \( \sim 0.5 \) nm. A computer recorded and analyzed the data and automatically positioned the monochrometer with a stepper motor. In order to remove the spectral sensitivity of the optical system, we calibrated the system by recording the spectrum from a lamp with a known power spectrum. The calibration lamp is a Optronics model 245C, 45 W tungsten-halogen coiled filament powered by an Optronics model 65DS constant current source. The spectrum recorded from the tungsten lamp was compared with the known spectral irradiance of the lamp to determine the spectral response of the photoluminescence system. The raw data from the GaN photoluminescence spectra was then corrected using the measured spectral response of the system to yield the real photoluminescence spectra.

We measured the photoluminescence at room temperature and at 82 K. The sam-
The GaN sample was mounted in the dewar for both the 293 K and 82 K photoluminescence measurements. This dewar consists of an inner jacket, which was filled with liquid nitrogen to a level just below the sample during the low temperature measurement, and an outer jacket, which was filled with liquid nitrogen to the top of the dewar during the low temperature measurement. The sample was mounted in the optical fin of the dewar, which consists of four glass windows through which light can propagate. Prior to cooling the dewar with liquid nitrogen, we purged the inner jacket with gaseous nitrogen for ~10 minutes to remove any moisture in the inner jacket. This process was a necessary step in the experimental process to prevent water vapor from freezing on the GaN sample and clouding the optical fin, thus impeding
a photoluminescence measurement.

The temperature of the GaN film was measured by a Lake Shore Cryotronic, Inc. carbon-glass resistor model CGR-1-2000. This device was developed for use with a Lake Shore temperature monitor device as an extremely accurate temperature sensor over a wide temperature range. We did not have access to a commercial temperature system. We built the system displayed in Fig. 4.11 to monitor the temperature. The resistance of the carbon-glass resistor is a function of temperature. By measuring the voltage drop across the carbon-glass resistor for a fixed current input, the resistance and, hence, temperature are measured. While this system is much less accurate than the commercial systems, the photoluminescence spectra of GaN at \( \sim 80 \) K is insensitive to temperature change on the order of a few K. Our system has the necessary temperature resolution to this level.

Figs. 4.12 and 4.13 display the photoluminescence for an undoped GaN/Al\(_2\)O\(_3\) sample. The data shows weak structure from \( \sim 390-410 \) nm (3.02-3.18 eV) at 293 K and a much stronger signal at 378.5 nm (3.276 eV). The difference in scale of the photoluminescence data indicates that the photoluminescence intensity is much stronger at lower temperatures. This data is consistent with shallow donor acceptor recombination. Lowering the temperature of the GaN/Al\(_2\)O\(_3\) sample increases the population in these states and, thus, facilitates photoluminescence.

Figs. 4.14 and 4.15 display photoluminescence spectra for an n-doped GaN sam-
Figure 4.11: Device to measure temperature of GaN during low temperature photoluminescence. The thick wires represent the four leads (two current, two voltage) to the carbon-glass resistor.

In the region near the band gap, ~400 nm, the doped samples exhibit a similar behavior as the undoped sample. Again this is attributed to donor-acceptor recombination. Unlike the spectra from the undoped sample, the doped sample spectra display a wide feature at ~2.2 eV. In contrast to the DA recombination feature, this feature is insensitive to temperature. This yellow band luminescence is ubiquitous in GaN samples. The oscillations in the yellow band are due to a microcavity formed by the front and back surfaces of the GaN film [61].
Figure 4.12: Photoluminescence spectrum of undoped GaN at 293 K
Figure 4.13: Photoluminescence spectrum of undoped GaN at 82 K
Figure 4.14: Photoluminescence spectrum of n-doped GaN at 293 K
Figure 4.15: Photoluminescence spectrum of n-doped GaN at 82 K
Chapter 5

Properties of GaN

In recent years, the electronic, optical, and structural properties of the III-V nitrides have been thoroughly investigated. Alloys with different atoms such as In, Ga, and Al with N produce semiconductor materials with band gaps ranging from 1.9 to 6.2 eV. The most significant motivation for these studies is the potential of III-V nitrides for short-wavelength laser diode applications.

Commercial applications of short-wavelength laser diodes include optical storage, laser printing, and display technologies. As an example of their superiority, we compare digital video disks (DVD) systems with conventional long-wavelength diodes to systems with short-wavelength diodes [62]. Short wavelength diodes are focused to a smaller spot size than long-wavelength diodes. Present DVD-ROM technology uses diode lasers that emit between 635 and 650 nm and read 0.4 μm pits separated by 0.74 μm tracks. Storage for these disks is 4.7 Gbyte. By comparison, GaN laser diode based DVD systems (operating at wavelengths of 400 to 430 nm) are projected to
read 0.2 μm pit lengths on a 0.4 μm track. The predicted storage density is 15 Gbyte.

Despite predictions of the commercially available short-wavelength laser diodes, the development of GaN based electro-optic devices has been hindered by a number of factors; these factors include lack of suitable substrates, difficulty in p-doping the nitrides, presence of large background electron concentrations, and lack of modern crystal growth techniques [63]. Only recently have advances by Nakamura and coworkers [19] in GaN laser diode lifetimes suggested that the goal of commercially available short-wavelength laser diodes by 2000 is within reach.

Although the commercial potential for GaN based laser diodes is enormous, we are concerned with the fundamental optical properties of GaN. Theoretical and experimental investigations have elucidated the structure of defects levels in GaN and have contributed to our understanding of self-compensation in GaN. Because a thorough understanding of material properties is essential for the interpretation of our spectroscopic data, in this chapter we briefly review the properties of GaN. The chapter is organized as follows. First we discuss the structural and electronic properties of GaN with an emphasis on the electronic properties near the valence band maximum and conduction band minimum. We then summarize the experimental and theoretical investigations of defects in GaN. Finally, we apply group theory to calculate all resonantly enhanced second-order nonlinear optical process in GaN.
5.1 Crystal Structure

A crucial obstacle impeding the growth of high quality, defect free GaN films is the lack of a suitable substrate. Traditionally, GaN has grown on the [0001] face of sapphire, despite the large lattice mismatch and thermal incompatibility [64]. In general, GaN crystallizes in the wurzite phase when grown on a hexagonal substrate and the zincblende phase when grown on cubic substrates (except for the [111] face of cubic substrates). Examples of substrates for wurzite GaN include Al₂O₃ [0001] [65], Al₂O₃ [11̅20] [15], Al₂O₃ [01̅10] [66], SiC 6H [67, 68, 69] and GaAs [111] [70]. Zincblende GaN has been grown on GaAs [001], 3C SiC [71], MgO [66], and Si [001] [72, 73]. For the remainder of this thesis, we will confine ourselves to wurzite GaN grown on Al₂O₃ [0001]. All of our GaN samples have this structure, which is the most common structure for GaN.

Before discussing the physical structure of GaN, a few definitions are required. Unlike cubic systems, the structure of GaN and Al₂O₃ are referred to using a four index label. The convention for hexagonal systems is a four axis system, e.g. [hkil] where the h, k, and i refer to the reciprocal of the intercept of the Miller plane with the lattice vector in the hexagonal plane [74]. The three indices are related to one another according to

\[ i = -(h + k). \]  \hspace{1cm} (5.1)

The fourth index, l, corresponds to the reciprocal of the Miller plane with the crystal
axis perpendicular to the hexagonal plane. The [0001] face of Al₂O₃ is referred to as the α face, the c-face, or the basal plane.

Structurally, wurzite (see Fig. 5.1) and zincblende crystals are very similar. Wurzite is formed by stacking planes of Ga and N atom in an ABAB... sequence along the (0001) direction, while zincblende is formed from an ABCABC... sequence along the (111) direction. The similarity of these structures results in equivalent nearest neighbors for both the wurzite and zincblende lattices. However, next nearest neighbors are inequivalent. The actual positions of the Ga and N atoms are determined by its space group, p6₃mc. The Ga atoms are located at (0, 0, 0) and (2/3, 1/2, 1/3), while the N atoms are located at (0, 0, u) and (2/3, 1/3, 1/2+u). Table 5.1 displays some of the physical properties of GaN. Note, u refers to the displacement of the Ga sublattice with respect to the N sublattice and has an ideal value of 0.375c.

5.2 Band Structure and Electronic Properties of GaN

In this section we discuss spectroscopic structure in the band gap region and we describe the measured electronic properties of GaN.

---

1 The point groups are listed in the Schoenflies and international notation respectively. The space groups are listed in notation of International Tables for X-ray Crystallography [75].
Figure 5.1: Wurtzite crystal structure. The white spheres represent Ga atoms and the gray spheres represent N atoms.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a lattice constant</td>
<td>0.3189 nm [76]</td>
</tr>
<tr>
<td>c lattice constant</td>
<td>0.5185 nm [76]</td>
</tr>
<tr>
<td>point group</td>
<td>C₆ᵥ or 6mm</td>
</tr>
<tr>
<td>space group</td>
<td>p₆₃mc (No. 186)</td>
</tr>
</tbody>
</table>

Table 5.1: Crystal Properties of GaN [0001].
5.2.1 Band Gap Physics

GaN is a direct band gap semiconductor with a band gap of 3.4 eV. Because a medium's response to an incident light field is enhanced when the photon has an energy nearly equal to an energy state of the system, the properties of the conduction band minimum and valence band maximum strongly influence the optical characteristics of GaN in the near band gap region. Therefore, in this section we focus mainly on the characteristics of the valence band maximum and the conduction band minimum. This section includes some discussion of group theory, which will be more thoroughly explained in section 5.4. Fig. 5.2 displays the calculated band structure of GaN. The band gap sits at the Γ point of the Brillouin zone (see Fig. 5.3). The valence band maximum is built (principally) of the N 2p states. In the absence of spin orbit splitting, the valence band maximum consists of Γ₆ and Γ₁ bands that are split by the hexagonal crystal field by \( \Delta_{cr} = 22 \text{ meV} \) \cite{78}. When spin is included, the Γ₆ band splits into Γ₉ and Γ₇ bands, separated by the spin-orbit energy of \( \Delta_{so} = 11 \text{ meV} \) \cite{78}. Inclusion of spin also transforms the Γ₁ band to Γ₇. Because spin orbit splitting is so small, matrix elements may be calculated from the representation of the point group without spin.

The conduction band minimum is built (principally) of the Ga and N s-states. Without spin, the state is labeled as Γ₁, and with the inclusion of spin, the band transforms as Γ₇. The valence and conduction bands are separated by 3.4 eV at room
Figure 5.2: Calculated GaN band structure. The method of calculation is the empirical pseudopotential method. This figure is adapted from [77].
Figure 5.3: Brillouin zone of the hexagonal lattice
### Table 5.2: GaN electrical properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>electron mobility</td>
<td>$\mu_e$</td>
<td>350 cm$^{-2}$/Vs [65]</td>
</tr>
<tr>
<td>electron concentration (undoped)</td>
<td>$n_e$</td>
<td>$\sim 10^{17}$ cm$^{-3}$ [81]</td>
</tr>
<tr>
<td>electron concentration (doped)</td>
<td>$n_e$</td>
<td>$\sim 10^{19}$ cm$^{-3}$ [82]</td>
</tr>
<tr>
<td>hole mobility</td>
<td>$\mu_h$</td>
<td>20 cm$^{-2}$/Vs [83]</td>
</tr>
<tr>
<td>hole concentration</td>
<td>$n_h$</td>
<td>$4.5 \times 10^{17}$ cm$^{-3}$</td>
</tr>
</tbody>
</table>

Control of the electrical properties of GaN is one of the largest obstacles to improving GaN electro-optical device properties. Undoped GaN displays high electron concentrations (see Table 5.2.) These high electron concentrations may result from the formation of native donors that introduce electrons with energies near the valence band [79]. These donors act as an efficient compensation mechanism that hinders p-doping of GaN. For example, incorporation of $\sim 6 \times 10^{19}$ cm$^{-3}$ Mg acceptors into the GaN lattice results in a hole concentration of $\sim 5 \times 10^{17}$ cm$^{-3}$ [80]. An overview of defects in GaN is presented in section 5.3.
5.3 Defects in GaN

Recently, intense experimental and theoretical effort has been applied to understand the nature of defect states in GaN. The goals of this effort include the identification of the prevalent defect species, determination of the growth conditions that lead to defects, and elimination of defect states to optimize GaN electro-optic performance characteristics. Defect states adversely affect the electrical characteristics of semiconductors by trapping carriers. This trapping degrades the mobility of the conducting material. Defect states also offer both radiative and nonradiative electron-hole recombination routes that compete with the preferred radiation channel, i.e. the defect states degrade the preferred luminescent properties of the material. We briefly review some of the experimental and theoretical work on this subject for two reasons. First, defect states are present in GaN regardless of growth technique or doping. Second, our study was motivated in part to elucidate the role of defect states on the nonlinear optical properties of GaN.

Perhaps the most commonly postulated defect state in GaN is the nitrogen vacancy, $V_N$ [53, 76, 84, 85, 86]. The ubiquitous high n-type conductivity of GaN suggests that the conduction electrons are due to a native defect, as opposed to a contaminant which has lower concentrations than the conduction electrons. Using *ab initio* molecular dynamics calculations, Boguslawski and coworkers identified $V_N$ and the gallium interstitial, I(Ga), as defect states most likely to be responsible for the
high intrinsic electron concentrations in GaN. However, other researchers Neugebauer and Van de Walle do not believe this mechanism for the n conductivity, i.e. \( V_N \) [87]. They instead suggest that the dominant defect in n-type GaN is \( V_{Ga} \) and in p-type GaN is \( V_N \).

Table 5.3 summarizes some of the experimental work in this field\(^2\). No consensus as to the nature of defects states in GaN has been reached, and this area remains a rich field for research.

### 5.4 Application of Group Theory to Optical Process

In this section, we analyze the relationship between the nonlinear optical properties of GaN and its band structure. This analysis is formulated in terms of group theory and selection rules. This section assumes the reader has some familiarity with abstract group theory, specifically character tables, irreducible representations, and group multiplication tables. The reader is referred to [36, 91, 92] for excellent discussions of abstract group theory and its application to solid state systems.

The general question we want to answer is: given the band structure of GaN, how can we determine which bands contribute to the nonlinear optical spectrum.

The quantum mechanical expression for the second-order nonlinear susceptibility.

---

\(^2\)In Table 5.3 "?" refers to an unidentified defect, \( cb \) refers to the conduction band level, and \( vb \) refers to the valence band level.
<table>
<thead>
<tr>
<th>ref.</th>
<th>sample</th>
<th>defect</th>
<th>energy</th>
<th>method</th>
</tr>
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<tbody>
<tr>
<td>[88]</td>
<td>undoped</td>
<td>$V_{Ga}$</td>
<td>vb + 1.0 eV</td>
<td>photocapacitance and optical</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>current deep level transient</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>spectroscopy</td>
</tr>
<tr>
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<td>p-type</td>
<td>I(Ga) or I(N)</td>
<td>vb + 1.8 eV</td>
<td>deep level transient spectroscopy</td>
</tr>
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<td></td>
<td></td>
<td>vb + .45 eV</td>
<td>spectroscopy and photoemission</td>
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<td></td>
<td></td>
<td>vb + .21 eV</td>
<td></td>
</tr>
<tr>
<td>[53]</td>
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<td>$V_{N}$</td>
<td>cb + .8 eV</td>
<td>very high pressure optical</td>
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<td></td>
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<td></td>
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<td></td>
<td></td>
<td>luminescence and Raman scattering</td>
</tr>
<tr>
<td>[89]</td>
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</tr>
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<td></td>
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<td></td>
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<td></td>
</tr>
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</tr>
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<td>photothermal current method</td>
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<td>cb - .042 eV</td>
<td>photoluminescence and</td>
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<td></td>
<td>and doped</td>
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<td></td>
<td>optically detected</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>vb + .19 eV</td>
<td>magnetic resonance</td>
</tr>
<tr>
<td></td>
<td>p-doped</td>
<td>?</td>
<td>vb + .5 eV</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3: Defects in GaN
equation (5.2), is represented using matrix elements of the form \( \langle m | r_i | l \rangle \) as

\[
\chi_{ijk}(\omega = 2\omega_0) = -2N\frac{e^3}{\hbar^2} \sum_{mnl} \rho_{ll}^{(0)} \left( \frac{\langle l | r_i | n \rangle \langle n | r_i | m \rangle \langle m | r_i | l \rangle}{(\omega - \omega_{nl}) + \gamma_{nl}} \right)
\]

\[
+ \frac{\langle l | r_i | n \rangle \langle n | r_i | m \rangle \langle m | r_i | l \rangle}{(\omega - \omega_{mn} + \gamma_{mn})}
\]

\[
+ \frac{\langle l | r_i | n \rangle \langle n | r_i | m \rangle \langle m | r_i | l \rangle}{(\omega + \omega_{mn} - \gamma_{nm})}
\]

\[
+ \frac{\langle l | r_i | n \rangle \langle n | r_i | m \rangle \langle m | r_i | l \rangle}{(\omega + \omega_{ml} - \gamma_{ml})}
\].

In equation (5.2), \(| l \rangle\), \(| m \rangle\), and \(| n \rangle\) are the quantum mechanical states of the system: \(\rho_{ll}^{(0)}\) is the unperturbed density of the state \(| l \rangle\); \(-e r_i\) is the dipole moment operator along the direction \(i\); \(\hbar \omega_{nm}\) is the energy difference between states \(| n \rangle\), and \(| m \rangle\); and \(\gamma_{nm}\) is a dephasing term. Determination of nonzero matrix elements is greatly simplified through group theory. Group theory assigns symmetries to states based on the underlying symmetry of the crystal.

The power of group theory to determine band symmetries becomes clear when we examine the relationship between the Hamiltonian, \(H\), the symmetry operations of the crystal, \(P(X_i)\), and the eigenstates of the Hamiltonian, \(\psi_{nj}\). Note the index \(n\) corresponds to the an eigenstate of energy \(E_n\) and \(j\) labels the \(l\)-fold degenerate states. In general, \(P(X_i)\) are all of the symmetry operations of the crystal including translations and point operations of the crystal. We will state without proof the following theorem.

*If \(H\) is invariant under the group \(G\) of \(P(X_i)\) then the eigenfunctions belonging to the same energy level, \(\psi_{nj}\), form a basis of the representation of \(G\).*
Let us examine this statement from a different viewpoint. Since all of the symmetry operations of the crystal $P(X_i)$ commute with $H$, the operation $P(X_i)$ on $\psi_{nk}$ produces another function with energy $E_n$. This function must be a linear combination of the degenerate functions $\psi_{nj}$,

$$P(X_i)\psi_{nk} = \sum_{j=1}^{l} \Gamma_n(X_i)_{jk} \psi_{nj}. \quad (5.3)$$

By applying equation (5.3) to all symmetry operations $X_i$, a set of matrices, $\Gamma_n$, are generated that form an irreducible representation of $H$. Thus the eigenstates $\psi_{nj}$ of $E_n$ transform as $\Gamma_n$. This leads naturally to selection rules and splitting of states under external perturbations. We will be concerned primarily with the former, specifically to determine contributions from various valence and conduction band states to the resonant components of $\chi^{(2)}_{ijk}(2\omega = \omega_o)$. Tables 5.4 and 5.5 are the character table and multiplication table for $C_{6v}$ symmetry, respectively.

### 5.4.1 Second-Order Nonlinear Optical Processes at $k = 0$

We will now explicitly calculate nonzero contributions to $\chi^{(2)}_{ijk}(\omega = 2\omega_o)$ at $k=0$. In general, the nonlinear susceptibility depends on all possible direct three photon processes in GaN. As stated in section 5.2.1, it is sufficient to use the point group representations of the band symmetries without spin; since spin orbit splitting is so small in GaN, it does not alter the symmetries of the bands significantly.

For spectroscopic measurements of GaN with a two photon energy near the band
Table 5.4: Character table for C\textsubscript{6v}

Adapted from [92]. Spin is contained in the $\Gamma_7$, $\Gamma_8$, and $\Gamma_9$ representations.
Table 5.5: Multiplication Table for $C_{6v}$

Adapted from [92].
gap, the nonlinear susceptibility is enhanced by processes that originate at the valence band maximum (the $\Gamma$ point in the Brillouin zone.) A general matrix element $\langle f|H|i \rangle$ with initial state $i$ that transforms at $\Gamma_i$, final state $f$ that transforms as $\Gamma_f$, and operator $H$ that transforms as $\Gamma_H$, transforms as

$$\langle \Gamma_f|\Gamma_H|\Gamma_i \rangle.$$ \hspace{1cm} (5.4)

This matrix is nonzero if the direct product $\Gamma_H \otimes \Gamma_i$ contains $\Gamma_f$. The matrix element is zero otherwise.

Using the above rule, it is quite clear how to determine selection rules. Let us calculate nonlinear process at the $\Gamma$ point for $\chi^{(2)}_{zzz}$. The dipole operator along the $z$ direction, $E \parallel c$, transforms as $\Gamma_1$. A simple allowed three photon process is shown in Fig. 5.4. This process consists of the following matrix elements that transform as

$$\langle \Gamma^a_1|\Gamma_1|\Gamma_1^b \rangle \langle \Gamma_1^b|\Gamma_1|\Gamma_1^c \rangle \langle \Gamma_1^c|\Gamma_1|\Gamma_1^a \rangle.$$ \hspace{1cm} (5.5)

Using Table 5.5 it is clear that all three matrix elements are nonzero. This three photon process contributes to the second-order nonlinear susceptibility as

$$-2Ne^3 \hbar^2 \frac{\langle \Gamma_1^a|r_z|\Gamma_1^b \rangle \langle \Gamma_1^b|r_z|\Gamma_1^c \rangle \langle \Gamma_1^c|r_z|\Gamma_1^a \rangle}{[(\omega - \omega_{\Gamma_1^a\Gamma_1^b}) + i\gamma_{\Gamma_1^a\Gamma_1^b}] [(\omega - \omega_{\Gamma_1^b\Gamma_1^c}) + i\gamma_{\Gamma_1^b\Gamma_1^c}]}.$$ \hspace{1cm} (5.6)

This process is resonant for $\hbar \omega \approx \hbar \omega_{\Gamma_1^a\Gamma_1^b} = E_g$ where $E_g$ is the bad gap energy.

For nonlinear process such as $\chi^{(2)}_{zzz}$, we need to distinguish between the dipole operators. The dipole operator for an electric field perpendicular to the $c$ axis, $E \perp c$. 

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Figure 5.4: Allowed three photon process for $\chi_{zzz}^{(2)}(\omega = 2\omega_0)$ of GaN. The dipole moment operator, $-ez$, transforms as $\Gamma_1$. $E_F$ is the Fermi level and $E_g$ is the band gap.

has $\Gamma_3$ symmetry. Table 5.6 displays all of the allowed three photon processes at the $\Gamma$ point that originate from the top of the valence band and are resonant when the second harmonic field has energy approximately equal to the band gap energy. This calculation assumes that the bands below the gap are completely full and the bands above the gap are completely empty. The three photon process shown in Fig. 5.4 corresponds to the first entry in the table. The states $l$, $m$, and $n$ are the same as in equation (5.2). Note, the band notation in Table 5.6 is derived from Fig. 5.5.

Also note, Table 5.6 lists the Feynman diagrams that correspond to the resonant three photon process. The two relevant Feynman diagrams are displayed in Fig. 5.6. In this figure, time is represented vertically. Photons are represented by wavy lines. The intersection of the photon with the straight line representing the ket or bra space corresponds to an interaction (emission or absorption) of the photon with the medium.
Figure 5.5: Band symmetries for GaN and the Γ point. The superscript is my notation to more clearly distinguish the bands. The approximate band energies are adapted from [77]. A three photon process is resonantly enhanced when the two photon energy is approximately equal to the band gap energy. These resonant interactions start from either $\Gamma_6^a$ or $\Gamma_1^a$. 
Table 5.6: Resonant three photon processes for $\chi_{zzz}^{(2)}(\omega = 2\omega_o)$, $\chi_{zzz}^{(2)}(\omega = 2\omega_o)$, and $\chi_{zzz}^{(2)}(\omega = 2\omega_o)$ at the $\Gamma$ point. The table contains all three photon process in which the last time ordered photon is the $2\omega_o$ photon corresponding to a virtual transition from the GaN conduction band to the valence band.

Thus, the Feynman diagrams graphically display the time ordering of photons in a three photon process and determine the structure of the energy denominator of equation (5.2).

We briefly describe Lee's and Gustafson's theory [93] of Feynman diagrams for second harmonic generation. The process is cast in terms of the perturbation of the density operator. The density operator is defined as the ensemble average over product of the ket and bra states

$$\rho = \langle \psi | \psi \rangle.$$

The $\rho$ can be expanded in a perturbation series as

$$\rho = \rho^{(0)} + \rho^{(1)} + \rho^{(2)} + \ldots$$

\[\text{Table 5.6: Resonant three photon processes for } \chi_{zzz}^{(2)}(\omega = 2\omega_o), \chi_{zzz}^{(2)}(\omega = 2\omega_o), \text{ and } \chi_{zzz}^{(2)}(\omega = 2\omega_o) \text{ at the } \Gamma \text{ point. The table contains all three photon process in which the last time ordered photon is the } 2\omega_o \text{ photon corresponding to a virtual transition from the GaN conduction band to the valence band.}

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$$\rho = | \psi \rangle \langle \psi |.$$  

The $\rho$ can be expanded in a perturbation series as

$$\rho = \rho^{(0)} + \rho^{(1)} + \rho^{(2)} + \ldots$$
Figure 5.6: Feynman diagrams for the resonant SHG in GaN. The diagrams represent the time evolution of $\rho^{(2)}$. From these diagrams, the terms in equation (5.2) are generated. See [93] for the conventions used with these diagrams.
where $\rho^{(0)}$ is the density operator in thermal equilibrium, and $\rho^{(i)}$ represent the $i$th order perturbation to $\rho^{(0)}$. Once $\rho$ is determined, the nonlinear polarization is calculated as

$$\langle \mathbf{P}^{(2)} \rangle = \langle \psi | \mathbf{P} | \psi \rangle = Tr(\rho^{(2)} \mathbf{P}). \quad (5.9)$$

We simplify the rules for Feynman diagrams by observing that the three virtual transitions for second-harmonic generation leave the state unaltered. Although each photon process induces a phase shift in $\rho^{(2)}$, the net phase shift is zero for SHG. Therefore, we will disregard the net phase shift caused by each photon process. The rules for double sided Feynman diagrams are as follows.

1. The state starts with $|l\rangle \rho^{(0)}_{ll} |l\rangle$. For SHG, the state also ends with $|l\rangle \rho^{(0)}_{ll} |l\rangle$.

2. For the ket side, a vertex that brings the state from $|l\rangle$ to $|m\rangle$ by absorption of a photon with angular frequency $\omega_1$ corresponds to the matrix element

$$\langle m | - er_i E(\omega_1) | l \rangle \over i\hbar. \quad (5.10)$$

where $-er_i$ is the dipole moment operator along the direction $i$ and $E(\omega_1)$ is the electric field. For an emission process, the matrix element is

$$\langle m | er_i E^*(\omega_1) | l \rangle \over i\hbar. \quad (5.11)$$

Similarly, the matrix element that represents absorption of a photon on the bra side is

$$-\langle l | er_i E(\omega_1) | m \rangle \over i\hbar. \quad (5.12)$$
Emission of a photon on the bra side is represented by

\[ -\langle l | - e r_i E^*(\omega_i) | m \rangle \frac{1}{i \hbar}. \]  

(5.13)

Fig. 5.7 displays the diagrams representing the emission and absorption of a photon on both the ket and bra side.

3. A propagator takes the state from one vertex to the next and corresponds to an energy denominator in equation (5.2). Second-harmonic generation involves three photon interactions (vertices) and therefore two propagators. If the propagator takes the state from the \( j \)th vertex to the \( (j+1) \)th vertex when the state is \( |m\rangle \langle l| \), the propagator has the form

\[ \Pi_j = \pm \left[ \sum_{i=1}^{j} (\omega_i - \omega_{mi} - i \gamma_{mi}) \right]^{-1}. \]  

(5.14)

where \( \omega_i \) is positive for absorption of a photon on the ket side or emission of a photon on the bra side. Conversely, \( \omega_i \) is negative for emission of a photon on the ket side or absorption of a photon on the bra side. The plus (minus) in front of the propagator corresponds to a \( (j+1) \)th vertex on the ket (bra) side.

4. The product of all of the matrix elements and the propagators yields a term in equation (5.2). In general, there are eight unique ways to arrange the photons in the Feynman diagrams for a three photon process. For second-harmonic generation, there are only four unique ways since the two of the photons are indistinguishable. The four unique photon time orderings correspond to the four unique terms the second-order susceptibility for SHG.
Figure 5.7: Graphical representation of photon emission and absorption. Diagram A (B) corresponds to absorption (emission) of a photon which alters the state from $|l\rangle$ to $|m\rangle$. Diagram C (D) corresponds to absorption (emission) of a photon which alters the state from $\langle m |$ to $\langle l |$. 
5.5 MOCVD Growth of GaN

Our GaN on Al$_2$O$_3$ [0001] samples were grown by Asif Khan and C. J. Sun at APA Optics by the procedures described in references [65, 94]. Here we review the growth techniques for high quality single crystal films of GaN on sapphire. A 1.25 cm $\times$ 1.25 cm basal plane sapphire substrate was degreased and etched in hot H$_3$PO$_4$:H$_2$SO$_4$ to remove surface defects and contaminants. A clean substrate is essential for MOCVD growth because surface impurities can physically block the deposition of a coating and affect the mode and amount of nucleation of the depositing material [95]. After placing the sapphire substrates onto a silicon carbide coated graphite susceptor in the reactor chamber, a 0.050 $\mu$m buffer layer of AlN was deposited by low pressure metalorganic chemical vapor deposition (LPMOCVD) at 1000$^\circ$ C. The AlN buffer layer helped initiate growth of the GaN film. GaN was then deposited at a temperature of 850$^\circ$ C and pressure of 76 Torr. Ga and N sources were triethylgallium (TEG) and ammonia, respectively. The TEG flux was 13 $\mu$m/min and the ammonia flow was 1 sl/min. SiH$_4$ was used as a source gas to intentionally n-dope some samples with Si. Fig. 5.8 illustrates the steps in the growth of GaN on Al$_2$O$_3$ by LPMOCVD. After growth, the GaN films were electrically characterized by van der Pauw and Hall measurements. The results of these measurements are displayed in Table 5.7. "Yellow band" refers to the presence of the yellow luminescence band measured by photoluminescence (see section 4.3.)
Figure 5.8: Flow diagram for LPMOCVD growth of GaN on Al₂O₃. Diagram A represents the general procedures for growth. Diagram B represents specific procedures involved in the growth of the AlN and GaN films. The box with the thick lines represents the steps in the nucleation of the film.
<table>
<thead>
<tr>
<th>#</th>
<th>dopant</th>
<th>thickness</th>
<th>mobility</th>
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<td>none</td>
<td>1.021 µm</td>
<td>20 cm²/V s</td>
<td>4.47×10¹⁷</td>
<td>no</td>
</tr>
<tr>
<td>G9273</td>
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<td>8.52×10¹⁷</td>
<td>yes</td>
</tr>
<tr>
<td>G9213</td>
<td>Si</td>
<td>2.995 µm</td>
<td>192 cm²/V s</td>
<td>2.13×10¹⁸</td>
<td>yes</td>
</tr>
</tbody>
</table>

Table 5.7: Electrical properties of GaN samples
Chapter 6

Nonlinear Optical Spectroscopy of GaN

In this chapter we present the results from our nonlinear optical spectroscopy of our GaN/Al$_2$O$_3$ samples [96]. By measuring the azimuthal dependence of SHG from GaN/Al$_2$O$_3$ we determined that our GaN films and sapphire substrates are miscut by 0.80°. We performed SHG spectroscopy of our GaN/Al$_2$O$_3$ samples in the s-in/p-out and p-in/p-out polarizations over a two photon energy range of 2.6 to 3.4 eV. Our measurements reveal a slight enhancement of $\chi^{(2)}_{xxx}$ at a two photon energy of 2.80 eV. In contrast, $\chi^{(2)}_{xxx}$ is spectrally flat. The 2.80 eV feature is clearly independent of yellow band luminescent defects, and we speculate that it may result from transitions involving an intrinsic midgap defect state. Finally, we probed the GaN/Al$_2$O$_3$ interface using SHG rotational symmetry techniques. No interface states were observed over a two photon energy range of 2.6 to 3.4 eV.
6.1 Nonlinear Optical Spectroscopy as a Probe of Condensed Matter Systems

Nonlinear optical spectroscopy is a unique probe of condensed matter systems as a result of its sensitivity to surfaces and interfaces, its long penetration depth, and its non-destructive nature. One application of nonlinear optical spectroscopy has been the investigation of the symmetry and structure of surfaces and interfaces. This includes the determination of the bonding angle of a molecule to a surface [6], the measurement of the pretilt angle of a liquid crystal [9], the observation of Angstrom scale roughness at the Si(100)/SiO$_2$ interface [97], and the observation of Si-O bonding arrangements at kinks on vicinal Si(111) surfaces [98]. Nonlinear optical spectroscopy has also been used to measure electronic properties at the interfaces between solid materials. Examples of these investigations include the spectral identification of antisite defects in Au/GaAs [10], the measurement of new bonding states at the CaF$_2$/Si interface [3], the observation of an interface quantum well state in ZnSe/GaAs [2], and the observation of a strain induced two photon resonances from Si-SiO$_2$ interfaces [4]. Our nonlinear optical investigations reveal both structural and electronic features of bulk GaN thin films. In addition, we did not observe any strain induced interface states by second-harmonic rotational symmetry measurements.
6.2 Nonlinear Rotational Symmetry of GaN

In section 2.3 we discussed the relationship between the allowed second-order susceptibility elements and the symmetry of the media. In this section we discuss our investigations of the symmetry of GaN by second-harmonic generation. By measuring second-harmonic intensity as a function of the angle between the incident beam and crystal axes for a variety of polarizations, we probed the symmetry of our GaN thin films. Fig. 6.1 displays the geometry of the sample and the fundamental and second-harmonic beams. Because SHG is mediated by a third rank tensor, second-harmonic generation is a more sensitive probe of crystal symmetry than linear spectroscopies, which are mediated by second rank tensors.

The second-harmonic response of GaN is determined by transforming the dipole allowed second-order nonlinearities in the crystal frame of reference to the lab frame of reference, i.e.

\[
\chi_{ijk}^{(2),lab} = R(\phi)_i R(\phi)_j R(\phi)_k \chi_{\alpha\beta\gamma}^{(2),\text{crystal}}
\]

(6.1)

where

\[
R = \begin{pmatrix} 
\cos \phi & \sin \phi & 0 \\
-\sin \phi & \cos \phi & 0 \\
0 & 0 & 1 
\end{pmatrix}.
\]

(6.2)

The calculated azimuthal dependence of SHG from GaN [0001] is displayed in Table 6.1.
Figure 6.1: Geometry of SHG from GaN/Al₂O₃. $\theta$ is the angle of incidence of the fundamental beam and $\phi$ is the angle between the laboratory axes and the crystal axes. Both the fundamental and second-harmonic fields are polarized in the plane of incidence (p-in/p-out polarization).

<table>
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<th>Polarization</th>
<th>$P^{(2)}(\omega = 2\omega_0)$</th>
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<tr>
<td>p-in/p-out</td>
<td>$2\chi^{(2)}<em>{zzz}E_z(\omega_0)E_z(\omega_0) + \chi^{(2)}</em>{zzz}E_x(\omega_0)E_x(\omega_0) + \chi^{(2)}_{zzz}E_z(\omega_0)E_z(\omega_0)$</td>
</tr>
<tr>
<td>p-in/s-out</td>
<td>0</td>
</tr>
<tr>
<td>s-in/p-out</td>
<td>$\chi^{(2)}_{yy}E_y(\omega_0)E_y(\omega_0)$</td>
</tr>
<tr>
<td>s-in/s-out</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 6.1: Azimuthal dependence of $P^{(2)}(\omega = 2\omega_0)$ from GaN [0001]
Figure 6.2: Rotational symmetry of SHG from GaN/Al₂O₃ [0001]. The angle of incidence is 15°. \( \phi \) is the angle between the miscut direction and the plane of incidence. \( \bigcirc \) (□) is the data from the p-in/p-out (s-in/p-out) polarized second-harmonic field. The solid (dashed) line is a fit to the p-in/p-out (s-in/p-out) data with the miscut angle as a free parameter. The fitted miscut angle, \( \alpha \), is 0.79° (0.82°) for the p-in/p-out (s-in/p-out) polarizations.
Fig. 6.2 displays the azimuthal dependence of SHG for GaN in the p-in/p-out and s-in/p-out polarizations at an angle of incidence of 15°. The p-in/p-out and s-in/p-out polarized SHG data exhibit a one-fold symmetric modulation. These data are inconsistent with misaligned polarizers, which would result in non-zero isotropic signals for both polarizations. On the other hand, a simple sample miscut model was applied successfully to interpret the data. A miscut between the normal to the surface and the z-axis of the crystal results in a precession of the z-axis about the surface normal during the azimuthal scan. This precession induces an azimuthally dependent coupling of the fundamental fields to generate the anisotropic second-harmonic signal.

Assuming the angle between the surface normal and the z-axis of the crystal is $\alpha$. $\chi^{(2)}_{ijk}^{l_ab}$ is related to $\chi^{(2)}_{\alpha\beta\gamma}^{crystal}$ by equation (6.1) but with equation (6.2) replaced by

$$
R^{miscut} = \begin{pmatrix}
\cos \phi & \sin \phi & 0 \\
-\sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\cos \alpha & 0 & -\sin \alpha \\
0 & 0 & 1 \\
\sin \alpha & 0 & \cos \alpha
\end{pmatrix}.
$$

(6.3)

Note, equation (6.3) assumes the [0001] axis is miscut in the xz plane. Since the x- and y-axes of GaN are equivalent, this assumption simply produces a phase shift between the experimental and calculated data. Table 6.2 displays the calculated azimuthal dependence of SHG from GaN [0001] with a small miscut angle, $\alpha$. Note that higher order terms in the miscut, i.e. terms with miscut dependences of $\sin^2 \alpha$ and $\sin^3 \alpha$, are not displayed. The best fits to the p-in/p-out and s-in/p-out data yield a sample miscut angle, $\alpha$, of $0.80^\circ \pm 0.05^\circ$. The data were fitted with a function that
Table 6.2: Azimuthal dependence of $P^{(2)}(\omega = 2\omega_0)$ from GaN [0001] with a small miscut angle, $\alpha$
includes the effects of pulse propagation through the GaN film (see section 6.3) and uses the second-order susceptibility determined by equations (6.1) and (6.3). SHG rotational symmetry measurements in the p-in/s-out and s-in/s-out polarizations were complicated by the sapphire birefringence and were not performed. The relationship between the sapphire birefringence and SHG from GaN/Al₂O₃ is discussed in Appendix E.

Fig. 6.3 displays SHG data from our 1.020 μm GaN/Al₂O₃ sample as a function of the angle of incidence. The maximum transmitted SHG response of GaN occurs at an angle of incidence of ~ 50°. The SH response of GaN as a function of the angle of incidence depends on three factors: the coupling of the incident fields to the susceptibility elements; the generation of a bound wave, which has a magnitude that depends on the propagation direction of the fields in the GaN film; and the Fresnel coefficients. The SHG responses of all of our GaN/Al₂O₃ samples are similar to Fig. 6.3. The film thickness affects the overall magnitude of SHG as a function of the angle of incidence, but does not alter the relative magnitude of the response, i.e. the ratio of the SHG response at two angles of incidence is independent of film thickness. This independence with respect to the film thickness arises because the interference of the bound and free waves is insensitive to the angle of incidence.
Figure 6.3: SHG as a function of angle of incidence from GaN/Al₂O₃. The polarization configuration is p-in/p-out. The minimum of the curve is at ~1°, which is consistent with the miscut angle determined from SHG rotational measurements. The anisotropy in the SHG response for positive and negative angles is due to the sample miscut [22].
6.3 Theory of Nonlinear Optical Spectroscopy from GaN/Al₂O₃

We performed SHG spectroscopy of GaN/Al₂O₃ over a two photon energy range of 2.6 to 3.4 eV in the s-in/p-out and p-in/p-out polarizations. As Table 6.1 indicates, our SHG measurements of GaN/Al₂O₃ in the s-in/p-out polarization probe a single second-order susceptibility element, $\chi^{(2)}_{yy}$. We also measured SHG from GaN/Al₂O₃ in the p-in/p-out polarization at several angles of incidence. We fitted these spectra for $\chi^{(2)}_{xx}$, but were unable to independently determine $\chi^{(2)}_{zz}$.

Determination of nonlinear optical susceptibilities from the SHG spectra requires precise knowledge of the linear optical properties, e.g. the index of refraction and sample thickness. The experiments in chapter 4 provide these numbers. Using the linear optical properties of our GaN and sapphire samples, we developed a model for second-harmonic pulse propagation through GaN/Al₂O₃. The model includes ultrafast nonlinear pulse propagation effects based on the methods developed in 2.4.2.

Accurate determination of the nonlinear susceptibility requires the inclusion of ultrafast effects for two reasons. First, although our GaN samples have thicknesses less than 5 μm, the highly dispersive nature of GaN affects the interference of the bound and free waves. We quantify the significance of ultrafast effects by defining the error, $\sigma$, with respect to the calculated SHG intensity that neglects these effects...
as

\[
\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \frac{(I_{i}^\text{mono} - I_{i}^\text{ultra})^2}{(I_{i}^\text{mono})^2}}.
\] (6.4)

In equation (6.4), \(I_{i}^\text{mono} (I_{i}^\text{ultra})\) is the calculated SHG intensity from GaN using the monochromatic (ultrafast) theory and \(i\) labels the wavelength at which \(I_{i}^\text{mono} (I_{i}^\text{ultra})\) is evaluated. For our 4.885 \(\mu\)m GaN sample, \(\sigma = 0.35\) over a fundamental wavelength range of 740 to 755 nm. The error between the monochromatic and ultrafast theories is especially large in this region due to the high dispersion of GaN at a second-harmonic wavelength of 370 to 378 nm. Second, the ultrafast analysis ensures compatibility of the calculated SHG signal from GaN with the calculated SHG from quartz. Note that the following calculations assume that both the GaN film and sapphire substrate are perfectly cut. Experimentally, we suppressed the effect of the miscut by measuring our nonlinear spectra at a crystal orientation of \(\phi = 90^\circ\).

Fig. 6.4 displays the geometry of our SHG from GaN/\(\text{Al}_2\text{O}_3\) at a non-normal angle of incidence. The fundamental light with angular frequency \(\omega\) propagates to the air/GaN interface and generates a reflected second-harmonic free wave \((E_{fR0})\), a second-harmonic bound wave that propagates through the GaN film \((E_{b1})\), and a second-harmonic free wave that propagates through the GaN film \((E_{f1})\). The bound and free nonlinear fields propagate to the GaN/\(\text{Al}_2\text{O}_3\) interface where they generate a free wave reflected from the GaN/\(\text{Al}_2\text{O}_3\) interface \((E_{f1R})\) and a free wave that is transmitted into the sapphire \((E_{f2})\). Table 6.3 summarizes the conventions for the
nonzero nonlinear waves in air, GaN, and sapphire, and defines phase relationships between the waves.

Our model includes all factors that affect the calculated second-harmonic signal by at least 10%. Thus, the model does not include the effect of bound wave reflection from the GaN/Al$_2$O$_3$ interface because the reflection coefficient is small, i.e. $|r_{s12}(\omega)|^2 \approx 0.03$ and $|r_{p12}(\omega)|^2 \approx 0.015$, where $r_{s12}(\omega)$ is the Fresnel reflection coefficient for s-polarized light with 1 (GaN) as the incident medium and 2 (sapphire) as the substrate medium. $r_{p12}(\omega)$ is the Fresnel reflection coefficient for p-polarized light at the same interface. However, we include $E_{fr1}$ in our analysis, which is the nonlinear wave that is reflected from the GaN/Al$_2$O$_3$ interface and undergoes one
Table 6.3: Nonlinear waves and phases

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{b1}$</td>
<td>bound wave in GaN</td>
</tr>
<tr>
<td>$E_{f1}$</td>
<td>free wave in GaN</td>
</tr>
<tr>
<td>$E_{f1r}$</td>
<td>free wave in GaN reflected from the GaN/Al$_2$O$_3$ interface</td>
</tr>
<tr>
<td>$E_{fr0}$</td>
<td>free wave in air reflected from air/GaN interface</td>
</tr>
<tr>
<td>$E_{f2}$</td>
<td>free wave in sapphire transmitted</td>
</tr>
<tr>
<td>$\delta$</td>
<td>round trip phase acquired by $E_{fr1}$</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>phase acquired by $E_{f2}$ during round trip of $E_{fr1}$</td>
</tr>
</tbody>
</table>

multiple reflection in the GaN film before transmission through the GaN/Al$_2$O$_3$ substrate. The fields generated at the air/GaN interface and $E_{fr1}$ propagate from point A to point C in Fig. 6.4. This field is related to $E_{f2}$, which is the nonlinear free wave initially transmitted through the GaN/Al$_2$O$_3$ interface as $|E_{fr1}| \approx 0.1|E_{f2}|$. Note that the fields generated at the air/GaN interface and $E_{f2}$ propagate from point A to point B in Fig. 6.4. Contributions of nonlinear waves that undergo more than one set of reflections in the GaN film affect the total transmitted SHG intensity by less than $\sim$2% and are therefore not included in our theory. The interference of $E_{f2}$ and $E_{fr1}$ is computed by summing their respective contributions at points B and C.

In our analysis, we express the nonlinear fields in terms of the wavevectors and
wavevector components. The free wavevectors are defined as

\[ k_{fi} = \frac{\pi n_{fi}\omega}{c} \]  
(6.5)

\[ k_{fiz} = -\cos\theta_{fi}k_{fi} \]  
(6.6)

\[ k_{fix} = \sin\theta_{fi}k_{fi}, \]  
(6.7)

where \( i \) is equal to 0, 1, 2 and denotes the air, GaN, and sapphire regions, respectively, and \( \omega \) is the angular frequency of the second-harmonic fields. The bound wavevectors are defined similarly with \( n_{b1} \) substituted for \( n_{fi} \). The free (bound) wave angle of incidence in region \( i \) is \( \theta_{fi} (\theta_{bi}) \) and is determined from \( \theta_0 \) and \( n_{fi} (n_{bi}) \) by Snell's law.

We now determine the nonlinear polarization induced in GaN by the applied fundamental field. The p-polarized fundamental light field generates a nonlinear polarization of the form

\[ P_z^{(2)} = 2t_{p01}^2(\omega_o)\chi_{zzz}^{(2)}E_xE_z \]  
(6.8)

and

\[ P_z^{(2)} = t_{p01}^2(\omega_o)(\chi_{zzz}^{(2)}E_xE_z + \chi_{zzz}^{(2)}E_zE_z). \]  
(6.9)

Note that \( E \) is the incident fundamental field and \( t_{p01}(\omega_o)E \) is the fundamental field transmitted into the GaN film. The nonlinear polarization generated by an s-polarized fundamental field is

\[ P_z^{(2)} = t_{s01}^2(\omega_o)\chi_{yy}^{(2)}E_yE_y. \]  
(6.10)
The bound wave fields are determined by the nonlinear polarization; the nonlinear wave equation,
\[ \nabla \times \nabla \times \mathbf{E}(\omega) + \frac{\varepsilon(\omega)}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{E}(\omega) = -\frac{4\pi}{c^3} \frac{\partial^2}{\partial t^2} \mathbf{P}^{(2)}(\omega); \] (6.11)
and the nonlinear version of Maxwell's equation,
\[ \nabla \cdot \mathbf{E}_{bl} = \frac{-4\pi \nabla \cdot \mathbf{P}^{(2)}}{\varepsilon_{bl}}. \] (6.12)

The bound wave is coupled to the nonlinear polarization and exists only in nonlinear media, e.g. GaN. If we assume the bound wave field has the form
\[ \mathbf{E}_{bl} = (\bar{z}\mathbf{E}_{blz} + \bar{x}\mathbf{E}_{blx})e^{i(k_{bl}r - \omega t)}, \] (6.13)
then the bound wave components are
\[ \mathbf{E}_{blz} = \frac{4\pi}{\varepsilon_{bl} - \varepsilon_{f1}} \left( P^{(2)}_z \left( 1 - \frac{k_{blz}^2}{k_{f1}^2} \right) - \frac{k_{blz}^2 k_{blz} P^{(2)}_z}{k_{f1}^2} \right), \] (6.14)
and
\[ \mathbf{E}_{blx} = \frac{4\pi}{\varepsilon_{bl} - \varepsilon_{f1}} \left( P^{(2)}_x \left( 1 - \frac{k_{blx}^2}{k_{f1}^2} \right) - \frac{k_{blx}^2 k_{blx} P^{(2)}_x}{k_{f1}^2} \right). \] (6.15)

The relationships among the bound wave field, the free wave field, and the nonlinear polarization are displayed in Fig. 6.5.

The three nonlinear free waves in this calculation are: the free wave generated at the air/GaN interface, \( \mathbf{E}_{f1} \), which propagates with the bound wave; the free wave reflected from the GaN/Al₂O₃ interface, \( \mathbf{E}_{f1r} \); and the free wave generated at the
Figure 6.5: Polarization and propagation directions of the nonlinear fields and second order polarization in GaN. $E(\omega)$ is the s-polarized fundamental field, $E_{fl}$ is the free wave, $E_b$ is the bound wave, and $P^{(2)}$ is the second order nonlinear polarization. The polarization of the free wave is perpendicular to the direction of propagation of the free wave. Although the polarizations of the bound wave and second order polarization are not perpendicular to their direction of polarizations, the polarization of the bound wave is in a direction that ensures $\nabla \cdot D = \nabla \cdot (E_b + 4\pi P) = 0$. Note that the refraction angles of the bound and free waves are approximately correct for the given angle of incidence. The polarization field has been offset from the bound and free wave electric fields to simplify the drawing (the polarization field is collinear with the bound wave electric field). Similar diagrams are found in [39].
GaN/Al₂O₃ interface, which propagates through the sapphire substrate. \( E_{f2} \). The free nonlinear waves have the form

\[
E_{fj} = (\hat{x}E_{fjx} + \hat{z}E_{fjz})e^{i(\pm k_{fj}x - wt)}
\]  

(6.16)

with \( j = 1, r1, \) or \( 2 \). The amplitude of the free wave components are

\[
E_{fjz} = \frac{k_{fjz}}{k_{fj}} E_{fj} \quad \text{and} \quad E_{fjx} = -\frac{k_{fjx}}{k_{fj}} E_{fj}.
\]  

(6.17)

Matching boundary conditions at the air/GaN interface determines \( E_{f1} \) as

\[
E_{f1} = \left( \frac{k^2_{f1}k_{f1z}}{k_{f0z}k_{f1}} - k_{f1} \right)^{-1} \left( \left( k_{b1z} - \frac{k^2_{f0}}{k_{f0z}} \right) E_{b1x} - k_{b1z} E_{b1z} \right).
\]  

(6.18)

Similarly, matching boundary conditions at the GaN/Al₂O₃ interface determines \( E_{f1r1} \) and \( E_{f2} \) as

\[
E_{f1r1} = -\left( \frac{k^2_{f2}k_{f1z}}{k_{f2z}k_{f1}} + k_{f1} \right)^{-1} \left( \left( k_{b1z} - \frac{k^2_{f2}}{k_{f2z}} \right) E_{b1x}e^{-i(k_{b1z} + k_{f1z})d} 
\right.
\]

\[
\left. -k_{b1z} E_{b1z}e^{-i(k_{b1z} + k_{f1z})d} + \left( k_{f1} - \frac{k^2_{f2}k_{f1z}}{k_{f2z}k_{f1}} \right) E_{f1}e^{-i2k_{f1z}d} \right).
\]  

(6.19)

and

\[
E_{f2} = \left( \frac{k^2_{f1}k_{f2z}}{k_{f1z}k_{f2}} + k_{f2} \right)^{-1} \left( \left( k_{b1z} - \frac{k^2_{f1r}}{k_{f1rz}} \right) E_{b1x}e^{-i(k_{b1z} - k_{f2z})d} 
\right.
\]

\[
\left. -k_{b1z} E_{b1z}e^{-i(k_{b1z} - k_{f2z})d} + 2k_{f1} E_{f1}e^{-i(k_{f1z} - k_{f2z})d} \right).
\]  

(6.20)

The previous calculations determine the magnitude of the nonlinear waves. The measured SHG signal also requires inclusion of the phase relationships between the
various free waves and summing these waves appropriately. Therefore, the measured
SHG field transmitted through GaN/Al₂O₃ is

\[ E_t(r, 2\omega) = \hat{c}t_{p20}(2\omega) \left( E_{f2} e^{i(k_{f2}r - k_{f2}d)} + r_{p10}(2\omega) t_{p12}(2\omega) E_{f1r} e^{i(k_{f1}r + k_{f1}d)} \right). \]

Note, that the round trip distance traversed by \( E_{f1} \) is

\[ \delta = \frac{2d}{\cos \theta_{f1}} \]

and the corresponding distance traversed by \( E_{f2} \) is

\[ \Delta = 2d \tan \theta_{f1} \sin \theta_{f1}. \]

The measured intensity is

\[ I_t = \frac{c}{8\pi} |E_t(r, 2\omega)|^2. \]

We can express these equations to explicitly define the transmitted second-
harmonic field in terms of the nonlinear optical susceptibilities, the fundamental fields,
and propagation effects. The second-harmonic field for the s-in/p-out geometry is

\[ E_{sp}(2\omega) = Y_{yy} \chi_2^{(2)} E_y E_y \]

where

\[ Y_{yy} = i^2 \gamma_{s01}(\omega_o) Y_{12} \]
and

\[ Y_{mn} = e^{4\pi t_{\omega_0}(2\omega_0)} \left[ \left( \frac{k_{f1}^2}{k_{f2}^2} + k_{f2} \right)^{-1} e^{ik_{f2}d} \left\{ \frac{C_m}{C_n} \left[ \left( k_{b1z} + \frac{k_{f1}^2}{k_{f2}^2} \right) e^{-ik_{b1z}d} + \left( k_{f1}^2 - \frac{k_{f2}^2}{k_{f2}^2} \right) e^{-ik_{f1}d} \right] \right\} \right] \]

\[ + 2k_{f1} e^{-ik_{f1}d} \left( \frac{k_{f0}^2}{k_{f0}^2} - k_{f1} \right)^{-1} \left( k_{b1z} - \frac{k_{f0}^2}{k_{f0}^2} \right) \]

\[ + C_n \left[ - k_{b1z} e^{-ik_{b1z}d} - 2k_{f1} k_{b1z} e^{-ik_{f1}d} \left( \frac{k_{f0}^2}{k_{f0}^2} - k_{f1} \right)^{-1} \right] \]

\[ - r_{p10}(2\omega_0) t_{p12}(2\omega_0) e^{ik_{f1}d} \left( \frac{k_{f0}^2}{k_{f0}^2} - k_{f1} \right)^{-1} \]

\[ \left\{ C_m \left[ \left( k_{b1z} - \frac{k_{f2}^2}{k_{f2}^2} \right) e^{-ik_{b1z}d} + e^{-ik_{f1}d} \left( k_{f1}^2 - \frac{k_{f2}^2}{k_{f2}^2} \right) \right] \right\} + C_n \left[ - k_{b1z} e^{-ik_{b1z}d} \right] \]

\[ - k_{b1z} e^{-ik_{f1}d} \left( k_{f1}^2 - \frac{k_{f2}^2}{k_{f2}^2} \right) \left( \frac{k_{f0}^2}{k_{f0}^2} - k_{f1} \right)^{-1} \]. \quad (6.27) \]

The coupling of the fields in the medium determines \( Y_{mn} \) with

\[ C_1 = - \frac{k_{b1z} k_{b1z}}{k_{f1}^2} \quad (6.28) \]

and

\[ C_2 = \left( 1 - \frac{k_{b1z}^2}{k_{f1}^2} \right). \quad (6.29) \]

The above equations include Fresnel transmission and reflection coefficients of the fundamental and second-harmonic fields. For example, \( t_{s01}(\omega_0) \) is the Fresnel transmission coefficient for s-polarized light from layer 0 to layer 1. The Fresnel reflection coefficient is denoted similarly with \( r \) substituted for \( t \). Equation (6.25) explicitly displays the three factors on which the nonlinear response of the media depends. These
factors are: the nonlinearity of the media, $\chi^{(2)}_{zzz}$, the applied fundamental fields, $E_y$; and the propagation of the nonlinear fields, $Y_{yy}$. Note that $Y_{yy}$ is a function only of the linear optical properties of the media and the GaN film thickness.

The second-harmonic response of GaN in the p-in/p-out geometry may be written similarly as

$$E_{pp}(2\omega_o) = Y_{xx} \chi^{(2)}_{zzz} E_x E_x + 2Y_{xz} \chi^{(2)}_{zzz} E_x E_z + Y_{zz} \chi^{(2)}_{zzz} E_z E_z$$

(6.30)

with

$$Y_{xx} = Y_{zz} = t_{p01}^2(\omega_o)Y_{12}$$

(6.31)

and

$$Y_{xz} = t_{p01}^2(\omega_o)Y_{21}.$$  

(6.32)

Equations (6.25) and (6.30) do not include the effect of the “walk-off” between the bound and free waves. “Walk-off” refers to the spatial separation of the bound and free waves that results from different directions of propagation of these waves in the nonlinear crystal. “Walk-off” decreases the overlap of the bound and free waves, and hence modifies the interference of these waves. For an 800 nm beam with an angle of incidence, $\theta_0$, of 46.0°, the corresponding free and bound waves propagate in GaN with angles of $\theta_{f1} = 16.4°$ and $\theta_{b1} = 18.0°$, respectively. After propagating through 5 $\mu$m of GaN, the spatial separation of the center of the free and the bound
waves is 0.15 μm. Our Ti:Al₂O₃ beams have a spot size of ~100 μm, and therefore “walk-off” is insignificant in our experiment.

Ultrafast effects are incorporated into the theory by modifying the phases of the nonlinear waves to include the finite duration of the pulses. The transmitted SHG wave is composed of a sum of waves that propagate through the film stack with various phase velocities. For example, we can rewrite a transmitted second-harmonic wave, \( E_{sp}(2\omega_0) \), to explicitly display its phase dependence as

\[
E_{sp}(2\omega_0) = D_{AB}^b e^{i(kf_2\Delta - k_{b1}z)} + D_{AB}^f e^{i(kf_2\Delta - k_{f1}z)}
+ D_{AC}^f e^{i(kf_2\delta - k_{b1}z)} + D_{AC}^b e^{i(kf_2\delta - k_{b1}z)}.
\]

(6.33)

Comparison of equation (6.33) with equations (6.25) - (6.29) reveals that the \( D \) coefficients consist of \( \chi^{(2)}_{xyy} \), \( E_y \), Fresnel coefficients, dielectric constants, and wavevectors in air, GaN, and sapphire. \( D_{AB}^b \) corresponds to the wave that propagates from point A to point B in Fig. 6.4 and has a phase that depends on the bound wavevectors in GaN. The other \( D \) coefficients are defined similarly. The time required for the \( D_{AB}^b \) and \( D_{AB}^f \) waves to propagate to point B and the \( D_{AC}^b \) and \( D_{AC}^f \) waves to propagate to point C is contained in the phase of each wave (i.e. a group velocity is associated with each wavevector). For example, the time required for the \( D_{AB}^b \) wave to propagate from point A to point B is

\[
t = \frac{\Delta}{v_f} + \frac{d \cos \theta_{b1}}{v_{b1}}
\]

(6.34)
where \( v_{f2} \) is the group velocity of the free wave in the sapphire and \( v_{b1} \) is the group velocity of the bound wave in GaN. We calculated this time by replacing each wavevector with the inverse of its group velocity. This transformation follows directly from a first-order expansion with respect to angular frequency of the wavevectors that appear in phases (see section 2.4.2). Thus, ultrafast effects are included in the \( D_{AB}^b \) wave by multiplying the phase by a Gaussian centered at the time required to propagate the wave from point A to point B, i.e.

\[
D_{AB}^b e^{i(k_{f2}A - k_{b1}d)} \rightarrow D_{AB}^b e^{i(k_{f2}A - k_{b1}d)} \exp \left( \frac{-\Delta \omega^2}{8} \left( t - \frac{\Delta}{v_{f2}} - \frac{\cos \theta_{b1} d}{v_{b1}} \right)^2 \right), \quad (6.35)
\]

where \( \Delta \omega \) is the angular frequency bandwidth of our Ti:Al_2O_3 laser. The ultrafast effects are incorporated into the other \( D \) waves by similar transformations.

### 6.4 Second-Harmonic Generation Spectra from GaN/Al_2O_3

In this section we discuss our SHG spectra from GaN/Al_2O_3 in the p-in/s-out and p-in/p-out polarizations. From these spectra we extract \( \chi^{(2)}_{zzz} \) and \( \chi^{(2)}_{zzz} \), respectively. In addition, from our rotational symmetry measurements as a function of the angle of incidence, we determined that the sample miscut does not induce any symmetry forbidden nonlinearities, e.g. \( \chi^{(2)}_{zzz} \) or \( \chi^{(2)}_{zzz} \).

In order to accurately calculate the effects of group velocity mismatch in our GaN films, we measured \( \Delta \omega \) at each wavelength by determining the wavelength distribution of the pulse with a monochromometer. In practice, group velocity mismatch is most
Figure 6.6: SHG spectrum of 1.020 μm GaN sample in the s-in/p-out polarization. The angle of incidence is $\theta_0 = 46^\circ$.

significant for our 4.885 μm sample below a fundamental wavelength of 750 nm.

Figs. 6.6 and 6.7 display our s-in/p-out raw data from our undoped 1.020 μm and our n-type 4.885 μm GaN samples. The data are referenced to the measured SHG from quartz in the same polarization configuration. The discrepancy between the spectra is due entirely to nonlinear interference effects, and is not due to differences in the nonlinear susceptibility.

Using the techniques developed in the section 6.3 and our measured values for the
Figure 6.7: SHG spectrum of 4.885 μm GaN sample in the s-in/p-out polarization. The angle of incidence is $\theta_0 = 46^\circ$. 

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linear optical properties of GaN, we extracted $\chi_{zzz}^{(2)}$ from the data. This parameter is displayed in Fig. 6.8. The magnitude of $\chi_{zzz}^{(2)}$ is approximately $2.4 \times 10^{-8}$ esu, which is consistent with Miragliotta's average value of $2.45 \times 10^{-8}$ esu measured at a single fundamental wavelength of 1064 nm [22]. This is lower than the other reported values for $|\chi_{zzz}^{(2)}|$ of $9.25 \times 10^{-8}$ esu [20] and $3.92 \times 10^{-8}$ esu [23]. The data also exhibits a weak but distinct peak centered at a two photon energy of 2.80 eV. This feature is inconsistent with the expected spectral dependence based on Miller's rule [99].

For measurements in the p-in/p-out polarizations, SHG couples to $\chi_{zzz}^{(2)}$ and $\chi_{zzz}^{(2)}$ in addition to $\chi_{zzz}^{(2)}$. Therefore, we measured the SHG response of GaN at several angles of incidence to fit the two unknown susceptibility elements (see Fig. 6.9). We observed that our spectra were very weakly dependent on $\chi_{zzz}^{(2)}$. The insensitivity of our spectra to $\chi_{zzz}^{(2)}$ results from the fact that our nonlinear signal is proportional to $|\bar{e}_{2\omega} \chi_{zzz}^{(2)} e_\omega e_\omega|^2 \leq 0.004|\chi_{zzz}^{(2)}|^2$. Therefore, we assume the theoretically predicted relationship between $\chi_{zzz}^{(2)}$ and $\chi_{zzz}^{(2)}$, i.e. $\chi_{zzz}^{(2)} = -2\chi_{zzz}^{(2)}$. Fig. 6.8 compares the measured value of $\chi_{zzz}^{(2)}$ to $\chi_{zzz}^{(2)}$ averaged over all of our samples. Although these elements are approximately equal, as predicted by the bound charge model [100], $\chi_{zzz}^{(2)}$ lacks a feature at a two photon energy of 2.80 eV.

We compared our data with the calculated values of $\chi_{zzz}^{(2)}$ and $\chi_{zzz}^{(2)}$ [25] in Fig. 6.8. Hughes and coworkers [25] calculated the second-order susceptibility elements with the full-potential linearized augmented plane-wave method within the local density...
Figure 6.8: Measured nonlinear susceptibility elements for GaN. \(\diamond (\Box)\) denotes \(\chi^{(2)}_{zzz}\) (\(\chi^{(2)}_{zzzz}\)). Data represent the average values for all of the GaN/Al\(_2\)O\(_3\) samples. The solid line (dashed) is the calculated value of \(\chi^{(2)}_{zzz}\) (\(\chi^{(2)}_{zzzz}\)) from reference [25].
Figure 6.9: SHG spectrum of 1.020 μm GaN sample in the s-in/p-out polarization. The ◆, □, and △ data points were measured at angles of incidence of 46°, 60°, and 30°, respectively.
approximation. The agreement between the magnitudes of the calculated and experimental second-order susceptibility elements is quite good. Note that the calculated data exhibits a larger dispersion in the second-order susceptibility elements than the experimental data. In addition, the calculated $\chi_{zzz}^{(2)}$ lacks a resonance at 2.80 eV. We speculate this feature may result from virtual transitions involving an intrinsic midgap defect state. Since, the calculation of the dispersion of $\chi_{zzz}^{(2)}$ includes only bulk band structures, the calculation cannot predict spectral features that couple to defect states.

6.5 Possible Origin of the 2.80 eV Resonance

By analyzing the nature of a resonance in $\chi_{ijk}^{(2)}$, the magnitude of this feature, and the symmetry of states that may participate in this resonance, we are able make some speculative suggestions about the nature of this feature. First, we consider possible origins of the feature at a two photon energy of 2.80 eV. The second order nonlinear susceptibility for second-harmonic generation is derived from quantum statistical mechanics as [46]

$$\chi_{ijk}^{(2)}(\omega = 2\omega_0) = -\frac{N e^3}{\hbar} \sum_{g,n,n'} \left[ \frac{\langle g|r_i|n\rangle\langle n|r_j|n'\rangle\langle n'|r_k|g\rangle}{(\omega - \omega_{ng} + i\Gamma_{ng})(\omega - \omega_{n'g} + i\Gamma_{n'g}) + \ldots} \right] \rho_g^{(0)}$$

where $N$ is the number of electrons per unit volume; $|g\rangle$, $|n\rangle$, and $|n'\rangle$ are states of the system, $\hbar\omega_{ng}$ is the energy difference between states $n$ and $g$; $\Gamma_{ng}$ is a dephasing term; $\rho_g^{(0)}$ is the equilibrium density of the initial state $g$; $-er_k$ is the dipole operator...
along direction \( k \); and the dots represent unique permutations of the states. The contribution of three photon processes to \( \chi^{(2)}_{ijk}(\omega = 2\omega_o) \) depends on several factors. First, resonant enhancement of \( \chi^{(2)}_{ijk}(\omega = 2\omega_o) \) occurs when \( \omega \approx \omega_{ng} \) (two photon resonance) or \( \omega \approx \omega_{n'g} \) (one photon resonance). Second, contributions to \( \chi^{(2)}_{ijk}(\omega = 2\omega_o) \) are constrained by the matrix elements in the numerator of equation (6.36). In other words, the matrix elements determine whether a process is allowed and influence the magnitude of allowed processes. Third, the occupancy of the states requires that the first virtual transition in the three photon process originates from an occupied state and connects to an unoccupied state.

These constraints limit the type of process responsible for a two photon resonance with energy 2.80 eV in \( \chi^{(2)}_{ijk}(\omega = 2\omega_o) \). Because GaN is a direct band gap semiconductor with a band gap energy of 3.4 eV, the two photon resonance cannot result from virtual transitions between valence and conduction band states only. In addition, the requirement that the process begin with a virtual transition between an occupied and an unoccupied state precludes any process that occurs only in the valence or conduction bands. Thus, it is unlikely that the 2.80 eV feature results purely from the band structure of GaN. On the other hand, it is well known that GaN contains a variety of defect states [63]. Thus, the spectral feature could result from a three photon process that involves both a defect state and the GaN bands. For example, a bulk defect state (or defect band) with energy 2.80 eV above the valence band (a
midgap state) could play a role in this resonance.

We present a simple analysis of the $\chi^{(2)}_{\text{zzz}}$ spectrum that can somewhat constrain the properties of the defect state within the simple model. We decompose the susceptibility into resonant and nonresonant terms [4] as

$$\chi^{(2)}_{\text{zzz}}(\omega = 2\omega_0) = \chi^{(2)}_{\text{zzz, res}}(\omega = 2\omega_0) + \chi^{(2)}_{\text{zzz, non}} = \frac{Ae^{i\phi}}{(2\omega_0 - \omega_{ng} + i\Gamma_{ng})} + \chi^{(2)}_{\text{zzz, non}} (6.37)$$

where the symbols have the same meaning as in equation (6.36) and $e^{i\phi}$ is a phase difference between the resonant and nonresonant components. The resonant term is attributed to a two photon resonance involving transitions to a midgap defect state and the nonresonant term is attributed to all other nonresonant bulk three photon transitions. This decomposition assumes that the only spectral dependence of $\chi^{(2)}_{\text{zzz}}(\omega = 2\omega_0)$ results from the denominator of the Lorentzian term. The other terms in equation (6.37) are expected to be slowly varying functions of $\omega_0$. Fitting this function to the data determines $\phi \approx -\frac{\pi}{2}$ and $\chi^{(2)}_{\text{zzz, res}} = 3.8 \times 10^{-9}$ esu at a two photon energy of 2.80 eV. If we assume the resonant component of $\chi^{(2)}_{\text{zzz}}$ results from defect states with a density of $N \sim 10^{20}$ cm$^{-3}$, then the hyperpolarizability associated with these states is $\alpha_{\text{zzz}} \sim 10^{-29}$ esu. This speculative analysis yields numbers that are large but not impossible.

We also determined possible three photon processes that contribute to $\chi^{(2)}_{\text{zzz}}(\omega = 2\omega_0)$, but not to $\chi^{(2)}_{\text{zzz}}(\omega = 2\omega_0)$, by analyzing the symmetry of the proposed midgap defect state. Defects in GaN are frequently characterized by s-like or p-like symmetry.
Our model assumes a defect state lies in the GaN band gap with s-like or p-like symmetry and that a three photon process originates at either the valence band maximum or at the defect state. This analysis applies group theory [92] to calculate the nonzero matrix elements in equation (6.36). In this calculation, we used the band symmetries determined by Bloom et al [77]. Fig. 5.5 displays the symmetries of the GaN bands at the Γ point and their approximate energies. Assuming $C_{6v}$ symmetry, s-like states have $A1$ ($\Gamma_1$) symmetry and p-like states have $E2$ ($\Gamma_6$) symmetry. Table 6.4 shows all nonzero resonant three photon processes for $\chi^{(2)}_{zzz}(\omega = 2\omega_o)$ and $\chi^{(2)}_{zzz}(\omega = 2\omega_o)$. All processes are at the Γ point of the Brillouin zone. In Table 6.4, $\Gamma_6^{defect}$ refers to a defect state with $\Gamma_6$ (p-like) symmetry. The labels $g$, $n$, and $n'$ refers to the states in equation (6.36). Of the cases examined, only the three photon process that originates from a p-like defect state is inconsistent with our observation of a 2.80 eV resonance in $\chi^{(2)}_{zzz}(\omega = 2\omega_o)$ but not in $\chi^{(2)}_{zzz}(\omega = 2\omega_o)$. Fig 6.10 displays three photon processes that may contribute to this resonance.

We now draw several conclusions from our spectroscopic data and speculate about the nature of the defect state. First, the spectroscopic feature at a two photon energy of 2.80 eV is likely to be an intrinsic midgap defect not associated with yellow band defects. This conclusion results from the presence of the 2.80 eV feature in samples with and without yellow band luminescence. Second, the defect is likely to be a point defect and not a defect complex. Defect complexes could arrange themselves
Figure 6.10: Three photon processes in GaN involving a midgap defect state. In Fig. A, the resonant transition is a transition between the defect state and the GaN valence band. In Fig. B, the resonant transition is a transition between the conduction band and the defect state. The virtual transitions are labeled by symmetry and by energy, e.g. $\hbar \omega_1$. The process is resonant for $\omega = \omega_1 + \omega_2$. 
Table 6.4: Possible contributions to $\chi_{xxx}^{(2)}(\omega = 2\omega_o)$ and $\chi_{xxx}^{(2)}(\omega = 2\omega_o)$ for a defect state in the band gap of GaN

<table>
<thead>
<tr>
<th>susceptibility</th>
<th>defect symmetry</th>
<th>origin</th>
<th>$g$</th>
<th>$n$</th>
<th>$n'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_{xxx}^{(2)}$</td>
<td>s-like</td>
<td>valence</td>
<td>$\Gamma_1^a$</td>
<td>$\Gamma_5^b$</td>
<td>$\Gamma_1^{\text{defect}}$</td>
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<tr>
<td>$\chi_{xxx}^{(2)}$</td>
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<td>defect</td>
<td>$\Gamma_1^{\text{defect}}$</td>
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<td>$\chi_{xxx}^{(2)}$</td>
<td>p-like</td>
<td>valence</td>
<td>$\Gamma_6^a$</td>
<td>$\Gamma_3^b$</td>
<td>$\Gamma_6^{\text{defect}}$</td>
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<td>$\chi_{xxx}^{(2)}$</td>
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<td>$\chi_{xxx}^{(2)}$</td>
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<td>$\chi_{xxx}^{(2)}$</td>
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</table>
in various bonding geometries within the lattice, and hence the hyperpolarizabilities of the individual complexes would tend to cancel in an assemble average. Third, there are several symmetries and energy positions within the band gap of the defect state that may contribute to $\chi^{(2)}_{zzz}$ but not $\chi^{(2)}_{zzz}$. Fourth, the position of this state in the band gap region is unknown. Unfortunately, second-harmonic generation does not unambiguously determine one- or two-photon excitations. Fifth, the defect state must be a bulk defect state and not an interface defect state. Although inhomogeneities at the interface may form defect states with large nonlinearities, significantly fewer defect states are produced at the interface than in the bulk. The volume density of interface defect states, $N_i$, is related to the surface density of interface defects, $N_{i\text{surface}}$, as $N_i = N_{i\text{surface}}d$, where $d$ is the number of defects perpendicular to the surface per cm. If we assume that the defect layer extends over 10 unit cells, one defect exists per unit cell, and the surface density of interface defect states is $10^{14}$ cm$^{-2}$, then $N_i = 10^{15}$ cm$^{-3}$. Thus, $N_i$ is several orders of magnitude smaller than the estimated volume density of bulk defects, $N_b = 10^{20}$ cm$^{-3}$.

6.6 Effect of Interface Strain

Finally we consider the influence of the sample miscut on possible strain induced defect states in GaN. Observation of strain and disorder effects on second-harmonic generation from vicinal Si(111)/SiO$_2$ and Si(100)/Si$_3$N$_4$ interfaces [102] suggests that
strain induced defect states may be generated at or near the GaN/Al₂O₃ interface. Strain is expected to couple most strongly to the components of the susceptibility elements that are perpendicular to the interface [11]. Thus, this effect may be most easily observed in \( \chi^{(2)}_{zzz} \) and \( \chi^{(2)}_{zzz} \). Note that the film coordinate, the xz plane is a mirror plane. Therefore, susceptibility elements such as \( \chi^{(2)}_{zzz} \) and \( \chi^{(2)}_{yzz} \) are forbidden. Note, these elements are defined to include only the effect of the strain induced nonlinearity and do not result from a coordinate transformation.

We performed rotational symmetry measurements in the p-in/p-out polarizations to probe GaN for these elements. We simplified our analysis by assuming \( \chi^{(2)}_{zzz} \). Thus, the second-order susceptibility, including the sample miscut and strain, transforms as

\[
\chi_{ijk}^{(2), \text{lab}} = R^{\text{miscut}}(\phi)_{i\alpha}R^{\text{miscut}}(\phi)_{j\beta}R^{\text{miscut}}(\phi)_{k\gamma} \chi_{\alpha\beta\gamma}^{(2), \text{crystal}} + R(\phi)_{i\alpha}R(\phi)_{j\beta}R(\phi)_{k\gamma} \chi_{\alpha\beta\gamma}^{(2), \text{strain}}. \tag{6.38}
\]

In equation (6.38), \( \chi_{ijk}^{(2), \text{crystal}} \) represents \( \chi_{zzz}^{(2)}, \chi_{zzz}^{(2)}, \) and \( \chi_{zzz}^{(2)} \), \( R^{\text{miscut}} \) is the matrix defined by equation (6.3), \( \chi_{ijk}^{(2), \text{strain}} \) represent \( \chi_{zzz}^{(2), \text{strain}} \) and \( \chi_{zzz}^{(2), \text{strain}} \). and \( R \) is the matrix defined by equation (6.2). We deduced the miscut angle of our films from the rotational symmetry data at an angle of incidence of 15° assuming \( \chi_{zzz}^{(2), \text{strain}} = 0 \). We repeated our rotational measurement over a two photon spectral range of 2.6 to 3.4 eV at an angle of incidence of 65° to fit for \( \chi_{zzz}^{(2), \text{strain}} \) with the miscut angle fixed from the 15° rotational scan. We were unable to detect any strain or miscut
Figure 6.11: $\chi^{(2)}_{zzz}$ of GaN determined by SHG azimuthal scans. We were unable to observe any strain induced nonlinearity. The magnitude of this effect may be compared with the magnitude of the bulk susceptibility elements by comparing this figure with Fig. 6.8

induced nonlinearity within the limit of our measurement and determined $\chi^{(2),\text{strain}}_{zzz} < 0.005\chi^{(2)}_{zzz}$. Fig. 6.6 displays $\chi^{(2),\text{strain}}_{zzz}$.

Interface states that do not result from miscut induced strain are not observable by our rotational symmetry technique. These states could result from bonding between the substrate and the thin film [3]. Due to symmetry at the interface, these states most strongly affect $\chi^{(2)}_{zzz}$. Unfortunately, sample geometry precludes a direct measurement
of this second order susceptibility element. We express the influence of the interface states on $\chi^{(2)}_{zzz}$ as

$$\chi^{(2)}_{zzz} = \chi^{(2),\text{bulk}}_{zzz} + \chi^{(2),\text{interface}}_{zzz}, \quad (6.39)$$

where $\chi^{(2),\text{bulk}}_{zzz}$ is the second-order susceptibility element due to the bulk band structure and $\chi^{(2),\text{interface}}_{zzz}$ is the second-order susceptibility element due to interface states. We calculated the minimum magnitude of $\chi^{(2),\text{interface}}_{zzz}$ that is observable by SHG spectroscopy using our theory of SHG from GaN in the p-in/p-out geometry (equation (6.30)). Our calculation assumed an angle of incidence of 88° to maximize coupling of the fields to $\chi^{(2)}_{zzz}$. The interface states are said to be observable if they influence the magnitude of the SHG signal by at least 10%. Our calculation determined the minimum observable $\chi^{(2),\text{interface}}_{zzz}$ in terms of the the bulk second-order susceptibility as $\chi^{(2),\text{interface}}_{zzz} = 0.35 \chi^{(2),\text{bulk}}_{zzz}$. If we assume $|\chi^{(2),\text{bulk}}_{zzz}| \approx 4.8 \times 10^{-8}$ esu and an interface defect volume density, $N_i$, of $10^{15}$ cm$^{-3}$, then the minimum observable interface defect hyperpolarizability is $\alpha^{\text{interface}}_{zzz} \approx 1.7 \times 10^{-23}$ esu. This is a nonphysical (too large) second-order hyperpolarizability, and illustrates that interface defect states associated with $\chi^{(2)}_{zzz}$ are not observable. Note that this analysis is not limited to GaN [0001]. The observation of $\chi^{(2),\text{interface}}_{zzz}$ is inhibited by the large index of refraction of GaN, which refracts the field polarization away from the $z$ direction. and the other nonzero susceptibility elements, which provide a large signal background.
Chapter 7

SHG Microscopy

The majority of this thesis describes completed experiments on the linear and nonlinear optical properties of GaN. This chapter details our ongoing work in a different field of study - nonlinear optical microscopy. We designed and constructed a nonlinear optical microscope to investigate the nonlinear optical properties of heterogeneous systems. In addition, we have begun investigations of the nonlinear optical properties of carbon nanotubes. While we have not observed distinct second-harmonic responses from isolated carbon nanoropes, we have made significant progress and are continuing our work.

Nonlinear optical microscopy differs substantially from our previous nonlinear studies. We briefly highlight the applications and limitations of this technique. Our studies of the nonlinear optical properties of GaN are characterized by highly detailed calculations and experimental techniques. Spectral features were determined from homogeneous films with an accuracy of $\sim 10\%$. In contrast, nonlinear optical
microscopy attempts to correlate relatively large changes in the nonlinear response of a medium with local changes in electronic or structural properties. Nonlinear optical microscopy probes the local structure or symmetry of a medium by focusing the fundamental beam to $\sim 3 \, \mu\text{m}$. Ideally, one probes structural changes that cannot be observed by linear optical techniques. For example, because of its high spatial sensitivity, the nonlinear optical microscope appears well suited to investigate the nonlinear optical properties of carbon nanoropes. Measurements of a single carbon nanorope have the potential to provide a more accurate determination of nanotube nonlinear optical properties than measurements of a sample that consists of an ensemble of tubes or nanoropes. In contrast to SHG experiments from a sample of randomly oriented nanoropes, SHG microscopy may isolate susceptibility elements from a single nanorope, or a dilute collection of oriented nanotubes.

This chapter is organized as follows. We first discuss the historical development of nonlinear optical microscopy. We then describe our nonlinear optical microscope. This section includes a discussion on the detectability limits of the microscope and determines an upper bound on the nonlinearity of the carbon nanotubes from this limit.
7.1 Historical Context of Second-Harmonic Generation Microscopy

In 1974 Robert Hellwarth and Paul Christensen imaged second-harmonic generation from a polycrystalline ZnSe film [26, 27]. Fig. 7.1 displays their experimental setup for SHG microscopy. The coupling of the fundamental light to the various orientations of the polycrystalline crystal axes produced a quasi-phase matching condition for certain propagation directions. Fundamental light incident on a particular grain produced SHG along the quasi-phased matched direction. Since the fundamental laser light covered many grains, second-harmonic light was scattered in various directions. These small beams of scattered SHG were called "beamlets" by Hellwarth and Christensen. By examining the distribution and intensity of these SHG beamlets, they determined the average size of the polycrystalline grains, the thickness of the grains, the preferred orientation of the normal to the grains, and the coverage of the grains. This experiment introduced techniques to probe local structure with second-harmonic generation. SHG microscopy has been used more recently to examine the local structure of Langmuir monolayers [103]; to probe the domain structure of magnetic garnet films [104], BaTiO$_3$ [105], and LiTaO$_3$ [105]; to measure concentration gradients of Sb on Ge (111) [106]; and to probe tissue [107].

The recent activity in nonlinear optical microscopy is probably a result, at least in part, of the success of conventional nonlinear optics as a probe of surfaces and interfaces. In addition, the introduction of Ti:Al$_2$O$_3$ lasers into the nonlinear optical
Figure 7.1: Experimental setup for SHG microscopy of polycrystalline ZnSe. The sample is placed at the focus of Nd:YAG laser pulse. SHG is observed on a screen behind the sample. The figure is adapted from [26].

spectroscopy community has dramatically improved the simplicity and signal to noise ratio of these experiments. In general, Ti:Al₂O₃ based experiments have higher signal to noise ratios than experiments that employ conventional laser systems. This higher signal to noise ratio is the result of the very high peak powers that are achieved with 100 fs pulses and the high repetition rate of the laser (76 MHz). Detection is further enhanced by lock-in detection, which is applicable to this system due to its high repetition rate. Therefore, the excellent SH generating capability of Ti:Al₂O₃ systems may be applied to experimental regimes that were previously inaccessible.

7.2 Nonlinear Microscope

In this section we discuss our experimental design and the development of nonlinear optical microscopy. We designed our microscope to measure simultaneously both the linear and nonlinear reflectivity of our samples. These measurements provided us with
complimentary information about our samples and were a gauge of the effectiveness of nonlinear optical microscopy as a unique structural probe. This section also discusses techniques for accurately and reproducibly determining sample position. We conclude this section with a discussion of the detection limits of our system and the nonlinearity of carbon nanoropes.

Figure 7.2: Experimental setup for nonlinear optical microscopy. The thin lines represent the fundamental beam and the thick lines represent SHG. The dashed lines represent electrical connections.
7.2.1 Optical Setup

The optical path of the laser light in the microscope is shown in Fig. 7.2. A mode-locked 800 nm pulse from the Ti:Al₂O₃ laser was collimated by a lens and enlarged by a telescope. The beam was then polarized and amplitude modulated by an optical chopper. A series of optics directed the fundamental beam to a 0.85 NA air coupled objective. Prior to this objective, a small fraction of the fundamental light was reflected to a reference nonlinear line containing a plate of phased matched KDP and a photomultiplier tube.

The objective focused the fundamental beam to a ~3 µm spot on a sample placed at the focal point of the objective (about 0.3 mm from the front of the objective). The intense fundamental light induced the emission of SH photons from the sample. The signal was emitted in reflection from the sample surface and was collected by the objective. The objective also collected the reflected fundamental light. Because the sample was positioned at the focal point of the objective, the reflected SHG light and the fundamental light propagated as collimated beams along the same path as the incident fundamental beam.

After exiting the objective, the SHG beam was reflected by a harmonic beamsplitter, which was engineered to reflect light at a wavelength of 400 nm and transmit light at a wavelength of 800 nm. In practice, a small fraction of the fundamental light was also reflected from the harmonic beamsplitter and propagated with the
second-harmonic light towards the detection apparatus (see Fig. 7.2). The detection apparatus is discussed in section 7.2.2.

We are able to probe a variety of nonlinear susceptibility elements of our samples by altering the polarization and the angle of incidence of the fundamental beam. We used a zeroth order half-wave plate to rotate the polarization of the fundamental beam from horizontal to vertical. The angle of incidence of the fundamental light was altered by positioning the beam center away from the microscope objective axis. Light in the image plane is related to light in the back aperture plane of the objective by a Fourier transform. Thus, translations in the back aperture plane became new incidence angles in the focal plane. This is illustrated schematically in Fig. 7.3. Unfortunately, a trade off exists between the angle of incidence and spot size in the focal plane. When we operated the microscope at normal incidence, we filled the back aperture of the microscope objective to minimize the spot size in the focal plane. Translating the beam off the objective axis necessitated reducing the beam size in the back aperture plane. Thus, the beam was focused at a non-normal angle of incidence but had a spot size larger than the normal incidence spot size. This trade off between angle of incidence and spot size limited our measurements to an angle of incidence of \( \sim 30^\circ \) with a corresponding spot size of 15 \( \mu \text{m} \).

Our highly focussed Ti:Al\(_2\)O\(_3\) beam cannot be adequately described by a plane wave representation. In particular, we observed a nonzero isotropic SH response.
Figure 7.3: Diagram of Ti:Al$_2$O$_3$ pulse incident on the microscope objective. Fig. A displays the Ti:Al$_2$O$_3$ beam (thick lines) incident on the back aperture of the microscope objective in the on axis geometry. The beam is focused to 3 $\mu$m at normal incidence in the focal plane. Fig. B displays the Ti:Al$_2$O$_3$ beam incidence on the back aperture of the microscope objective in the off axis geometry. The beam is focused to 15 $\mu$m at non-normal incidence in the focal plane. The back aperture, or exit pupil, of the microscope is also displayed.
Figure 7.4: SHG rotational symmetry of Si (100) and Si (111) measured by the nonlinear optical microscope. ◊ is the experimental data from Si (100) and the solid line is an isotropic fit to the data. □ is the experimental data from Si (111) and the dashed line is an isotropic fit to the data.

from Si (111) and Si (100) (see Fig. 7.4). We used silicon as a reference material to test the alignment of the nonlinear optical microscope. Sipe and coworkers [108] have calculated the second-harmonic response for the (100), (111), and (110) faces of Si. They determined that second-harmonic generation from both the surface and the bulk is forbidden from Si (100) excited by a plane wave fundamental beam at normal incidence. Although a nonlinear polarization is generated in Si (100) excited
by a plane wave for both the surface and bulk, the polarization cannot radiate a second-harmonic wave in the vacuum. Note that SHG is forbidden from Si (100) in this geometry for the electric quadrupole and magnetic dipole contributions to the nonlinear polarization.

The discrepancy between theory and experiment is resolved by incorporating a more sophisticated description of the fundamental beam in the focal plane. The electric field of a Gaussian beam in the focal plane \((z = 0)\) has the form

\[
E(x, y, z = 0) = \hat{z} E_0 \exp \left( -\frac{x^2 + y^2}{w_0^2} \right),
\]

(7.1)

where \(w_0\) is the spot size or beam waist of the focused beam. Because silicon has inversion symmetry, its nonlinear polarization is related to the fundamental fields as

\[
P^{(2)}_i = \Gamma_{ijkl} E_j \nabla_k E_l.
\]

(7.2)

Equation (7.2) is a nonlocal response of the nonlinear polarization to the fundamental fields. The nonlocal response is mediated by a fourth rank tensor, \(\Gamma_{ijkl}\), which includes electric quadrupole and magnetic dipole terms. A plane wave at normal incidence induces only a nonlinear polarization that has a component perpendicular to the silicon surface, i.e. the silicon surface is defined by the xy plane with z normal to the plane, and the only nonlinear polarization is directed along z. From equation (7.2), the second-order nonlinear polarization induced in Si (100) by an x polarized plane
wave at normal incidence is

\[ P_z^{(2)} = k \Gamma_{zzzz} E_x E_z, \]  \tag{7.3} 

where \( k \) is the wavevector of the fundamental field. The nonlinear polarization expressed in equation (7.3) cannot radiate a second-harmonic wave into the vacuum. In contrast, the transverse profile of the Gaussian wave varies appreciably in the focal plane, and the Gaussian wave induces a nonlinear polarization with components parallel to the silicon surface, i.e. \( P_x^{(2)} \) and \( P_y^{(2)} \). The nonlinear polarization induced in Si (100) excited by a x-polarized Gaussian wave at normal incidence, i.e. equation (7.1), is

\[ \mathbf{P} = \left( -i \Gamma_{zzzz} \frac{2x}{w_o^2} \Gamma_{yxyz} \frac{2y}{w_o^2} + i \frac{k \Gamma_{zzzz}}{2} \right) E^2 \exp \left( - \frac{2(x^2 + y^2)}{w_o^2} \right). \]  \tag{7.4} 

This nonlinear polarization has components along x and y, and can radiate a SH field into the vacuum. Thus, unlike our SHG spectroscopy of GaN, which is adequately described by plane waves, SHG microscopy requires a Gaussian wave description.

An additional significant effect in nonlinear optical microscopy is the anomalous behavior of the polarization of a highly focussed beam. Carter [109, 110] determined that tightly focused Gaussian beams consist of a longitudinal field in the focal plane, i.e.

\[ \mathbf{E}(x, y, z = 0) = \hat{x} E \exp \left( - \frac{x^2 + y^2}{w_o^2} \right) - i \hat{z} \frac{x}{kw_o^2} E \exp \left( - \frac{x^2 + y^2}{w_o^2} \right). \]  \tag{7.5} 

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In particular, this effect could dominant nonlocal effects for samples with large non-linear susceptibilities that have components perpendicular to a surface. An example of such a sample is a film of rod-like nonlinear molecules that lie nearly perpendicular to a substrate.

It is instructive to analyze this effect on the nonlinear polarization generated in Si (100). A normally incident wave of the form of equation (7.5) induces a nonlinear polarization in Si (100) directed along the x direction due to the transverse gradient of the standard field polarized along the x direction and the anomalous field polarized along the z direction. We can compare the nonlinear polarization induced by each effect as

\[
\frac{P_x^{(2)\text{standard}}}{P_x^{(2)\text{anomalous}}} = \frac{\Gamma_{xxxx}}{\Gamma_{xxxx}^{(2)}} \frac{E^2 \exp\left(- \frac{x^2 + y^2}{w_o^2}\right)}{E^2 \exp\left(- \frac{x^2 + y^2}{w_o^2}\right)}.
\]

(7.6)

where \(P_x^{(2)\text{standard}}\) is the nonlinear polarization induced by the transverse gradient of the standard field, i.e. the first term in equation (7.5), and \(P_x^{(2)\text{anomalous}}\) is the nonlinear polarization induced by the transverse gradient of the anomalous field, i.e. the second term in equation (7.5). The SHG signal detected is simply the SHG intensity integrated over the area of the SHG beam. Therefore, the ratio of the intensities is

\[
\frac{I(2\omega)\text{standard}}{I(2\omega)\text{polarization}} = \frac{16\Gamma_{xxxx}^2}{15\Gamma_{xxxx}^2} (kw_o)^4.
\]

(7.7)

If we assume \(\Gamma_{xxxx} = \Gamma_{xxxx}\); the fundamental wavelength, \(\lambda\), is 800 nm; and the spot size, \(w_o\), is 3 \(\mu m\), then this ratio is \(\sim 3 \times 10^5\). Therefore, the anomalous fundamental
polarization is negligible for Si (100) because it affects the nonlinear polarization by
the same mechanism as the standard fundamental polarization, i.e. both effects are
nonlocal effects, but the magnitude of the anomalous polarization is smaller than the
magnitude of the standard polarization. The anomalous polarization is significant
when it acts locally while the standard polarization acts nonlocally. e.g. nonlinear
microscopy of GaN [0001] at normal incidence, or when it is applied to unusual
geometries, e.g. rod-like nonlinear molecules at near normal incidence.

7.2.2 Detection

Due to the vast difference in the magnitudes of the linear and second-harmonic light,
we used two detection schemes. (Typically, the ratio of second-harmonic photons to
fundamental photons transmitted through the system was 1 to 10^{12}.) Prior to the de­
tection apparatus, a small fraction of the light was reflected from a glass slide to a Si
photodiode. The output from the photodiode was measured by a Stanford Research
Systems SR530 lock-in amplifier. The measurement recorded the light reflected lin­
early from the sample. The light transmitted through the glass slide was polarized
and the linear light was separated from the second-harmonic light by a short pass
filter. A monochrometer set to pass light at 400 nm removed almost all of the back­
ground light, while transmitting the second-harmonic light to a cooled Hamamatsu
side-on PMT model R4220P. An image of the sample was formed by translating the
sample and measuring its local second-harmonic response. Although this technique lacks the speed of directly imaging the entire second-harmonic response with a large area excitation beam, it has a greater sensitivity to the nonlinearity of the sample. This increased sensitivity is due to the tighter focusing of the beam, and therefore higher intensity of the beam, as compared to a direct imaging method.

Our detection apparatus was designed to measure extremely low light signals by photon counting. Photon counting requires a PMT with high gain, low noise, and a fast response time. Our PMT has a bialkali photocathode with a gain of $1.2 \times 10^7$ at a bias voltage of $1150\,\text{V}$, a rise time of $2.2\,\text{ns}$, and a quantum efficiency of $\sim 20\%$ at a wavelength of $400\,\text{nm}$. These characteristics ensure that a measured second-harmonic photon was converted into a current pulse with an amplitude substantially above the background electrical noise. The PMT was cooled to $-20\,^\circ\text{C}$ by a Products For Research liquid heat exchanged, thermoelectric cooled housing model TE177RF. Because photocathodes have low work functions, electrons are thermally excited and emitted from the photocathode. These thermally excited electrons constitute noise. Cooling the PMT reduced the dark counts by decreasing the energy available to thermally excite electrons above the photocathode work function. A typical dark count rate for the cooled PMT was 1 to 2 counts per second.

While the cooled PMT suppressed dark counts, optical noise was not eliminated. We accounted for the optical noise from our measurements by detecting the signal
Figure 7.5: Relationship between the optical chopper and photon counter gates. The count rate from the signal, which is detected only when the chopper is open, is much larger than the background count, which is always detected.

from the PMT with a Stanford Research Systems gated photon counter model SR400. The gated photon counter is an integrated photon counting system that consists of amplifiers, discriminators, gate generators, and counters. The dual channel photon counter has a variety of counting modes including synchronous detection (A-B counting). In synchronous detection, an optical chopper modulates a light source. During the experiment, the reference output from the optical chopper triggered the gates of the photon counter. The A Gate of the photon counter was positioned to coincide with the open phase of the chopper. This is displayed in Fig. 7.5. Similarly, the B Gate of the photon counter was positioned to coincide with the closed phase of
the chopper. The photon counter counted the number of photons in both gates and reported the difference between the two gates, i.e. A-B.

Although the A Gate and B Gate parameters may be set independently, accurate A-B counting requires that the gates have identical characteristics. In a typical measurement, we amplitude modulated the Ti:Al$_2$O$_3$ laser light at 1 kHz. Both the A Gate and B Gate widths were set to 400 μs and the gates were delayed 50 μs from the start of the open and closed positions of the chopper, respectively. By setting the gate durations less than the period of the open and closed chopper positions, we ensured that signal photons were always counted in A Gate. However, signal photons can be counted in the B Gate due the finite width of the Ti:Al$_2$O$_3$ beam. For a finite sized beam, the transmission of light through the chopper is not a series of step functions but rather is a series of step functions with tails. These tails represent the partially blocked beam, and the length of the tail is proportional to the size of the beam. Thus, a fraction of light is transmitted through the nonlinear optical microscope when the optical chopper has a closed phase. We eliminated this systematic error by placing the chopper at the focal point of the telescope lenses.

We now discuss the photon generated current pulses and their relationship to the measured counts. The number of detected counts depends on two parameters: the discriminator level and the shape of the current pulse. Our PMT was ideally suited for photon counting because it generates high amplitude current pulses when a single
Figure 7.6: Distribution of pulse voltages from photon counting PMT. The vertical line represents the discriminator setting. The noise distribution is described by exponential distribution.

Therefore, we set the discriminator level of the gated photon counter to a level above the noise but below the pulse amplitude. We determined the ideal level by measuring the height distribution of the pulses from the PMT. A typical pulse height distribution for our PMT is displayed in Fig. 7.6. Thus, the experimentally determined ideal setting for the discriminator is -30 mV for a PMT bias of 1150 V. In addition, we modified the shape of the current pulse to suppress multiple counting of the same pulse. Typically, a PMT current pulse consisted of
Figure 7.7: Snubber schematic to reduce current pulse ringing. A signal is reflected from the short coaxial cable and reshapes the current pulse from the PMT. The length of the cable determines the delay of the reflected pulse and the resistance of the variable resistor determines the magnitude of the reflected signal. We adjusted the variable resistor while observing the current pulse on an oscilloscope to minimize pulse ringing. This figure was adapted from reference [111].

A main pulse followed by several smaller pulses. If the height of these secondary oscillations had been above the discriminator level, the pulse was counted twice. By placing a variable resistor at a distance of 6 inches from the PMT and in parallel with the signal cable to the photon counter [111], we introduced electrical feedback into the signal (see Fig. 7.7). This feedback reshaped the pulse and damped the pulse ringing. Hence, we ensured each signal pulse was counted only once.

7.2.3 Registering and Positioning Samples

In contrast to second-harmonic generation from a Si wafer, which is homogeneous, many applications of second-harmonic microscopy require accurate and reproducible control of the sample position. Reproducibility and accuracy of the sample position
depend on two components: a highly accurate translation stage and an optical de­
tection scheme to correlate sample features with the focused Ti:Al$_2$O$_3$ beam. Our
translation staged consists of a Newport three axis translation stage model 462-XYZ-
M. We positioned the stage with a long travel, high resolution, i.e. 0.25 µm, Newport
micrometer model HR-1. The micrometers were attached to computer controlled
stepper motors. We briefly summarize the unique features of our stepper motors. A
more complete description of stepper motors is found in reference [112]. We operated
our 4-phase stepper motors in the half step mode. This extended the number of steps
per rotation from 200 to 400, which corresponds to a minimum step size of 1.25 µm.
Since our beam size was 3 µm, the beam was overlapped with its previous position.
Thus, complete scanning of the sample was ensured. During the experiment, we po­
positioned the sample at the focal point of the objective by adjusting the height of the
sample to produce a collimated fundamental beam. We subsequently made a finer
adjustment of the sample height to maximize the SHG signal.

Second-harmonic generation microscopy is most useful as a probe of heterogeneous
systems. In particular, SHG microscopy enhances the visualization of and provides
contrast to heterogeneous systems with similar linear optical properties. In addition,
SHG microscopy can distinguish between linear and nonlinear regions. One such sys­
tem consists of carbon nanotubes and carbon nanoropes deposited on glass. Although
carbon nanotubes have symmetries that allow second-harmonic generation, the sam­
samples are usually dissolved in solution. Thus, the second-harmonic contributions from individual nanotubes or ropes average to zero. Therefore, nonlinear investigations of carbon nanotubes have been limited to third harmonic generation [113]. We suggest that second-order nonlinear effects in carbon nanotubes may be examined by isolating the response of a single tube or rope. Isolating the second-order nonlinear response of a single tube may be achieved by careful sample preparation and sample examination with a nonlinear optical microscopy.

We now briefly discuss our carbon nanorope sample preparation and highlight sample features relevant to our nonlinear microscope. The carbon nanorope samples and sample masks were prepared entirely by Radoslav Antonov in Prof. Alan Johnson’s laboratory. In addition, Radoslav Antonov examined our nanorope samples with atomic force microscopy (AFM). The nanorope sample was grown by Prof. Richard Smalley’s group at Rice University. The raw samples consisted of tangled nanoropes and carbonaceous material. These ropes had lengths on the order of a few microns and widths less than or equal to 100 nm. In order to isolate the effect of a single nanorope, the raw material was dissolved in dichloroethane and sonicated for 10 minutes. This process separated the tangled nanoropes. The dissolved material was then deposited on a mask by spin coating at 1000 rpm or simply evaporating the solvent. This process deposited single nanoropes separated by several microns on the mask.

The sample mask was designed to register a nanotube within a few microns. We
used photolithography to etch several 25 μm squares on a chromium film deposited on glass. The squares were positioned in an asymmetric pattern to facilitate identification of a single square. After depositing the carbon nanoropes on the mask, we examined the mask with a Zeiss Axiophot microscope using an air coupled 0.60 NA differential interference contrast (DIC) objective. Typically we deposited the dilute carbon nanorope solution on 15 etched squares. On average, one or two carbon nanoropes were visible on the squares. Fig. 7.8 displays a diagram of the masks with deposited nanoropes. After identifying potential candidates using DIC optical microscopy, the samples were examined by AFM. AFM determined if any non-optically visible nanoropes or carbonaceous material were close to, i.e. within ~5 μm, our
Figure 7.9: Video microscopy apparatus to align sample. The thick lines represent light from the attenuated Ti:Al$_2$O$_3$ beam and the thin lines represent light used to illuminate the sample.

Once we identified a single isolated nanorope on the substrate mask, we positioned the mask in our nonlinear microscope using video microscopy. We imaged the sample using transmitted light placed behind the sample. Fig. 7.9 displays the experimental apparatus for viewing the sample position. To position the sample with respect to the incident Ti:Al$_2$O$_3$ beam, we attenuated the Ti:Al$_2$O$_3$ beam to $\sim$0.1 mW. A 50/50 cube beamsplitter was inserted into the optical path of the microscope. Note that this beamsplitter was removed prior to the measurement. Thus, approximately 50%
of light reflected from the sample was redirected along an optical line containing a video camera with a macro zoom lens focused to infinity. This camera collected and imaged the reflected light from the back aperture of the infinity conjugated microscope objective. We observed this image and identified the sample position on a video monitor. We then positioned the corner of the sample mask with the Ti:Al₂O₃ beam using the computer controlled stepper motors.

Fig. 7.10 displays an SHG micrograph of carbon nanoropes on our mask. The only detectable signal results from the metal surrounding the glass island. Signal from the glass/nanorope region is at the level of the noise. Note that glass is an ideal substrate on which to deposit the carbon nanoropes because it has no SHG response when excited by a normally incident fundamental beam. In a typical experiment, we scanned only over the glass/nanotube region. Our investigation of the nonlinear properties of carbon nanoropes consists of 30 SHG microscopy scans on 10 samples. We were unable to clearly identify SHG signal from the glass/nanotube region in any of these measurements.

The high intensity generated by the focussed Ti:Al₂O₃ beam may potentially damage the nanorope sample. We used a 30 mW average power Ti:Al₂O₃ beam during our SHG microscopy scans. We examined the nanotube sample prior to and subsequent to the SHG microscopy scan by DIC microscopy. We did not observe any changes in the nanorope appearance. Thus, we do not believe that we exceeded the damage
7.2.4 Detection Limits and Noise

Detection is limited by optical noise, i.e. background photons, and photon statistics. The distribution of detected photons in a time $T$ is described by the Poisson distribution, which is

$$P_n(T) = \frac{\bar{n}^n}{n!} e^{-\bar{n}}. \quad (7.8)$$

The Poisson distribution determines the probability of detecting $n$ photons in time $T$ if the average number of photons detected in time $T$ is $\bar{n}$. The uncertainty, i.e. the
mean square deviation, of the photon number is

\[ \delta n = \sqrt{n}. \] (7.9)

We determined the uncertainty in the number of counts reported by the photon counter using Poisson statistics. Our detection system uses synchronous detection and reports a number of counts \( n \) as

\[ n = n_A - n_B, \] (7.10)

where \( n_A \) (\( n_b \)) is the number of counts detected in the A (B) Gate. \( n_A \) includes both SHG photons from the sample and background counts, while \( n_B \) includes only background counts, i.e.

\[ n_A = n_{SHG} + n_{back}, \] (7.11)

and

\[ n_b = n_{back}. \] (7.12)

Thus, the uncertainty in \( n \) is

\[ \delta n = \sqrt{2n_{back} + n_{SHG}}. \] (7.13)

Equation (7.13) assumes that the background is truly random, i.e. the background counts during the A Gate are uncorrelated with the background counts during the B Gate. We define a detected signal as

\[ n_{SHG} > 2\delta n. \] (7.14)
From this criteria, we determine the time required to satisfy this inequality. The count rate is expressed as

\[
r_i = \frac{n_i}{T},
\]

where \( i \) represents SHG or back. The critical detection time, \( T_d \) is therefore

\[
T_d = \frac{4(r_{SHG} + 2r_{back})}{f_{dc} r_{SHG}^2},
\]

where \( f_{dc} \) is the duty cycle ratio of the the gate, e.g. \( f_{dc} = 0.4 \) for a 400 \( \mu \text{s} \) gate and a chopper frequency of 1 kHz. Equation (7.16) illustrates the importance of reducing the background count to the lowest possible value. For example if the SHG photon count rate is 100 Hz and the background count rate is 1000 Hz. then \( T_d = 19 \text{ s} \). In contrast, lowering the background rate to 100 Hz with the same signal count rate reduces the detection time to 0.27 s. In practice, we were able so far to lower the background count rate to \( \sim 15 \text{ Hz} \) by placing the detection apparatus in a nearly light tight box and covering the entire apparatus with black cloth.

During a typical measurement of the nonlinear response of carbon nanotubes, we scanned a 10 \( \mu \text{m} \times 10 \mu \text{m} \) area of the sample mask at a rate of one pixel per 10 s. So far we have not been able to unambiguously detect the carbon nanotubes in our measurements. Using the above analysis, we determined that \( r_{SHG} < 6 \text{ Hz} \).
7.3 Calculated SHG Signal from Carbon Nanoropes

In this section, we present two calculations to estimate the limits of our nonlinear optical microscope as a probe of molecular systems. The first calculation uses the SHG signal upper limit from carbon nanotubes to determine the second-order hyperpolarizability of a single carbon nanotube. The second calculation determines the SHG signal from a surface film of aligned nonlinear molecules with the same area as our carbon nanotube sample. We chose p-nitrobenzoic acid (PNBA) as the nonlinear molecule in our calculation because its nonlinear optical properties have been thoroughly investigated [6]. This calculation demonstrates that SHG microscopy from a small collection of molecules is feasible.

We calculate the maximum nonlinearity of carbon nanotubes using a simple model that assumes the carbon nanotubes act as a nonlinear surface layer on the glass substrate. We assume that the carbon nanorope is composed of 100 nanotubes. We further assume that each nanotube has $C_{5v}$ symmetry [30] and that the dominant hyperpolarizability of each nanotube is $\alpha_{zzz}^{(2)}$, i.e. the dominant hyperpolarizability is along the axis of the molecule. The surface second-order nonlinear susceptibility is related to the second-order hyperpolarizability by

$$\chi_{S,ijk}^{(2)} = \frac{1}{A} \sum_{n=1}^{N} (\hat{i} \cdot \hat{\beta})(\hat{j} \cdot \hat{\gamma})(\hat{k} \cdot \hat{\delta}) \alpha_{\beta\gamma\delta}^{(2)}(n),$$

with $N$ nanotubes lying in an area $A$. If we assume that a nanotube has equal probability of lying parallel to or antiparallel to the $z$ axis, then on average there will be a
net alignment of $\sim \sqrt{100} = 10$ nanotubes for a nanorope composed of 100 nanotubes. Note that equation (7.17) assumes the nanotubes are non-interacting. Since our calculation yields only an approximate value for the second order hyperpolarizability of carbon nanotubes, this is a reasonable assumption.

Shen [46] has determined the nonlinear intensity reflected from a surface layer excited by a normally incident fundamental wave as

$$I(2\omega) = \frac{32\pi^3\omega^2}{c^3} |\mathbf{e}_\omega \cdot \chi^{(2)}_S : \mathbf{e}_\omega \mathbf{e}_\omega|^2 I^2(\omega), \quad (7.18)$$

where $\mathbf{e}_\omega = \mathbf{L}(\omega) \cdot \mathbf{e}_\omega$. Note that $\mathbf{e}_\omega$ denotes the unit polarization vector of the field at frequency $\omega$ and $\mathbf{L}(\omega)$ is a Fresnel factor dyadic with the relevant element

$$L_{xx}(\omega) = \frac{2}{1 + \epsilon(\omega)}. \quad (7.19)$$

We can recast equation (7.18) as

$$|\chi^{(2)}_{S,xx}|^2 = \frac{S_{SHG} A^2 \tau}{U^2 A_{eff} f} \frac{c^3}{32\pi^3 \omega^2 L_{xx}^2(\omega) L_{xx}(2\omega)} \frac{1}{L_{xx}(2\omega)}. \quad (7.20)$$

The variables in equation (7.20) are defined with their corresponding values in Tables 7.1 and 7.2. Note that $\chi^{(2)}_{S,ijk}$ is defined in a coordinate system with $z$ normal to the substrate while $\alpha^{(2)}_{\beta\gamma\delta}$ is defined in a coordinate system with the nanotube axis aligned along $z$. Equation (7.20) determines the surface nonlinear susceptibility in terms of the energy of the SHG photons radiated in one second, $S_{SHG}$, the Ti:Al$_2$O$_3$ laser parameters, and the sample geometry. Note that our analysis assumes that
Table 7.1: Ti:Al₂O₃ laser parameters for calculating SHG from carbon nanotubes and PNBA

<table>
<thead>
<tr>
<th>parameter</th>
<th>symbol</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>laser repetition rate</td>
<td>$f$</td>
<td>$7.6 \times 10^7$ s⁻¹</td>
</tr>
<tr>
<td>applied fundamental energy/pulse</td>
<td>$U$</td>
<td>$4 \times 10^{-3}$ ergs</td>
</tr>
<tr>
<td>applied CW power</td>
<td>$P$</td>
<td>$3.0 \times 10^5$ ergs s⁻¹</td>
</tr>
<tr>
<td>beam area</td>
<td>$A$</td>
<td>$7 \times 10^{-8}$ cm²</td>
</tr>
<tr>
<td>fundamental angular frequency</td>
<td>$\omega$</td>
<td>$2.35 \times 10^{15}$ s⁻¹</td>
</tr>
<tr>
<td>pulse duration</td>
<td>$\tau$</td>
<td>$10^{-13}$ s</td>
</tr>
<tr>
<td>speed of light</td>
<td>$c$</td>
<td>$3 \times 10^{10}$ cm/s</td>
</tr>
<tr>
<td>fundamental wavelength</td>
<td>$\lambda$</td>
<td>$8.0 \times 10^{-5}$ cm</td>
</tr>
</tbody>
</table>

$S_{SHG}$ is related to the upper limit of photon count rate, $r_{SHG}$, which we determined in section 7.2.4 based on our null detection:

$$S_{SHG} = h\omega r_{SHG}$$ (7.21)

where $h\omega$ is the energy per photon.

Equation (7.17) may be rewritten as

$$\chi^{(2)}_{S,zzz} = N_s \alpha^{(2)}_{zzz},$$ (7.22)

where $N_s$ is the surface density of nanotubes. Note that $N_s$ is the inverse of the area of a single nanotube. The calculation determines an upper limit of the hyper-
<table>
<thead>
<tr>
<th>parameter</th>
<th>symbol</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>surface density</td>
<td>$N_s$</td>
<td>$1.4 \times 10^{11}$ cm$^{-2}$</td>
</tr>
<tr>
<td>effective beam area</td>
<td>$A_{eff}$</td>
<td>$7 \times 10^{-11}$ cm$^2$ (area of nanotubes)</td>
</tr>
<tr>
<td>SHG Signal</td>
<td>$S_{shg}$</td>
<td>$3 \times 10^{-11}$ ergs</td>
</tr>
<tr>
<td>fundamental susceptibility</td>
<td>$\epsilon(\omega)$</td>
<td>$3.93 + 3.62i$ [114]</td>
</tr>
<tr>
<td>second-harmonic susceptibility</td>
<td>$\epsilon(2\omega)$</td>
<td>$3.57 + 3.07i$ [114]</td>
</tr>
</tbody>
</table>

Table 7.2: Properties of carbon nanotubes for calculating SHG from carbon nanotubes

The polarizability of the nanotubes as $\alpha_{zzz}^{(2)} = 1.1 \times 10^{-27}$ esu. Although this number is extremely large for conventional nonlinear molecules, e.g. $10^{-30}$ esu [6, 115, 116], a 0.5 μm carbon nanotube is composed of approximately 10,000 atoms, and the length of the tube suggests that very high hyperpolarizabilities may be achieved.

A second calculation shows that local domains of nonlinear molecules are easily observable by SHG microscopy. We calculated the number of SHG photons emitted from a domain of aligned $p$-nitrobenzoic acid (PNBA) with the same area as our carbon nanotube sample. PNBA is an organic molecule that has a permanent dipole moment and lacks inversion symmetry. The $\pi$-electrons contribute to the hyperpolarizability along the molecular axis, $\alpha_{zzz}^{(2)}$. Calculations show that $\alpha_{zzz}^{(2)}$ typically exceeds other hyperpolarizability elements by at least one order of magnitude [115]. Thus.
we assume the second-harmonic signal from a film of aligned PNBA molecules results solely from $\alpha_{zzz}^{(2)}$.

The calculation of the nonlinear signal from a surface of aligned PNBA molecules includes the parameters in Tables 7.1 and 7.3. This calculation is nearly identical to the calculation of the hyperpolarizability of the carbon nanotubes. The distinction between the calculations is that the nanotube calculation uses an SHG signal to determine the hyperpolarizability, while the PNBA calculation assumes a hyperpolarizability to determine the SHG signal. We determined that $\sim 1.8 \times 10^4$ SH photons are generated from a PNBA film per second. This SHG response is substantially greater than the SHG upper limit from carbon nanotubes (6 photons per second). Thus, SHG microscopy can easily probe domains of nonlinear molecules. However.
imaging carbon nanoropes with the SHG microscope may require techniques to align several nanoropes together to increase the SHG signal.
Chapter 8

Conclusion

In this brief chapter, we summarize our experimental results and review our conclusions from these experiments. We motivate our nonlinear optical experimental studies as a probe of GaN and describe the relationship between the various experimental techniques. Finally, we discuss the future of nonlinear optics as a probe of condensed matter systems and suggest further avenues for experimentation.

The primary question that this thesis has attempted to answer is: what are the nonlinear optical spectroscopic properties of GaN and how are these properties related to the underlying physics of GaN? In other words, we were motivated to understand the electronic and optical properties of bulk GaN and its interfaces using nonlinear optical spectroscopy as a probe. Determination of these properties required both experimental and theoretical investigations. These investigations included linear optical spectroscopy, photoluminescence, nonlinear optical spectroscopy, and a theory of ultrafast nonlinear spectroscopy of GaN.
Our nonlinear optical spectra and ultrafast nonlinear optical spectroscopy theory of GaN form the core of this thesis. The nonlinear optical spectroscopy theory required the solution to the nonlinear wave equation for a thin film geometry. We then incorporated ultrafast effects into the theory, which explicitly accounted for group velocity mismatch. We performed second-harmonic generation spectroscopy of GaN in the s-in/p-out and p-in/p-out polarizations over a two photon energy of 2.6 to 3.4 eV. We observed a slight enhancement in $\chi^{(2)}_{xzx}$ at a two photon energy of 2.80 eV. By contrast, $\chi^{(2)}_{zzx}$ is spectrally flat. We attributed the sub-band gap resonant enhancement to an intrinsic bulk defect state. This conclusion is derived from the magnitude of the effect and its presence in all of our GaN samples. We further investigated the role of our sample miscut on the nonlinear optical properties of GaN. We used rotational SHG to determine the sample miscut to be 0.8°. In addition, we were unable to observe any strain induced nonlinearity of GaN by rotational SHG; this effect could be produced by the sample miscut.

While further investigations of the nonlinear optical properties of GaN are certainly of interest, our future investigations lie in nonlinear optical microscopy. We have studied the spectra of GaN, and now must move on to other investigations. Nonlinear optical microscopy combines the strengths of nonlinear optical spectroscopy, e.g. sensitivity to symmetry, with the spatial sensitivity of optical microscopy. We suggest that this technique is well suited for the investigation the nonlinear optical
properties of carbon nanotubes. Such an investigation may lead to a technique to determine nanotube structure. In general, nonlinear optical microscopy is useful to investigate samples that have spatial inhomogeneity despite constant linear optical properties. Such systems include Langmuir Blodget films, polycrystalline films, and liquid crystals.
Appendix A

Justification of First Order Expansion of the Phase

In sections 2.4.4 and 2.4.5, we truncated the expansion of $k(\omega)$ to first order in $(\omega - 2\omega_o)$ for any $k(\omega)$ which appeared in a phase. In this appendix, we justify this expansion by demonstrating that the second order term is negligible for the second harmonic pulse generated in quartz or GaN from a Ti:Al$_2$O$_3$ fundamental source. The calculation follows the analysis developed by Silverstri et al [117].

The first order term in the expansion of $k(\omega)$ about $(\omega - 2\omega_o)$ gives rise to the group velocity mismatch which damps the interference of the bound and free waves. The second order term in the expansion accounts for the broadening of the pulse in time. This effect, known as group velocity dispersion (GVD), occurs because the frequency components of the pulse do not have the same group velocity. The pulse broadening increases as the distance through which pulse propagates increases or the dispersion is increased.

In equation (2.42) we defined the general form of the nonlinear ultrafast waves
that propagate through quartz as

\[ E(r, \omega) = \tilde{x}\zeta_m(\omega)e^{i\kappa_m(\omega)y} \]  

(A.1)

where the subscript \( m \) denotes either \( b \) or \( f \) for the bound or free waves. In the time domain, we can write the field at the beginning of the crystal \( (y = 0) \) as

\[ E_m(r, t) = \tilde{x}E_m\exp\left(-\frac{2ln2t^2}{\tau_{in}^2}\right)e^{i\omega t} \]  

(A.2)

with \( \tau_{in} \) as the FWHM of the pulse duration. The field acquires a phase \( \phi = k(\omega)y \) as it traverses the crystal. This phase perturbs the shape of the pulse and leads to an increase in the width of the pulse at the end of the crystal, \( \tau_{out} \), as

\[ \frac{\tau_{out}}{\tau_{in}} = \sqrt{1 + \frac{\phi''}{4\beta^2}}. \]  

(A.3)

In equation (A.3) \( \phi'' \) is defined as the second derivative of the phase of the wave, \( k(\omega)d \), with respect to \( \omega \), i.e.

\[ \phi'' = \frac{\partial^2 \phi}{\partial \omega^2} \bigg|_\omega \]  

(A.4)

with

\[ \phi = k(\omega)d = \frac{n(\omega)\omega L}{c}. \]  

(A.5)

\( \beta \) is defined as

\[ \beta = \frac{\tau_{in}^2}{8ln2}. \]  

(A.6)

It is easy to show that \( \phi'' \) can be rewritten as

\[ \phi'' = \frac{L\lambda^3}{2\pi c^2} \frac{d^2n(\lambda)}{d\lambda^2}. \]  

(A.7)
We calculate the effect of GVD on our second harmonic pulse of the form equation (A.1) that propagates through a 3 mm piece of quartz. We used the dispersion relationship listed in equation (2.67) and Table 2.3. We assume the fundamental pulse has a pulse width of 130 fs. For the parameters stated above, the pulse broadens less than $2 \times 10^{-6}\%$ for both the free and bound waves over a fundamental wavelength range of 740 nm to 1 $\mu$m for a film thickness of 3 mm. For GaN, the free wave pulse broadens by .43% and the bound wave pulse broadens by less than $10^{-6}\%$ for a film thickness of 5 $\mu$m over a wavelength range of 740 nm to 1 $\mu$m. These values were calculated using the Sellmeier dispersion relation for GaN with the parameters listed in Table 4.2.2. This justifies our first order expansion of $k$ with respect to $\omega$. Note, since the bound wave propagates with a wavevector twice that of the fundamental field, the broadening of the fundamental wave can be related to the broadening of the bound wave by

$$\tau_{\text{out}}^{\text{fundamental}} \sim 8\tau_{\text{out}}^{\text{bound}}.$$  

(A.8)

Thus, the fundamental wave does not appreciably broaden during propagation through the GaN film or quartz crystal.
Appendix B

Theory of Nonlinear Response Functions

In this appendix, we formally derive the relationship between the nonlinear polarization, $P_i^{(2)}(\omega = \omega_1 + \omega_2)$, the applied electric fields, $E_j(\omega_1)$ and $E_k(\omega_2)$. This relationship is applied to calculated SHG from the ultrafast Ti:Al$_2$O$_3$ laser system.

We start with a generalized second order nonlinear response function in time [118]

$$P_i^{(2)}(t) = \int_{-\infty}^{\infty} \chi_{ijk}^{(2)}(t - \tau_1, t - \tau_2) E_j(\tau_1) E_k(\tau_2) d\tau_1 d\tau_2. \quad (B.1)$$

$P_i^{(2)}(t)$ is the second order nonlinear polarization at time $t$ resulting from the application of fields $E_j(\tau_1)$ and $E_k(\tau_2)$ at all times before $t$. Since the system cannot respond before the electric fields are applied,

$$\chi_{ijk}^{(2)}(t - \tau_1, t - \tau_2) = 0 \quad \text{if} \quad t - \tau_1 < 0 \quad \text{or} \quad t - \tau_2 < 0. \quad (B.2)$$

This condition is known as causality.

We wish to solve the nonlinear wave equation and calculate the nonlinear fields from the nonlinear polarization in angular frequency space. The angular frequency
space representation allows the simplification of the nonlinear wave equation from
a partial differential equation to an algebraic equation. Therefore, we must derive
the generalized second order nonlinear response function in angular frequency space.
This may be effected by Fourier transforming equation (B.1). The Fourier transforms
are defined in the usual way as

\[ E(t) = \int_{-\infty}^{\infty} E(\omega) e^{-i\omega t} d\omega \]  

(B.3)

and

\[ E(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} E(t) e^{i\omega t} dt \]  

(B.4)

with

\[ \int_{-\infty}^{\infty} e^{i(\omega - \omega_0)t} dt = 2\pi \delta(\omega - \omega_0). \]  

(B.5)

The frequency space representation of \( \chi^{(2)}(t - \tau_1, t - \tau_2) \) follows as

\[ \chi^{(2)}_{ijk}(t - \tau_1, t - \tau_2) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi^{(2)}_{ijk}(\omega_1, \omega_2) e^{-i\omega_1(t - \tau_1)} e^{-i\omega_2(t - \tau_2)} d\omega_1 d\omega_2. \]  

(B.6)

Therefore, the time representation of the nonlinear polarization may be written ex-

cplicitly as

\[ P^{(2)}_i(t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi^{(2)}_{ijk}(\omega_1, \omega_2) e^{-i\omega_1 t} e^{-i\omega_2 t} \]

\[ (E_j(\omega_1) e^{i\omega_1 \tau_1} d\tau_1) (E_j(\omega_2) e^{i\omega_2 \tau_2} d\tau_2) d\omega_1 d\omega_2. \]

(B.7)

Using the Fourier transform equations, equation (B.7) can be expressed as

\[ P^{(2)}_i(t) = 4\pi^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi^{(2)}_{ijk}(\omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2) e^{-i\omega_1 t} e^{-i\omega_2 t} d\omega_1 d\omega_2. \]  

(B.8)
Fourier transforming equation (8.8) from time to frequency yields

$$P_{i}^{(2)}(\omega) = 4\pi^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi_{ijk}^{(2)}(\omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2) \delta(\omega - (\omega_1 + \omega_2)) d\omega_1 d\omega_2. \quad (B.9)$$

Equation (B.9) represents a general expression that determines $P_{i}^{(2)}(\omega)$ as a function of the incident fields $E_j(\omega_1)$ and $E_k(\omega_2)$. For monochromatic fields, i.e.

$$E_j(\omega_1) = \frac{\delta(\omega_1 - \omega_o)}{2\pi}. \quad (B.10)$$

Equation (B.9) reduces to the usual expression

$$P_{i}^{(2)}(\omega) = \chi_{ijk}(\omega = 2\omega_o) E_j(\omega_o) E_k(\omega_o). \quad (B.11)$$
Appendix C

Justification of Zeroth Order Expansion of the Coefficients in the Ultrafast Nonlinear Pulse Calculation

In section 2.4.4, we used a zeroth order expansion of $\omega$ about the central angular frequency of the pulse, $2\omega_o$, for all coefficients that appear in the wave equation. In this appendix, we restate the simplified form of the bound wave field and demonstrate that the simplification leads to a negligible correction to the SHG intensity.

From equation (2.38), we derived the relationship between the bound wave, $E_b$, and the second order nonlinear polarization, $P^{(2)}_z$, as

$$
\left[ k_b^2(\omega) - \frac{\epsilon(\omega)\omega^2}{c^2} \right] E_b(y, \omega) = \frac{4\pi\omega^2}{c^2} P^{(2)}_z(y, \omega).
$$

We then simplified this relationship by assuming

$$
\omega = 2\omega_o.
$$

This leads to the approximations

$$
k_b^2(\omega) = \left( \frac{2n(\omega_o)\omega_o}{c} + \frac{\omega - 2\omega_o}{\nu_b} \right)^2 \rightarrow \left( \frac{2n(\omega_o)\omega_o}{c} \right)^2 = \frac{4\epsilon_b\omega_o^2}{c^2}.
$$
and

\[
\frac{\epsilon(\omega)\omega^2}{c^2} \rightarrow \frac{4\epsilon_f\omega_0}{c^2}
\]  \hspace{1cm} (C.4)

with \(\epsilon_b \equiv \epsilon(\omega_0)\) and \(\epsilon_f \equiv \epsilon(2\omega_0)\). These simplification lead to the relationship

\[
E_{b_\perp}(\omega) = \frac{4\pi P_x^{(2)}(\omega)}{\epsilon_b - \epsilon_f}.
\]  \hspace{1cm} (C.5)

We compare this to the relationship between \(E_{b_\perp}\) and \(P_x^{(2)}\) without the zeroth order expansion, namely

\[
E_{b_\perp}(\omega) = \frac{4\pi \omega^2 P_x^{(2)}(\omega)}{c^2} \left[ k_b^2 - \frac{\epsilon(\omega)\omega^2}{c^2} \right]^{-1}.
\]  \hspace{1cm} (C.6)

The quantity that we measure is the SHG intensity averaged over all angular frequencies. Note, this is obviously identical to the SHG intensity averaged over the pulse duration. As stated previously, the SHG intensity depends on both the bound wave and free wave fields. The free wave is related to the bound wave by factors that are independent of \(\omega\). Therefore, it is sufficient to compare the intensities of the bound waves with and without the zeroth order phase approximation to determine if the phase approximation is valid. For GaN (quartz), the discrepancy between the zeroth order approximation and the full approximation is less than .17% (.06%) over the fundamental wavelength range of 740 nm to 1 \(\mu\)m. Thus, the zeroth order expansion of \(\omega\) is valid for the coefficients of the bound wave field.
Appendix D

Derivation of Optical Transmission through a Thin Film Equations

In this appendix, we derive several of the equations used in the calculation of light transmission through a thin film (see section 4.2.2).

D.1 Derivation of equation (4.15)

Equation (4.14) expresses the continuity of the tangential magnetic fields at boundary b as

\[ \mathcal{H}_{2b}^+ = \mathcal{H}_{1b}^+ + \mathcal{H}_{1b}^- . \]  

(D.1)

The positive going electric and magnetic fields in layer i are related by \( \nabla \times \mathbf{E}_i = -\frac{1}{c} \frac{\partial \mathbf{H}_i}{\partial t} \) as

\[ \mathbf{k}_i^+ \times \mathbf{E}_i^+ = \frac{\omega}{c} \mathbf{H}_i^+ \]  

(D.2)

or

\[ n_i \mathbf{k}_i \times \mathbf{E}_i^+ = \mathbf{H}_i^+ . \]  

(D.3)

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The polarization, \( \hat{e}_i^+ \), of the positive going field is determined by \( \nabla \cdot \mathbf{E}_i = 0 \) and \( \mathbf{k}_i^- \) (equation (4.8)) as

\[
\hat{e}_i^+ = -\sin \theta_i \hat{z} + \cos \theta_i \hat{x},
\]

and therefore

\[
\mathbf{E}_i^+ = \hat{e}_i^+ \mathbf{E}_i^+.
\]

Thus, equation (D.3) can be written as

\[
n_i \hat{y} \mathbf{E}_i^+ = \mathbf{H}_i^+.
\]

Using equations (4.9) and (D.4) we can express the positive going electric field in terms of the positive going tangential electric field as

\[
\hat{z} \times \mathbf{E}_i^+ = \hat{z} \times \hat{z} (\hat{x} \cdot \mathbf{E}_i^+) = \hat{y} \cos \theta_i \mathbf{E}_i^+.
\]

Combining equations (D.6) and (D.7) leads to

\[
\eta_i (\hat{z} \times \mathbf{E}_i^+) = \mathbf{H}_i^+
\]

with

\[
\eta_i = \frac{n_i}{\cos \theta_i}.
\]

A derivation for the negative going waves leads to an equation similar to equation (D.8), and thus to equation (4.15).
D.2 Derivation of equation (4.21)

The boundary condition for the electric fields at boundary \( b \) (equation (4.13)) can be written as

\[
\hat{z} \times \mathcal{E}_{2b}^+ = \hat{z} \times \mathcal{E}_{1b}^+ + \hat{z} \times \mathcal{E}_{1b}^-.
\]  

(D.10)

The boundary condition for the magnetic fields at boundary \( b \) can be expressed using equations (4.14) and (4.15) as

\[
\frac{\mathcal{H}_b}{\eta_1} = \hat{z} \times \mathcal{E}_{1b}^+ - \hat{z} \times \mathcal{E}_{1b}^-.
\]  

(D.11)

Combining equations (D.10) and (D.11) determines the positive going tangential electric field in layer 1 at boundary \( b \) in terms of the tangential electric and magnetic fields at boundary \( b \) as

\[
(\hat{z} \times \mathcal{E}_{1b}^+) = \frac{1}{2} \left( \frac{\mathcal{H}_b}{\eta_1} + (\hat{z} \times \mathcal{E}_b) \right).
\]  

(D.12)

The other expressions in equation (4.21) are derived by a similar analysis.

D.3 Derivation of equation (4.33)

In this section, we derive the reflection amplitude from a thin film. The boundary conditions for the electric and magnetic fields at boundary \( a \) are

\[
(\hat{z} \times \mathcal{E}_{0a}^+) + (\hat{z} \times \mathcal{E}_{0a}^-) = (\hat{z} \times \mathcal{E}_{1a}^+) + (\hat{z} \times \mathcal{E}_{1a}^-)
\]  

(D.13)
and

\[ \mathcal{H}_{0a}^+ + \mathcal{H}_{0a}^- = \mathcal{H}_{1a}^+ + \mathcal{H}_{1a}^-, \tag{D.14} \]

respectively. Equation (D.14) can be rewritten using equation (D.8) as

\[ \eta_0 \left( (\hat{z} \times \mathcal{E}_{0a}^+) - (\hat{z} \times \mathcal{E}_{0a}^-) \right) = \mathcal{H}_{1a}^+ + \mathcal{H}_{1a}^- . \tag{D.15} \]

In equation (4.26), we normalized the output tangential electric field, and thus determined the ratio of the tangential magnetic and electric fields at boundary a to be

\[ \frac{\mathcal{H}_a}{(\hat{z} \times \mathcal{E}_a)} = \frac{C}{B} . \tag{D.16} \]

where \( B \) and \( C \) are defined in equations (4.27) and (4.28), respectively. Now, equation (D.15) can be expressed in terms of equation (D.16) as

\[ \eta_0 \left( (\hat{z} \times \mathcal{E}_{0a}^+) - (\hat{z} \times \mathcal{E}_{0a}^-) \right) = \frac{C}{B} (\hat{z} \times \mathcal{E}_a) . \tag{D.17} \]

Multiplying equation (D.13) by \( \frac{C}{B} \) and subtracting equation (D.17) determines the reflection amplitude as

\[ r = \frac{(\hat{z} \times \mathcal{E}_{0a})}{(\hat{z} \times \mathcal{E}_{0a}^+)} = \frac{\eta_0 B - C}{\eta_0 B + C} . \tag{D.18} \]

**D.4 Derivation of equation (D.23) for complex indices of refraction**

The transmission coefficient for the case of absorption, i.e. complex indices of refraction, can be derived by analyzing the Poynting vectors at boundaries a and b. In
generally, the time averaged value of the Poynting vector is

$$\overline{S} = \frac{c}{8\pi} \text{Real}(EH^*)\hat{k}$$

(D.19)

where $\hat{k}$ is a unit vector in the direction of the net propagation of the fields. At boundary b, the time averaged Poynting vector, is

$$\overline{S}_b = \frac{c}{8\pi} \eta_2 E_2^2 \hat{k} = u_2 \hat{k}$$

(D.20)

where $E_2$ is the total electric field in the substrate and $u_2$ is the energy flux transmitted into region 2 per unit time. Similarly, the Poynting vector at boundary a is

$$\overline{S}_a = \frac{c}{8\pi} \text{Real}(BC^*)E_2^2 \hat{k} = (1 - R)u_0 \hat{k}$$

(D.21)

where $u_0$ is the incident energy flux per unit time in region 0 transmitted through boundary a. Therefore, the transmission coefficient of the thin film is

$$T = \frac{u_2}{u_0} = \frac{\eta_2(1 - R)}{\text{Real}(BC^*)}.$$  

(D.22)

Equation (D.22) can be rewritten using equation (D.18) and $R = r r^\ast$ as

$$T = \frac{\eta_2}{\eta_0} t t^\ast$$

(D.23)

where

$$t = \frac{2\eta_0}{\eta_0 B + C}.$$  

(D.24)
Appendix E

Effect of Sapphire Miscut on Nonlinear Optical Measurements

In section 6.2 we stated that rotational symmetry measurements of GaN in the s-out polarization are not useful as probes of thin film symmetry. Difficulty in extracting GaN symmetry data from this measurement stems from the birefringence of the sapphire substrate. In this appendix we discuss the effect of the miscut sapphire substrate on the nonlinear optical symmetry measurements of GaN.

Sapphire is a negative uniaxial crystal. For samples in which the extraordinary axis is miscut slightly from the normal to the sample, rotation of the sample about its normal causes the precession of the extraordinary axis. This results in transmission of p-polarized light, which depends on the rotation angle of the crystal.

We can model this effect as follows. We define three coordinate systems: the coordinate system of the polarizer, the coordinate system in which the laser beam is incident on the GaN/sapphire sample, and the coordinate system of the sample. These will be denoted by superscripts as p (polarizer), l (lab), and c (crystal), respec-
Figure E.1: Coordinate system of transmission through GaN/Sapphire. \( p \) (l) denotes the polarizer and lab reference frames, respectively. The crystal frame is not shown. 

This section uses the Jones vector and matrix notation, which is described in reference [119].

The field transmitted through the \( p \)-polarizer is

\[
E_p^p = \tilde{\varepsilon} E_{\parallel}^p e^{ikz} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} E_{\parallel}^p e^{ikz} \tag{E.1}
\]

The subscript \( \parallel \) denotes the \( p \)-polarized incident field. We can transform this field into the coordinate system of the angle of incidence of the GaN/sapphire substrate by

\[
E^l = R^p \mathbf{E}^p \tag{E.2}
\]
with

\[
R_{\text{lp}} = \begin{pmatrix}
\cos \theta & 0 & -\sin \theta \\
0 & 1 & 0 \\
\sin \theta & 0 & \cos \theta 
\end{pmatrix}.
\]  \hfill (E.3)

The superscript \( \text{lp} \) represents a transformation to the lab system from the polarizer system.

We non-rigorously treat the effect of the birefringence. Birefringence introduces a phase difference between the components that couple to the ordinary axis and the extraordinary axis. This may be represented by the matrix

\[
\Phi_c = \begin{pmatrix}
e^{ik_o d} & 0 & 0 \\
0 & e^{ik_e d} & 0 \\
0 & 0 & e^{ik_e d}
\end{pmatrix} \hfill (E.4)
\]

where \( k_o \) and \( k_e \) are the ordinary and extraordinary wave vectors, respectively, and \( d \) is an effective thickness of the crystal. This matrix represents the phase shift of the components in the crystal frame of reference. \( \Phi_c \) may be transformed to the lab frame of reference by

\[
\Phi^{\text{li}}_{ij} = R^{\text{lc}}_{i\alpha} R^{\text{lc}}_{j\gamma} \Phi_{\alpha\gamma} \hfill (E.5)
\]

with

\[
R^{\text{lc}} = \begin{pmatrix}
\cos \phi & \sin \phi & 0 \\
-\sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{pmatrix} \begin{pmatrix}
\cos \alpha & 0 & -\sin \alpha \\
0 & 1 & 0 \\
\sin \alpha & 0 & \cos \alpha
\end{pmatrix}.
\]  \hfill (E.6)
As usual, $\phi$ is the angle between the crystal axis and the lab axis and $\alpha$ is the miscut angle of the sample. Thus, the phase shift induced by the birefringence of the film may be accounted for by

$$E_t^i = \Phi E_{||}^i$$  \hspace{1cm} (E.7)

This is the wave that is transmitted through GaN/sapphire and is denoted by the subscript $t$. We can now project this onto the coordinate system of the polarizer by

$$E_t^p = (R_t^{pn})^T E_t^i$$  \hspace{1cm} (E.8)

where $T$ denotes the transpose of the matrix. The field transmitted through the s-polarizer is

$$E_{\perp}^p = P_\perp E_t^p$$  \hspace{1cm} (E.9)

with

$$P_\perp = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \hspace{1cm} (E.10)$$

This field may be expressed in terms of the incident field as

$$E_{\perp}^p = \frac{(e^{i\kappa d} - e^{i\kappa d})}{2} \left( \sin 2\alpha \sin \phi \sin \theta - \cos \theta \sin^2 \alpha \sin 2\phi \right) E_{||}^p \hspace{1cm} (E.11)$$

Because $\alpha$ is a small angle, this expression is dominated by $\sin \phi$, as opposed to the more conventional dependence of $\sin 2\phi$. 

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Let us compare the light transmitted through a birefringent thin film with the s-polarized SHG light from a GaN sample excited by a p-polarized fundamental beam. The nonlinear polarization is

\[ P^{(2)} = \frac{1}{2} \left( 2\chi^{(2)}_{xzz} - \chi^{(2)}_{zzz} - \chi^{(2)}_{zzz} + 2\chi^{(2)}_{zzz} \cos 2\alpha \right) \]

\[ + \chi^{(2)}_{zzz} \cos 2\alpha \sin \alpha \sin \phi \sin^2 \theta E^2(\omega_0) \]

\[ + (2\chi^{(2)}_{xzz} \cos^2 \phi - 2\chi^{(2)}_{zzz} \cos^2 \alpha \cos^2 \phi - \chi^{(2)}_{zzz} \cos^2 \alpha \cos^2 \phi) \]

\[ - \chi^{(2)}_{zzz} \sin^2 \phi \sin \alpha \sin \phi \cos^2 \theta E^2(\omega_0) \]

(E.12)

to lowest order in \( \alpha \).

Equations (E.11) and (E.12) have azimuthal dependences of \( \sin \phi \). For p-polarized excitation, the GaN film generates second-harmonic light in the p-polarized direction and a small fraction of light in the s-polarized direction, which is due to the miscut. The birefringence of the sapphire film rotates \( \sim 0.5\% \) of the p-polarized light into the s-direction. The SHG light that is generated in the p-polarized direction is rotated by the linear optical properties of sapphire and dominates the GaN miscut induced SHG light. Because the azimuthal dependences are similar, the miscut of the GaN film cannot be accurately measured in the p-in/s-out geometry. This argument applies to the s-in/s-out measurements as well. Note that this effect is insignificant for both the p-in/p-out and s-in/p-out measurements.
Appendix F

Code for Fitting Index of Refraction to Transmission Data

The following is a listing of the code used to extract the index of refraction of GaN from the transmission data through GaN/Al₂O₃. This program is a variation of the amoeba.c simplex optimization program found in Numerical Recipes in C [120]. The program performs a least squares fit of the transmission data to the calculated transmission of of light through GaN/Al₂O₃ (see section 4.2.2). I have used a variation of this program for all of the curve fitting and analysis in this thesis. I have found this routine to be very robust and have not had any problems with convergence to local minimum, as opposed to global minimum. I have verified this by changing the starting point of the fit and observing convergence to the same fitting value.

The code is compiled as

\[ g++ \text{ fit\_n.cpp ran0.c nrutil.c -lm -o fit\_n} \]

and the code is executed as

\[ \text{unix\_prompt> fit\_n <transmission data file> <wavelength in microns>} \]
/**************************************************************
  **
  ** fit.a.c : curve fitting program
  **
  ** fit a
  **
  ** by Bill Angerer
  **
  ** version 1.2 10/1/96
  **

  ** Note: This program is modified from the one in S Recipes to
  ** include curve fitting to data. The program minimizes
  ** a least squares fit between the modelling function and
  ** the data. The program passes the data (both in-
  ** dependent and dependent variables) and the number of
  ** data points to the subroutines of the program.
  **
  **
  *****************************************************************/

#include <math.h>
#include <stdio.h>
#include <stdlib.h>
#include <complex.h>
#include <iostream.h>
#include "arutil.h"

define Pi 3.1415926
#define MAX 3000    /* max # of iterations */
#define NP 2        /* number of vertices */
#define NF 1        /* number of parameters to fit */
define FTOL .000001

define GET_SUM '
for (j=1;j<endim;j++) {
  for (sum=0.0;i=1;i<plots;i++) sum+=y[i][j];
  prem[j]=sum;}
define SWAP(a,b) {swap=(a),(a)=(b),(b)=swap;}
typedef double_complex Complex;
void nnebea(double *p, double y[], int ndim, double ste1,
  double (*fun1)(double [], double [], double [], int, double),
  int *afun, double t[], double w[], int num, double lam);

double enetry(double *p, double y[], double psun[], int ndim,
  double (*fun1)(double [], double [], double [], int, double), int thi,
  double fsc, double t1[], double w1[], int num1, double lam1);

double testfunc(double x[], double t2[], double w2[], int num2, double lam2):

main(int argc, char *argv[]) {
  FILE *fp, *gp;
  int i, j, k, xdim;
  double *x1, *y1, *p1;
  double *ind, *dep;
  int count, count_max;
  double data;
  int n;
  long int seed;
  double lambda;
  cout << "Type in seed\n";
  cin >> seed;
  ndim=XP;
  x1=vector(1,XP); /* coordinate of a single vertex */
  /* this is used as a starting point for */
  /* simplex */
  y1=vector(1,XP);
  /* value of the function at the vertex */
  p1=matrix(1,XP,1,XP);
  /* coordinates of each vertex */
  nfunc = 0;

  if (argc<3) {
    cout << "USAGE: a.out <datafile> <wavelength in microns>\n";
    exit(0);
  }
  /************* OPEN THE DATA FILE *************/

if ( fgets(fp, argv[1], "r") == NULL )
{
    printf("unable to open file for reading");
    exit(0);
}

lambda = (double) atof(argv[2]);

/********** GET DATA POINT FROM FILE **********/

count = 0;
while( fscanf(fp, "%lf", &data) != EOF) {
    count++;
}

count_max = count / 2;

ind = dvector(1, count_max);
dep = dvector(1, count_max);

rewind(fp);
for (count=1; count<count_max; count++) {
    fscanf(fp, "%lf", &ind[count], &dep[count]);
}

/********** DRAW SIMPLEX AROUND THE BEST GUESS **********/

xi[1] = 0.0;
++ = 1;
while (xi[1] < 2.2 || xi[1] > 2.7) {
    printf("interaction number %d\n", n);
    xi[1] = 1.25 * rand0(1.0+1.0);
    for (i=1; i<n+1; i++) {
        for (j=1; j<=np; j++) {
            if (i == (j+1)) xi[j] = xi[j] + 0.25xi[i];
            pi[i][j] = xi[i];
        }
        y1[i]=testfunc(xi, ind, dep, count_max, lambda);
    }
    amosah(pi, y1, dim, PMUL, testfunc, &func, ind, dep, count_max, lambda);
    xi(0) = pi[1][1];
    n++;
}


```c
printf("values are \left\{x1, x2\right\};
}

printf("the maximised parameters are\n");
for(j=0;j<NP;j++) printf("%f\n", p[i][j]);
printf("\nmaximised value is \lf: y(\lf));
printf("\nnumber of iterations = \lf: nfunc\n");
free_dmatrix(p,1,1,NP);
free_dmatrix(y,1,1,NP);
free_dmatrix(x,1,1,NP);
free_dmatrix(n,1,count_max);
free_dmatrix(x0p,1,count_max);

fclose(fp);
return 0;
}

void anneal(double **p, double **y, int ndim, double ftol,
double (*funk)(double *, double *, int, double),
int *nfunc, double *x, double *y, int *sum, double *lam)
{
    int i, j, k, l, m, ppts=ndim+1;
    double rtol, sum, swap, yvase, ytrv, *psum;

    psum=director(1,ndim);
    *nfunc=0;
    GET_SUM
    do {
        i=2; 
        yhi=y[i][2] * (inhi<2.1) : (inhi<1.2);
        for (i=ppts;i++)
            if (y[i]>y[i-1]) ihi=i;
        if (y[i]=y[ihi])
            inhi=ihi;
        yhi=ihi;
    } else if (y[i]=y[ihi] && i< ihi) inhi=i;
```
\begin{verbatim}
rtol=2.0*fabs(y1[ih])-y1[llo])/(fabs(y1[ih])+fabs(y1[llo]));
if (rtol<rtol) {
    SWAP(y1,y[llo])
    for(i=1;i<ndim;i++) {
        SWAP(p1[i][j],p[llo][j])
    }
    break;
}
if (*nfunk>=NMAX) {
    printf("NMAX exceeded");
    exit(0);
}
*ytry*=metry(y,pmum,ndim,funk,hi,-1.0, t, w, num, lam);
*nfunk+=2;
    cout << "nguess # " << *nfunk;
if (ytry>y1[llo]) {
    ytry=metry(y,pmum,ndim,funk,hi,2.0, t, w, num, lam);
} else if (ytry>y1[ih]) {
    ysave=y1[llo];
    ytry=metry(y,pmum,ndim,funk,hi,5.0, t, w, num, lam);
    if (ytry>ysave) {
        for(i=1;i<empt;i++) {
            if (i!=1) {
                for (j=1;j<ndim;j++)
                    p[i][j]=pum[i][j]+0.5*(p[i][j]+p[llo][j]);
                y[i]=(*funk)(pmum, t, w, num, lam);
            }
        }
        *nfunk+=ndim;
        GET_SUM;
    } else --(*nfunk);
    while (rtol>rtol);
}
free_vector(pmum, 1, ndim);
}
\end{verbatim}
double testfunc(double x[], double t[], double w[], int num, double lam2)
{
    float lam0; // center wavelength of light
    float ng, na; // indices of refraction
    float ang1, ang2, ang3; // angles in air, GaN, and Sapphire
    Complex E, H; // electric and magnetic fields
    Complex t; // transmission coefficient
    float delt1, delt2; // phase shifts in GaN and sapphire
    float w1, w2, w3; // effective indices of refraction
    int i, j; // loop variables
    float d, l; // GaN and sapphire thicknesses
    float T; // intensity transmission coefficient
    float lam; // wavelength
    float funcvalue; // parameters used in least squares
    // fitting
    float normalize, calc_temp;

    lam0 = lam2;
    d = 1.020;
1 = 2500.0;

ng = x[1]; // fit for GeM index

as = sqrt(1 + 1.023798*lam0+lam0/(lam0+lam0 - 0.0377588)
 + 1.058254*lam0+lam0/(lam0+lam0 - 0.12544)
 + 5.280792*lam0+lam0/(lam0+lam0 - 321.3656));

calc_temp = 0.0;
normalize = 0.0;
funcvalue = 0.0;

angle0 = 0.0;
for (i = 1; i<= num; i++) {  // loop over data points
    angle0 = t2[i]/pi/180.0;
    angle1 = asin(sin(angle0)/ag);
    angle2 = asin(sin(angle0)/ns);
    eta0 = 1.0/cos(angle0);
    etag = ng/cos(angle1);
    etas = ns/cos(angle2);
    for (j = -500; j <= 500; j++) {  // loop over bandwidth of light
        lam = lam0+0.0075*j/250.0;
        deltag = 2*pi-ng/lam+d*cos(angle1);
        deltas = 2*pi-ns/lam+l*cos(angle2);
        // printf("%d\%d\%d\%d\%d\", deltag, deltas);
        E = cos(deltag)*cos(deltas) - etas*sin(deltag)*sin(deltas)/etag +
            eta0*(Complex(0,1)*cos(deltas)*sin(deltag)/etag +
            Complex(0,1)*cos(deltag)*sin(deltas)/etas);
        X = Complex(0,1)*etag*cos(deltas)*sin(deltag) +
            Complex(0,1)*etas*cos(deltag)*sin(deltas) +
            etas0*(cos(deltag)*cos(deltas) -
            etag*sin(deltag)*sin(deltas)/etas);
        t = 2*eta0/(etas0*X + 0);
        T = norm(t);
        calc_temp += T*exp(-j*j/(750.0+250.0));  // weight transmission
    }
}

// by Gaussian frequency

// distribution

normalize = exp(-j*j/(250.0+250.0));
}
calc_temp/=normalize;
funcvalue = (w2[i]-calc_temp)*(w2[i]-calc_temp);
calc_temp = 0.0;
    normalize = 0.0;
}
    return funcvalue;  // minimize this function
}
Bibliography


