STUDIES OF RADIATION DAMAGED GALLIUM ARSENIDE USING COHERENT ACOUSTIC PHONON SPECTROSCOPY

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CHAPTER I

INTRODUCTION

Aims and Motivations

The characterization of materials is one of the basic aims of the materials sciences. With some exceptions, the primary goal of materials characterization is to establish a correlation between microstructure and macroscopic properties. Investigation of microstructure resulting from different processing methods ultimately allows prediction of macroscopic properties (strength, electrical performance, etc.). Traditionally, microstructural characterization has focused on the identification of "macroscopic" defects, e.g. grain boundaries or dislocations (1). As the size scale of devices rapidly approached the nanoscale and samples or devices consisted of a "finite" number of atoms, interest shifted from the investigation of macroscopic defects to single atom defects and their effect on overall material properties (2).

Single atom point defects may in reality refer to different things. Generally, though defects may be perceived in a negative light, many device applications rely on their precise control and function (3, 4). The term may refer to substitutional defects purposefully introduced (known as doping) to modify electronic properties such as the ubiquitous use of doped silicon in diodes and transistors for use in electronics. The development of InGaN-based diode lasers, now found in high information density disc readers such as Blu-Ray players, proceeded from early attempts at growing p-doped GaN. InGaN emitters are also sensitive to the presence of lattice
dislocations, which tends to impart higher current density thresholds (4). Impurities (as opposed to doping to enhance the electronic properties) may be intentionally used to modify the mechanical properties of a material, such as use of ternary compound buffer layers in thin film growth applications that are more conducive to epitaxial growth of a particular film. On the other hand, the term may refer to unwanted defects such as a missing atom (vacancy) or an atom sitting in between lattice points (interstitial). Often, these types of defects are undesirable products of some processing technique or the environment in which the devices must operate. The growth of silicon carbide crystals via physical vapor transport has long been hampered by defect formation (though recent breakthroughs have been made in growing large, defect-free wafers) (5). Radiation damage from operation in nuclear or extra-atmospheric environments can cause electrical breakdown in semiconductors leading to device degradation and failure. Unintentional impurities usually refer to foreign atomic species inside the host lattice, such as hydrogen or carbon incorporation during a growth process. Inside the crystal lattice, impurities can occupy either a lattice site (substitutional) or the space in between lattice sites (interstitial). Additionally, self-substitutional and interstitial defects may exist where an atom moves from a lattice point to a space between lattice points, forming one vacancy and one self-interstitial defect. In compound materials, for example a binary compound with a stoichiometry of $A_nB_m$, an atom of element A may assume a lattice position of element B, giving rise to “antisite” defects. These type of intrinsic point defects can act as impediments to dislocation glide or otherwise modify mechanical properties, while vacancies can act
as charge traps and lead to degradation of electrical performance, among other
effects. Furthermore, different types of defects in close proximity to each other may
interact to form defect complexes, which can play critical roles in material
properties. For instance, strong evidence has been shown for an interaction
between an $\text{As}_{\text{Ga}}$ antisite defect and a self-interstitial (EL2 defect) giving rise to the
semi-insulating properties of GaAs (6).

One critical aspect of the presence of defects in the crystal lattice is strain effects
resulting from lattice relaxation. Depending on the type and symmetry of a defect or
defect complex, the surrounding lattice will relax, shifting the electronic potentials
in the nearby lattice, and hence modifying the electronic structure. This is the point
defect analog to strain-induced band bending at a surface or interface (often
considered two dimensional defects). Depending on the elastic behavior of the host
crystal, a single point defect can potentially modify a large number of neighboring
lattice points. When considered within the context of ever-shrinking electronic
devices, single defects could have a tremendous impact on overall device
performance.

The critical importance of point defects in nanomaterials motivates the need for
accurate measurement of where and in what quantities point defects are located
inside the crystal lattice. Traditionally techniques such as scanning electron (SEM)
or transmission electron (TEM) microscopy (7, 8), Rutherford backscattering
spectroscopy (RBS) or channeling (7, 8), scanning tunneling microscopy (STM) (9-
11), or in some rare cases, positron analysis have been employed (12). However, the
high resolution of the TEM and STM techniques usually restricts studies to single
defects, not aggregate defect concentrations \((11)\). Confocal microscopy is an optical technique with single defect resolution, but does not have the flexibility to measure aggregate concentrations \((13)\). Other optical techniques such as linear absorption or x-ray photoelectron spectroscopy (XPS), or electrical resistivity measurements, may yield quantitative data on the total number of defects present, but are incapable of giving information on the spatial distribution. It should be noted that microscopy techniques typically yield 2D information in the surface plane and have limited depth resolution limited to the near surface region. Measurements of the spatial distribution in the bulk are not possible beyond cross-sectional techniques, which can be arduous and are destructive. Channeling can often give a good estimate of defect distributions, but has low depth limits, medium resolution in terms of defect concentration, requires a beam line and analysis hardware, and damages the crystal lattice. Therefore, there exists a very real need for a convenient, nondestructive method for quantitative measurement of the depth-dependent distribution of point defects. Ideally, such a technique would have high depth limits and be sensitive to low defect concentrations. For ease integration into laboratory or industrial settings such a method should in principle be of table-top design and not require more “exotic” instrumentation such as beam lines or facility-type light sources.

**Overview**

In this thesis, we develop a technique known as *coherent acoustic phonon* (CAP) spectroscopy and show that it meets all of the above requirements in a proof-of-principle demonstration. The CAP technique is an ultrafast time-resolved optical
pump-probe technique that measures transient changes in reflectivity from surface-generated picosecond strain waves monitored as they travel into the sample (Figure 1.1). During propagation, the strain wave causes a small change in the optical properties, most notably the index of refraction. This small change ($\Delta \tilde{N}$) reflects the probe pulse, which is detected as the strain wave travels through the sample. Generally, the complex index of refraction is uniquely determined by a material’s electronic structure, and therefore only a function of the probe photon energy. However, as the strain wave travels through the crystal, the lattice is “squeezed” in a small region. Therefore, $\Delta \tilde{N}$ becomes dependent in a complicated fashion on the elastic properties of the crystal, as well as the photoelastic constant at the specific probe photon energy. A simple but conceptually helpful relationship could be written as

$$\Delta R \propto \Delta \tilde{N} = \tilde{N}_0 + \eta \frac{\partial \tilde{N}(E_{probe})}{\partial \eta}$$

[1.1]

where $\eta$ is the applied strain, $\tilde{N}_0$ the unperturbed index of refraction, and the derivative term represents the change in $\tilde{N}$ as a function of strain, at the applied photon energy. Considering this relationship, one immediately sees that any measurement of $\Delta R$ will contain a wealth of information unique not only to the sample, but to the local region of the sample being probed. For example, near a heterostructure interface strain will distort the band structure, which will modify the derivative term. This effect will then be apparent in the optical measurement. These considerations make CAP an ideal technique to measure defects and defect-
Figure 1.1: Conceptual diagram of the coherent acoustic phonon spectroscopic process. Here, an intense pump pulse causes rapid heating of the near surface region, giving rise to strain wave that travels into the bulk. The strain wave is monitored by a probe pulse as it propagates into the bulk.
induced effects in a crystal lattice. A detailed explanation of the CAP experimental setup, strain pulse generation and detection, and multiple experimental examples are discussed in Chapter 3.

To perform defect measurements, our model system was gallium arsenide with high concentrations of vacancy and self-interstitial defects created through helium ion bombardment. He\(^+\) radiation is representative of the alpha particles present in nuclear reactions or cosmic rays. As the alpha particles traverse the lattice they collide with the lattice, losing energy through inelastic collisions, knocking atoms from their lattice positions, until they come to rest (14). The result is a strongly depth dependent damage profile consisting of point defects, whose concentration and penetration depth is controlled via the total radiation dosage and incoming ion energy (15). The optical CAP response is compared for as-grown samples and samples exposed to varying radiation doses. Comparing the two shows a very distinct modification in the response of the irradiated samples. A methodology is established to correlate the changes in the optical response with an experimentally measured defect profile. Ultimately, we show that the CAP technique has enormous potential to serve as a depth-dependent point defect measurement tool, with high depth limits and nanometer-scale resolution, a wide range of applicability, and high sensitivity to defect concentration.

Secondly, we demonstrate that the CAP technique is sensitive to the type of defect strain-induced electronic structure modifications mentioned above. Moreover, we show that it is precisely this electronic structure change in regions of high defect concentration that are responsible for the differences in optical response. As a
result, we show that CAP operates not only as a defect measurement tool, but also as a sensitive probe to an electronic structure phenomenon known as “band tailing”. It is shown that by repeating the CAP experiments in damaged GaAs over a range of doses, one is able to watch how band-tailing phenomena develop as a function of increasing defect concentration.

Finally, we use the CAP technique to make novel observations on the electronic behavior of irradiated GaAs. We show that band-tailing effects appear at modest concentrations and rapidly grow over a relatively small increase in defect concentration. After a rapid initial rise, the band tailing effects are shown to essentially level off, or saturate, at defect concentrations orders of magnitude below the amorphization threshold. By analyzing this behavior further, we are able to make an estimation of the length of nearest neighbor elastic interactions surrounding a point defect, concluding that a single point defect may alter the electronic structure of neighboring lattice points out to 3-4 nearest neighbors. This range of interaction compares favorably with other experimental and theoretical work.

The organization of this thesis begins with a short review of the technical background necessary to have a comfortable understanding of the CAP process and presented results. This includes a brief review of light-matter interactions in semiconductors, a description of phonon propagation in crystals, an expansion on the discussion of defects and their role in semiconductors, and a detailed explanation of the generalized optical pump-probe technique. In reality, these
fields are quite broad, and attention is focused on specific aspects that help illuminate the results presented in later chapters.

Following this technical review, Chapter 3 is devoted entirely to specific description of the CAP process, how the strain pulse is generated and how various input parameters control the pulse characteristics. A review of past, relevant work is given, highlighting previous studies using CAP as a characterization technique. A mathematical basis for the CAP optical response is derived following procedures set forth in seminal works from Thomsen and Maris (16-18), which highlight the various dependencies of the optical response, and ultimately demonstrates the sensitive dependence on electronic structure.

Chapter 4 begins with a discussion of the ion irradiation process in semiconductors (specifically GaAs), followed by CAP data definitively showing that the technique is able to quantitatively measure depth-dependent defect concentrations. Data showing the influence of varying ion energy and total dosage is shown, as well as data showing the sensitivity of the optical response to the probe photon energy. In addition to clearly demonstrating the profiling capabilities, Chapter 4 lays the groundwork for the analysis presented in Chapter 5, which is an extension of the data in Chapter 4. Chapter 5 begins by clearly defining how intentional versus unintentional doping modifies the semiconducting electronic structure. The main focus, however, centers on the interpretation of CAP profiles as an indicator of regions of the crystal lattice where the electronic structure has been modified (instead of a direct interpretation as defect profiles). This concept is then used to demonstrate the ability of CAP to measure how electronic structure changes under
increasing radiation conditions. These chapters summarize current work regarding defect profiling using coherent acoustic phonon spectroscopy.
CHAPTER II

TECHNICAL BACKGROUND

Introduction
The CAP process involves many complex physical interactions, from the surface generation of the strain pulse to the relationship between the optical signal and the specific material properties. The two most basic processes involved are (a) the interaction of electromagnetic radiation (light) with the semiconductor, and (b) the propagation of the coherent phonon pulse through the lattice. The optical pump pulse is absorbed via charge carrier excitations, and an understanding of the microscopic processes occurring during photoexcitation is necessary to understand how external parameters (pump intensity, photon energy, etc.) modify the strain pulse and observed optical response. On the other hand, a few picoseconds after initial absorption the pulse propagates away from the surface, and the major consideration becomes lattice dynamics. This chapter illuminates the underlying physics of these two processes.

Here, a brief overview of the interaction between light and matter in semiconductors is given, providing a framework for a general explanation of time-resolved pump-probe spectroscopy. Next, the case of general pump-probe spectroscopy is narrowed down to the specific case of coherent acoustic phonon spectroscopy. From this, detailed explanations of the two important processes described above are given, namely (a) how the initial light-matter interactions can
influence the acoustic pulse and (b) how the lattice dynamics evolve as the pulse propagates away from the surface. These details form the physical foundation for the data interpretation and analysis in Chapters 4 and 5 and lend themselves to an intuitive grasp of what occurs on a microscopic level in the CAP process.

**Light-Matter Interactions in Semiconductors**

Generally, the properties that define a metal, insulator, or semiconductor are collectively known as a material’s band structure. Band theory argues that the discrete electronic energy levels of isolated atoms overlap when two atoms are brought into close proximity, providing multiple states for each electron. When an immense number of atoms are brought together in a solid (~$10^{22}$ atoms/cm$^3$) the available states become infinitesimally separated and may be considered as broad energy “bands”. Band “structure” then refers to the description of all allowed energy states for electrons in a given solid. The highest occupied band at finite temperatures is known as the conduction band, while the next lowest band is known as the valence band. The separation between these two bands, known as the band gap ($E_g$), determines whether a material is classified as a metal (no separation), insulator (multiple eV separation), or semiconductor (moderate separation). Though the definition of a semiconductor is somewhat arbitrary, it is usually defined by the ease at which electrons may be excited across the energy gap by some external energy input equal to or greater than $E_g$. Often, as is the case in optical pump-probe experiments on semiconductors, electromagnetic radiation of frequencies $h\nu > E_g$ (where $h$ is Planck’s constant and $\nu$ is the frequency) is used to
excite electrons across the energy gap. Therefore, one might argue that the energies of visible light define the range of band gaps over which a material is considered a semiconductor, and that roughly speaking materials with $E_g < 3.5$ eV fall into this category. The band structure is most often portrayed as in the case of Fig. 2.1(a), representing the band structure of GaAs, where the energy bands are plotted in momentum space. Plotting the bands in such a way provides a convenient method of seeing available transitions and the corresponding energy gaps.

The stimulation of an electron across the energy gap via absorption of a photon is known as photoexcitation. When an electron is excited from state $S_1$ to $S_2$, a “hole” is left behind in $S_1$, which may be thought of as a charge carrier identical to an electron, but with positive charge. Figure 2.1(b) shows a few of the basic processes involved in the photoabsorption and excitation process. Upon absorption of a light beam or pulse, a nonequilibrium distribution of electrons is set up in the conduction band. These “hot” electrons quickly thermalize amongst themselves through electron-electron collisions. Next, the electrons begin to lose energy through electron-lattice interactions and phonon emission, until they reach the bottom of the conduction band. After a given amount of time (typically nanoseconds), the electrons will relax from the conduction band to the valence band via electron-hole recombination. If the material is an ideal direct gap semiconductor (e.g. GaAs) there will be only radiative decay pathways, and the recombination will proceed via spontaneous emission of a photon whose energy is equal to $E_g$. The timescales of these processes are explored in the following section.
Figure 2.1: (a) Band diagram of GaAs from Ref. (19). The direct transition studied here is between $\Gamma_7$ and $\Gamma_6$. (b) A schematic diagram of some possible photoexcitation and relaxation processes.
The study of band theory and structure is an extremely broad field, and the qualitative explanations given here are meant to help illuminate the pump-probe process. Even the intuitive behavior of photoabsorption and relaxation requires time-dependent perturbation theory to provide a full physical description. References (19-22) provide excellent descriptions and derivations of many aspects of band theory and its effect on the macroscopic material properties.

Analogous to the band structure in \( k \)-space, the electronic structure describes the electron densities and crystal potentials in real space. Taken together, the two descriptions determine almost the full spectrum of a crystal's properties—conductivity, optical transparency or reflectivity, elasto-mechanical properties, etc.

In a dielectric crystal the fundamental light-matter interaction is the force of the electric field of the light on the electron densities, which creates a time-dependent charge polarization. The amount of electronic displacement (\( \vec{D} \)) is proportional to the electric field strength (\( \vec{E} \)) through the dielectric constant \( \varepsilon_r \) as:

\[
\vec{D} = \varepsilon_r \vec{E}
\]  \[2.1\]

\( \varepsilon_r \) is a critical parameter in describing how light propagates through a dielectric crystal. By solving Maxwell’s equations the speed of light (\( v \)) inside a dielectric may be written as (ignoring the magnetic permittivity)\(^1\):

\[
v = \frac{1}{\sqrt{\varepsilon_r}} c
\]  \[2.2\]

where \( c \) is the speed of light in a vacuum. The index of refraction (\( n \)) is defined as the ratio of the speed of light in the medium and \( c \), so that:

---

\(^1\) Excellent derivations may be found in appendix A of Ref. (22).
In reality, because the optical frequency ($\omega$) response of a crystal is dependent on its band structure, which may introduces effects such as photoexcitation or plasmonic absorption at different photon energies, $n$ more conveniently represented by a complex number:

$$\tilde{n}(\omega) = n(\omega) + i\kappa(\omega)$$  \hspace{1cm} \text{[2.4]}$$

Here $\kappa$ represents dissipative effects and is related to the absorption coefficient ($\alpha$):

$$\alpha(\omega) = \frac{4\pi\kappa(\omega)}{\lambda}$$  \hspace{1cm} \text{[2.5]}$$

where $\lambda$ is the optical wavelength. $\tilde{n}(\omega)$ completely describes the optical response of a material over the entire spectral range. Fresnel equations determine the reflection and transmission at an interface or optical discontinuity through $\tilde{n}(\omega)$. The reflection coefficient may be written as:

$$R(\omega) = \left| \frac{\tilde{n}(\omega) - 1}{\tilde{n}(\omega) + 1} \right|^2$$  \hspace{1cm} \text{[2.6]}$$

Because of its central role in determining the absorption, reflection, and transmission of light, as well as the photoelastic response, the complex index of refraction is the most important optical property influencing CAP experiments.

**Ultrafast time-resolved pump-probe spectroscopy**

Ultrafast time-resolved pump-probe spectroscopy studies the dynamics of condensed matter systems on timescales far shorter than is possible by traditional electronics. The “time-resolved” part refers to the measurement of transient changes in material properties as a function of time, $t$, distinguishing it from linear
spectroscopic techniques such as linear absorption, Fourier transform spectroscopy, ellipsometry, or photoluminescence. The “ultrafast” aspect refers to the time-resolution, typically on the order of 1-100 fs. Transient effects are induced by an optical “pump” pulse, and measured with a “probe” pulse- hence the term “pump-probe”. The value of the pump-probe technique lies in its ability to measure ultrafast electronic (or optical, magnetic, etc.) behavior at different points in the band structure by varying the photon energy. This technique may be applied using pulsed, coherent radiation sources ranging from x-rays to terahertz in fields such as chemistry, physics, biology, and engineering. There exist many unique experimental combinations depending on the subject of interest. Here focus is kept on measurement of transient changes in reflectivity, using a degenerate (hν_{pump}= hν_{probe}) pulse train originating from a self-modelocking oscillator cavity with a Ti:sapphire gain crystal. The laser pulses exiting the cavity are characterized by a 120 fs pulse width, with photon wavelengths tunable from 700-900 nm (1.77-1.38 eV). For reviews on other various types of pump-probe experiments, and the wide variety of applications, please see References (23, 24).

Figure 2.2(a) shows the setup of a general pump-probe experiment. Noticeable is the versatility in design- small "downstream" adjustments in the sample orientation and measurement device allow easy transition between measurements of reflectivity, transmission, luminescence, etc. This allows whole new dynamical systems to be probed without large experimental overhaul. Examining the setup in
Figure 2.2: (a) Schematic of a typical time-resolved pump-probe setup in multiple geometries (reflection, transmission, etc.). (b) Time-resolved pump-probe response of GaAs at 300K, probed about .03 eV above the direct band gap.
Fig. 2.2(a), the optical beam is split into two paths, one of which is sent through a variable delay line. The delay line is adjusted to change the relative time delay ($\Delta t$) between the two pulses arriving at the sample. For each position of the variable delay stage the probe pulse is measured. Taking multiple steps and compiling each data point yields the time-resolved response of the sample. If one considers that the speed of light $c=3\times10^8$ m/s, a step of one micron in the variable delay stage will change $\Delta t$ by roughly 3.3 fs, allowing extremely high time resolution. Typically the probe pulse is of much smaller intensity and spot size, and the observed signal is technically the *pump-induced* change in reflectivity (or transmission, absorption, etc.), $\Delta R=(R-R_0)/R_0$, where $R_0$ is the non-pump-induced reflectivity. Figure 2.2(b) shows a typical pump-probe transient reflectivity measurement of GaAs. A fast transient spike is observed near $t=0$ (here zero time delay is arbitrarily defined), followed by an exponential relaxation.

To interpret the time-resolved response in Fig. 2.2(b) it is necessary to understand the excitation dynamics in direct gap semiconductors during the first 10 fs to 10 ps, as these are the timescales of the light-matter process described in Section 2.1. Initially, electrons are excited from the valence to conduction band, setting up transient non-equilibrium electron and hole populations. This process happens instantaneously with respect to the timescale of the pulse, and sets up a delta-like distribution of electrons (holes) in the conduction (valence) band. Each step of the excitation-relaxation process causes a redistribution of the occupation of the density of states (DOS), which in turn modifies the absorption coefficient, and therefore the
reflectivity. If one neglects many body effects the change in absorption can be approximated as (25):

\[ \alpha(h\nu) = \left[ 1 - f_e(h\nu) - f_h(h\nu) \right]\alpha_0(h\nu) \]  \hspace{1cm} [2.7]

where \( f_{e,h} \) is the occupation of the DOS of the electrons (or holes) at the photon energy \( h\nu \), and \( \alpha_0 \) is the unperturbed absorption coefficient. An alternate way to consider this is that the absorption coefficient for a two level system is directly proportional to the quantum transition rate defined by:

\[ W_{1\rightarrow2} = \frac{2\pi}{\hbar} |M|^2 g(h\omega) \]  \hspace{1cm} [2.8]

where \( M \) is the quantum mechanical matrix element, and \( g \) is the DOS at a given energy \( h\omega \). The transition probability for the pump pulse can be described by a \( W_1 \), with an initial \( g_1(h\omega) \). After photoexcitation by the pump pulse, the density of states is modified by the redistribution of electrons amongst energy levels, and the time-delayed probe pulse sees a transition rate \( W_2 \) with a DOS of \( g_2 \), and hence a modified absorption coefficient.

After excitation the electrons (holes) initially exist in a coherent state, maintaining the polarization of the incoming light, but dephase on the order of 10 fs after termination of the optical pulse. For laser pulse widths on the order of 120 fs, as in Fig. 2.2(b), this process will appear instantaneously. After dephasing, a “hot” distribution of incoherent electrons exists, which gradually lose energy through electron-electron scattering until a quasi-thermal distribution characterized by an electron temperature \( T_e \) is reached (25, 26). At this point (~100 fs after excitation) the electrons (holes) begin to lose energy to the lattice through phonon emission via
electron-phonon interactions until the electron and lattice temperatures reach equilibrium. This process takes 1-10 ps after excitation and corresponds to the exponential relaxation seen in Fig 2.2(b). Interestingly, because the physical process behind the exponential decay is governed by statistical electron-phonon coupling, it is often possible to correlate the electron-phonon coupling constant with the rate of decay in simple systems (25-27). After relaxation, the long-term response is governed by photorelaxation between charge carriers (electron-hole recombination) and occurs on the timescale of nanoseconds. It is clear that many of the complex interactions that happen on the femtosecond timescale are outside the resolution of a typical 120 fs pulse laser, however, many systems designed specifically for such studies may reach as low as 5 fs and provide insight into such coherent interactions (28). Our main concerns here are identifying the initial excitation, and the subsequent electron-phonon relaxation mechanism that launches the coherent strain pulse. We will see that the acoustic oscillations propagate on the order of tens of picoseconds, allowing separation from the initial photoexcitation dynamics, simplifying the CAP analysis.

**Coherent acoustic phonon spectroscopy**

CAP spectroscopy may be considered as a time-resolved pump-probe technique that focuses on long-term dynamics that proceed from the initial excitation over time delays of about 10–1000 ps. In the CAP experiments the optical pump pulse is absorbed in the near surface region of a sample, either by the sample itself or by a thin absorbing layer grown on the surface. Following the processes described
previously, the absorption corresponds to photoexcitation of charge carriers, which
decay through various processes eventually transferring their excess energy to the
lattice via acoustic phonon emission. This in turn causes rapid heating and thermal
expansion, resulting in a diffusive component of incoherent thermal phonons and a
coherent component of longitudinal acoustic phonons, which quickly travels away
from the incoherently heated region. Ignoring piezoelectric effects (29, 30), there
are generally two independent strain generation mechanisms- electronic strain
through the deformation potential as electrons transiently populate the conduction
band, or thermally during the rapid expansion of the top layer after charge carriers
decay to the band valleys through phonon emission (17, 31, 32). The deformation
potential represents strain resulting from transient redistribution of the charge
carriers (33). As valence band electrons help bind the atoms more so than
conduction electrons, photoexcitation will cause a shift in the atomic lattice
positions, resulting in a transient strain. This effect occurs during the excitation
process, and dominates on timescales similar to the pulse width, roughly 100-200 fs.
After excitation the charge carriers will have excess energy depending on the
difference between photon and band gap energies, \( E' = E_{hv} - E_g \). If \( E' \) is greater than the
energy of a single longitudinal optical (LO) phonon, the carriers will couple
efficiently (26, 34) and decay through LO channels to longitudinal acoustic (LA)
modes in a few picoseconds. If \( E' \) is less than \( E_{LO} \) the carriers will couple
inefficiently to LA modes, and the thermal decay can take longer than 100 ps, an
insufficient timescale to produce coherent strain waves (31).
In CAP experiments, these microscopic considerations can be neglected assuming sufficiently short decay into LA modes. Matusda, et al., gave a detailed quantum mechanical description (31), however a macroscopic thermoelastic model is usually sufficient. From a macroscopic view, rapid thermal expansion launches a picosecond acoustic wave into the bulk. From a microscopic view, the coherent phonons released during electron phonon relaxation comprise the strain wave. In either case, the strain pulse begins propagation into the sample roughly 1-2 ps after initial excitation.

As the strain wave travels through the sample it creates a local change in density of the lattice that can be estimated as (16):

\[ \Delta \rho = \frac{M}{\Delta V} = \frac{\sigma_{\text{pulse}}}{B} = \frac{C\eta_{\text{pulse}}}{B} \]  

[2.9]

Here \( \sigma \) is the pressure of the strain pulse, \( C \) is the elastic constant, and \( \eta \) is the magnitude of the strain. The change in density results in a change in the index of refraction that can be estimated by the Gladstone-Dale law:

\[ \frac{\rho_0}{\rho_i} = \frac{n_0 - 1}{n_i - 1} \]

[2.10]

Here the subscript 1 indicates times when the lattice is under strain. Although the strain profile resembles a bipolar version of the heat deposition profile, for CAP analysis it usually suffices to think of the strain wave as representing a travelling optical discontinuity, ignoring details of the strain profile itself. Under this approximation, the strain wave may be thought of as a travelling “mirror” located at a depth \( z = v_s \Delta t \), where \( v_s \) is the acoustic speed of sound and \( \Delta t \) is the time after the initial excitation.
Figure 2.3(a) shows a schematic of the CAP experimental design used here. At some time delay $\Delta t$ after the pump pulse a probe pulse is brought to the sample. The probe pulse reflects partially off the sample surface, and partially transmits into the bulk. When it encounters the strain wave, it partially reflects off the “mirror”. Both reflected components combine at the photodetector, adding to form the measured time-dependent change in reflectivity $\Delta R(t)$. However, because the strain wave travels at the acoustic speed of sound, a continuously varying phase relationship exists between the two reflected beams, causing periodic interference. In the CAP response, $\Delta R(t)$ is seen to have a long lasting oscillatory tail. Fig. 2.3(b) shows this phenomena for a GaSb(20 nm)/GaAs(100) sample.

Upon comparison with Fig. 2.2(b), we see that the only difference is a thin layer of GaSb grown on top of the GaAs substrate. The band gap of GaSb is much less than that of GaAs ($E_{\text{GaSb}} \sim 0.72$ eV, $E_{\text{GaAs}} \sim 1.43$ eV (35)), which allows the photon energy to be tuned such that $E_{\text{GaSb}} < E_{\text{photon}} < E_{\text{GaAs}}$. Under this condition, the majority of the optical absorption, and therefore thermal expansion, will take place in a relatively narrow region (20 nm). Thus we see that depositing intense heat over a small depth generates a strain pulse coherent enough to observe strong oscillations in $\Delta R(t)$, as opposed to bare GaAs which has penetration depths on the order of microns in the NIR.

The CAP oscillations are strongly dependent on the material properties, and analysis yields a wealth of information regarding the sample. Because the wave travels at the acoustic speed of sound, the time-resolved data is easily correlated with depth if $v_s$ is known.
Figure 2.3: (a) Schematic of the pump-probe setup used in the experiments described here. (b) Time-resolved pump-probe response of GaAs sample capped with 20 nm of GaSb at 300K, probed just beneath the GaAs direct band gap. The persisting oscillatory signal corresponds to the travelling CAP wave.
The period of the oscillations may be written as (16):

\[ T = \frac{\lambda_{probe}}{2nv_x \cos \theta} \]  

[2.11]

Here \( \lambda_{probe} \) is the wavelength of the probe light, \( n \) is the real part of the index of refraction, and \( \theta \) is the angle between the pump and probe beams, usually approximated as \( \theta \approx 0^\circ \). In the absence of phonon scattering, \( \kappa \) may be found by measuring the decay of the oscillation amplitudes (\( \gamma \)):

\[ \frac{\gamma}{2} = \frac{4\pi \kappa}{\lambda_{probe}} \]  

[2.12]

The factor of \( \frac{1}{2} \) comes from the fact that the probe must pass through the sample both before and after reflection off the strain wave, so that amplitudes will decay twice as fast as the absorption coefficient.

These straightforward consideration make CAP a powerful tool for probing thin layered structures of unknown optical properties, as interfaces will manifest as a sharp change in the oscillatory behavior. Alternatively, the elastic constants may be measured if the optical constants are known by measuring \( v_s \). In the case of radiation-damaged GaAs we show in Chapter 4 that while the defect profiles may be extracted from analysis of the oscillatory signal, the relationships are not as simple as Eqns. [2.11-12].

**Factors influencing acoustic pulse characteristics**

Since the propagation of the CAP pulse is separated from the initial excitation dynamics in timescale, it is helpful to think of the CAP technique as two separate,
but combined processes. The first process concerns the absorption of the optical pump pulse in the near surface region of the sample and all the microscopic processes therein. This initial stage determines the spatial and temporal characteristics of the strain wave. The strain wave may be thought of as the conclusion of this first process, which is then used as an “input” into the second process, where the probe pulse monitors the strain wave as it travels through the bulk sample or through a region of interest. Such qualitative thinking is justified in the event that the pulse duration is much less than the acoustic velocity of the strain wave times the depth over which the heat is deposited. In this approximation the optical pulse will completely arrive prior to significant travel by the strain pulse. For experiments in GaAs, the optical pulse is roughly 120 fs, compared to an acoustic speed of 4.73 nm/ps (35), satisfying such conditions. Each process develops independently on a separate timescale— the initial absorption and strain generation occurs a few hundred femtoseconds to one picosecond after the arrival of the optical pump pulse, while the travel and observation of the strain wave happens on the order of tens to hundreds of picoseconds afterwards. Here we discuss aspects of the optical pulse and absorbing properties influencing the spatial-temporal characteristics of the strain wave.

In planning the CAP experiment, consideration must be given to the material response at the specific photon energy, specifically how much light will be absorbed or reflected, and over what depths the absorption occurs. On one hand, this motivates using materials with low penetration depths (high $\alpha$), so the heat is deposited over small region. However, it is also necessary for the probe pulse to
pass through the sample (twice) with enough intensity to register at the photodiode. High absorption, though conducive to generating strong strains, will act to damp out the probe pulse before considerable depths are reached. For example, a penetration depth of 100 nm will limit the depth resolution to about 500 nm. These two competing considerations, high strain versus high depth resolution, limit the amount of light absorbed at the surface and make appropriate materials selection a crucial step. Often it is preferable to use an absorbing layer and vary the photon energy so that the majority of light is absorbed in the top layer, not the sample of interest (consider the heterostucture in Fig. 2.3(b)). Absorbing layer thicknesses may be quite thin, 5-10 nm for metals and 10-50 nm semiconductor layers. If the sample under investigation is sufficiently transparent to the probe light, the strain wave can be observed up to 10 microns or more without significant signal attenuation. Examples of the CAP response in different materials are given Figure 2.4. Fig. 2.4(a) shows the optical response of different Si and SiO$_2$ combinations capped with a few nanometers of gold, with 0, 200, and 300 nm of thermally grown SiO$_2$ on Si, along with the response from fused quartz. The silicon response shows strong attenuation for probe wavelengths of 400 nm, near the Si direct gap. Figure 2.4(b) shows an example of single crystal diamond ($v_s \sim 17.1$ nm/ps) with a 5 nm Au absorbing layer. Diamond is both very conducive to phonon transport as well as transparent to visible wavelengths, and the acoustic pulse is observed almost 10 microns deep into the bulk diamond.
Figure 2.4: (a) The CAP response in Si samples with different combinations of doping and oxide thicknesses, probed near the Si band edge. All samples have been capped with 5 nm Au. (b) The CAP response in single crystal diamond (capped with Au) at 10K. The 600 ps time delay corresponds to 10 microns deep into the bulk.
A particular note about various absorbing layers should be given. As a rough consideration, metallic films may be grown at thicknesses equal to their penetration depths while many common semiconductors have penetration depths on the order of hundreds of nanometers for wavelengths in the visible and near infrared spectral region. Metal films also benefit from ease of growth, with many sputtering techniques available for quick deposition, while many semiconductors require molecular beam epitaxy (MBE) for reliable films. On the other hand, many metals are highly reflective in the near IR, meaning low absorption and low CAP response. Furthermore, an MBE-grown semiconductor has a greater degree of lattice matching, reducing the acoustic impedance at the interface. Materials selection is an important part of any CAP experiment. Here, unless otherwise noted, all GaAs samples have been deposited with a 20 nm MBE-grown GaSb film.

If the absorption takes place at a free surface the relaxation of the heated region will launch a rarefaction wave, resulting in a bipolar strain profile. The spatial extent of the strain wave is often approximated as twice the depth of heat deposition (or twice the absorption layer). Figure 2.5 shows the (a) initial thermal stress in a 50 nm Au layer and (b) the resulting strain profile as it propagates into GaAs. The result is a ~10 ps bipolar strain pulse traveling normal to the surface into the sample. To a first order approximation, this conceptual description is correct and may be applied to either metal or semiconductor layers. Thomsen, et al. (16), provided a straightforward method of determining the strain profile as a function of depth (z) and time (t) that yields a decent approximation at low laser intensities, discussed below. One can see that the majority of the strain exists near the profile
Figure 2.5: (a) The temperature rise and resulting thermally-induced strain in a 50 nm gold film, and (b) the resulting strain profile propagating into bulk GaAs. Note that the initial strain profile has become bipolar.
peak, so that the majority of the strain wave passes in a time much shorter than
the 10 ps it takes for the entire profile to traverse a given point.

One subtle point lost in the macroscopic conceptualization is that for materials with
high electron diffusivity (D_{el}) and/or low g_{el-ph}, the energy deposition profile may be
distributed over a depth much larger than the penetration depth of the light. In this
case the electrons travel a significant distance before relaxation. This effect is
important in metals where the thickness greatly exceeds the penetration depth,
applications requiring ultrafast strain pulses, or highly focused laser spots where
lateral diffusion may play a role (36). Comparison between experiment and models
has shown that initial heat diffusion can have a significant effect on the spatial pulse
profile for certain materials (32). Though an important consideration in
applications where the specific strain profile is critical, the 20nm GaSb layer used
here limits diffusion and constrains the initial heat deposition to the top layer.

Because of the rapid, simultaneous generation, the phonons may be considered to
be “coherent”. Much like an optical pulse, the strain pulse has a distinct center
frequency and bandwidth. The center frequency (v_0) may by considering the spatial
width of the strain pulse. For a 20 nm film, at an acoustic speed of 4.73 nm/ps, v_0 is
approximately 118 GHz. It should be pointed out that it can be tempting to associate
the oscillations in the optical response with phonon frequencies, a common mistake.
Instead, the only method to directly probe the phonon frequencies is a Fourier
transform of the pulse shape, which must be measured either via echoes (37, 38) or
a two-sided setup (39).
For all experiments considered here, the particular spatial-temporal details of the strain wave are unimportant, provided sufficient probe light is reflected. Likewise, the phonon frequencies are not relevant, assuming $v_0$ is low enough in the Brouillon zone so that acoustic speeds may be assumed.

**Important issues concerning pulse propagation**

It is often convenient to employ a macroscopic thermodynamic framework where the strain pulse is modeled as an elastic wave moving through a continuous elastic medium. In this case the time dependent lattice response is depends entirely on macroscopic quantities such as stress, strain, bulk modulus, etc. However, since the pulse is generated by phonon emission during charge carrier relaxation, the discrete phonon-phonon, phonon-lattice, or (in metals) phonon-electron interactions must be kept under consideration. Often a quantum mechanical description can be helpful in exploring the various possible reactions, but unnecessary in describing many observed effects in CAP experiments. The macroscopic description often suffices and is more conducive to modeling, and is used predominately in the following explanations.

The advantage of modeling the crystal as a continuous elastic medium is the intuitive description of stress ($\sigma$) and strain ($\eta$) it provides, which leads to simple derivations of bulk crystal properties such as the elastic stiffness tensor ($C_{mn}$), speed of sound ($v_s$), and elastic energy density ($U_{el}$).

Within the elastic limit, the strain is linearly dependent on the applied stress through the elastic stiffness coefficient C, so that $\eta = C \sigma$ (measured in units of GPa).
or dynes/cm²). A full description of an applied stress on a crystal, however, requires denoting the force vector and the crystal face it acts on. For example, a force acting in the \( \hat{x} \) direction on the \( y-z \) face will produce a longitudinal stress, while a similar force acting on the \( x-y \) face will produce a sheer stress. To fully describe all possible combinations, the stress and strain are written as second-rank tensors related through the fourth-rank elastic stiffness tensor (40):

\[
\sigma_{mn} = C_{mnpq} \eta_{pq}
\]  

[2.13]

Here the indices are the three orthogonal axes. As a high rank tensor, \( C_{mnpq} \) has 81 coefficients, however, this total is reduced by symmetry considerations to 32 for the general crystal. GaAs has isotropic cubic symmetry, further reducing the number of independent constants to three (35). For such cases \( C_{mn} \) may be written as (41):

\[
\begin{align*}
\text{[2.14]} \\
\text{These three elastic constants are of great importance because of their role in determining the speed of sound, the extent of nearest neighbor interactions, and phonon frequencies along high symmetry crystal directions. The wave equation in an elastic medium may be solved to determine acoustic velocities, e.g. along the [100] direction the speed of sound may be written as:}
\end{align*}
\]

\[
v_s = \sqrt{C_{11}/\rho}
\]  

[2.15]

where \( \rho \) is the density of the material. On the other hand, each phonon has an energy and momentum of:

\[
E = nh\nu
\]  

[2.16a]
where \( n \) is an integer, \( h \) is Planck’s constant, and \( \nu \) is the phonon frequency, and \( k \) is the phonon wave vector. Taking into account interactions between multiple neighboring atoms, a dispersion relationship may be written as:

\[
\omega^2 = \frac{2}{m} \sum_{p>0} C_p (1 - \cos(pk))
\]  

[2.17]

where \( \omega \) is the angular frequency \((\omega = 2\pi\nu)\) the index \( p \) represents the \( p \)-th plane away from the plane of motion, and \( a \) is the atomic planar spacing. From this the wave speed may be alternatively derived as

\[
v_s = \frac{\partial \omega}{\partial k}
\]

[2.18]

Considering the form of [2.17], at low frequencies the propagation speed will be constant, while high frequency components will travel slower than low frequency components. The roughly 100 GHz phonons in the CAP experiments fall far down the Brouillon zone, with wavelengths orders of magnitude larger than the atom unit cell. Thus the phonon will experience little dispersion, especially for propagation distances on the order of microns. Studies have demonstrated that typical CAP pulses must travel on the order of hundreds of microns to experience significant pulse broadening from dispersion \((39, 42, 43)\).

There are many aspects of lattice dynamics that cannot be accounted for within the harmonic elastic potential approximation, most notably in the case of the CAP experiments is phonon-phonon scattering which may tend to attenuate the acoustic pulse during propagation. For many applications the depth limits of the acoustic wave are critical and estimates of how far the wave will travel without attenuation
from phonon scattering is important. Picosecond ultrasonics has in fact been used as a tool to study phonon-phonon interactions and phonon lifetimes in the frequency range of 1-500 GHz (37, 38). If significant attenuation of the CAP pulse is occurring via phonon scattering processes the decay of the CAP oscillations may not be attributed solely to optical effects.

Attenuation through anharmonic phonon-phonon scattering is typically described using the phonon mean free path ($l_{ph}$) or lifetime ($\tau_{ph}$). For thermal phonons such a model suffices, however, it is not always clear how to give a complete description of an attenuation coefficient ($\alpha_{ph}$) due to the complicate dependence on frequency, temperature, phonon polarization, and crystalline disorder (44). The Landau-Rumer mechanism suggests a three-phonon decay process is expected to dominate at high $\omega$ and low $T$, while Akhieser mechanisms become important at low $\omega$ and low $T$ (38). Herring showed that Landau-Rumer theory could hold for certain crystals at lower frequencies due to collisions allowed by crystalline anisotropy (45, 46). Daly, et al., pointed out that for CAP experiments at room temperature, the 100 GHz phonons fell in between the two models, probably being described either by both, or more, processes (38). Experimentally, it was observed that room temperature CAP pulses were detectable even after 200 microns of travel.

Relevant information can be taken from studies on amorphous materials (37, 47-50), or on single crystals out but in somewhat different ranges of $T$ and $\omega$ (51-54). Generally, at higher temperatures a steep drop off in propagation distance via anharmonic interactions at high frequencies is observed, for example the attenuation of 440 GHz CAP phonons was shown to have two orders higher
magnitude than 75 GHz frequencies. As the temperature increases, the phonon DOS changes considerably, adding strong temperature dependence to the attenuation, which changes behavior at low and high temperatures. However it was shown that temperature effects remain relatively constant over the 100-300 K range (39) in CAP experiments. Experimental attenuation of 100 GHz phonons in SiO$_2$ was observed to be on the order of $10^4$ cm$^{-1}$ (37), and the mean free path in quartz was estimated to be about 10 microns at 100 GHz (43, 55, 56). Comparing phonon interactions between ideal crystals and disordered systems may be flawed due to extra possible processes in glasses, and there is ambiguity how disordered a quartz sample may be. It should be pointed out however that 100 GHz was deemed a “critical point” in quartz, beyond which attenuation increased almost five orders of magnitude between 100-1000 GHz.

In our studies, the atomic displacement from ion collisions during irradiation create strongly depth dependent defect profiles within the first 2-3 microns of the surface. Any effect of phonon attenuation on the observed optical signal can be assumed negligible based on the orders of magnitude higher attenuation length of low energy phonons in both ordered and disordered systems. Furthermore, experimental results suggest that the attenuation of the CAP oscillation may be fit to optical attenuation within experimental error (for instance, the silicon response of Fig. 2.4(a) matches well with reported optical penetration depths). Additionally, many other simplifications may be made in our experiments. For instance, the frequency distribution is irrelevant as long as sufficient strain exists to yield reasonable signal to noise ratio in the detected response. Dispersion and pulse broadening may be
ignored for due to the relatively short propagation distances. The primary effects of the presence of defects mainly manifest as electronic structure distortion, as discussed in Section 3.4.
CHAPTER III

COHERENT ACOUSTIC PHONON SPECTROSCOPY

Introduction

Since the discovery of residual acoustic signatures in pump-probe experiments (16-18, 57), CAP spectroscopy has been used in a wide number of different material systems, to measure many different material properties. The technique has been applied not only as a tool for probing subsurface structural characteristics, but also to investigate the behavior of hypersonic acoustic pulse propagation (as mentioned in the previous chapter) in different material class (i.e. amorphous, single crystal, liquid, etc.). In this Chapter, especially relevant work is highlighted. One of the most important results is the derivation of a mathematical description of the observed $\Delta R(t)$ oscillatory response, allowing phenomenological observations to be tied to specific physical effects. The original derivation in Reference (16) based on thermodynamic considerations still suffices to explain observed data almost twenty years later. In the specific case of irradiated semiconductors, such a model ultimately gives insight into the interplay between lattice defects and electronic structure. Here we follow the previous derivation, with emphasis on particular mathematical terms that may be influenced by the presence of crystalline point defects. This is followed by brief comments on the advantages of CAP spectroscopy over traditional characterization techniques.
The study of irradiation-induced point defects, and their effect on GaAs properties, represents a unique application of CAP spectroscopy. For defect concentrations on the order of $10^{21}$ cm$^{-3}$ the line between ordered and disordered systems becomes blurred. Therefore, it is important to understand what types of point defects dominate the irradiation process, and how these defects modify acoustic propagation. Furthermore, it is important to identify the effects such point defects have on the lattice and electronic structure of a crystal, and correlate them with specific mathematical terms in the description of $\Delta R(t)$. Section 3.4 lays out many of these concerns and discusses their impact within the situation of low energy irradiation, as is the case here.

**Previous work**

Observations by Thomsen and Maris in the mid-eighties on transient echoes in the pump-probe reflectivity response of $\text{As}_2\text{Te}_3$ gave birth to the field of picosecond ultrasonics (18). Their initial work was followed by a more detailed paper highlighting strain pulse generation and detection, where a depth- and time-dependent expression for the strain was reached (16). The derived expression based on the equations of elasticity included both diffusive and coherently propagating components. At the time, in addition to the non-invasive depth profiling capability, the ability to generate coherent strain pulses on the order of 100 GHz was viewed as a major advance in the field of acoustics. The discovery led to wide application in a diverse set of materials. The oscillatory response has been observed in semiconductors (29, 31, 32, 39, 42, 43, 58-65), metals (66-68) and
dielectric crystals (69, 70). It has been used to study unconventional or non-solid materials such as ice (71), glycerol (72), and water (73). It has proved a convenient tool in the study of elastic mechanics of thin films (29, 74). The effective elastic and optical properties of superlattices has been studied (58, 60, 62). The technique has been used to investigate microstructures (75, 76) and nanostructures (67, 77, 78). “Nanoacoustic” waves with nanometer lateral dimensions have been generated (79). Daly, et al., demonstrated submicron imaging with acoustic pulses (80), and a conceptually identical technique has used to image cancerous tissue in vivo in mice (81).

As material growth methods gain more control over the stoichiometric ratios in doping or compound growth, CAP provided a convenient way of measuring the composition-dependent properties. Hudert, et al., studied changes in the elasto-mechanical properties of piezoelectric In$_x$Ga$_{1-x}$As were studied as a function of concentration by (59). Changes in the elastic tensor of chemical vapor deposition grown diamond samples were investigated for varying levels of N$_2$ gas used during the growth process (74).

As mentioned, CAP has played a large role in the study of phonon-phonon interactions for GHz-THz phonons by measuring the decrease in wave intensity after significant propagation. In another paper, Daly, et al., showed that the acoustic pulse in silicon has strong temperature and $\omega$ dependencies that can only be explained by a combination of current phonon scattering models (38). Daly also investigated acoustic dispersion in Si wafers, showing effects become noticeable
only after propagation distances on the order of hundreds of microns (39). Acoustic attenuation was also explored across various T and ω ranges in SiO₂ (37, 50, 82).

It has been shown that CAP is able to both make measurements on hot electron diffusion, as well as be modified by diffusive effects (36, 83, 84). For metallic absorbing layers much thicker than the optical penetration depth, the spatial form of η(z,t) may be significantly altered by ballistic electron transport prior to electron-phonon coupling. Wu, et al., developed a model consistent with experiments to predicting spatial broadening of the strain wave from such effects (32).

Interest has also grown in the generation and detection of shear acoustic waves. A model for detection of shear and longitudinal acoustic waves taking into account obliquely scattered light with arbitrary polarization was given by Matsuda, et al. (85). Pezeril, et al., detected shear waves in liquid samples under a metal-coated lens (72). Generation and detection using canted gold films was theorized (86) and later demonstrated (87), and shear waves were reportedly observed through acoustic diffraction effects (88).

Quite recently, interest has grown in using the strain waves as a method of transient altering material properties in a nondestructive, nonthermal way. In our experiments, the strain wave is monitored in a “passive” manner, as it passes through a region of interest. The response provides depth-dependent information for material analysis. However, it is true that in the local region under strain the electronic potentials have shifted in a transient manner. Although this phenomenon is ignored when analyzing the optical response, it is this discontinuity that reflects a portion of the probe pulse, allowing the CAP wave to act as a “mirror”. Recent
studies have been performed investigating the use of this transient perturbation for ultrafast materials control. Examples include picosecond shifts in the band gap of CdSe (89) on the order of a few meV, and ultrafast control of photoemission from quantum dot structures (90, 91). These techniques are extremely attractive due to the non-thermal nature of the strain wave, allowing control over lattice effects without the diffusive nature of heating. Indeed, it appears that a new branch of picosecond ultrasonics, that of nonthermal ultrafast transient control of material properties is developing as a future area of much potential.

A few of the above studies have specific relevance to the work here and are heavily cited throughout this thesis. Thomsen and Maris (16-18) described the optical response based on an analytical solution of the equations of elasticity and the wave equation (see the following section for a discussion on the results). Their result remains the seminal work in the field, and gives good agreement with experiment based on the complex index of refraction $N$, acoustic speed of sound $v_s$, and the photoelastic constants. Miller, et al., demonstrated the strongly increased sensitivity of the optical response when the probe photon energy is tuned near the band gap energy in GaAs (61). This in turn accounts for the extreme sensitivity to the presence of defects in the GaAs lattice discussed in Chapters 4 and 5. Likewise, Devos, et al., demonstrated similar effects near the direct band transition in silicon, motivating the possibility of similar experiments (92). Hudert, et al., investigated the CAP response in Si:GaAs samples, observing distinct amplitude modulations, similar to the type discussed in Chapter 5 (59). However a direct link to profiling the Si concentration was not demonstrated. All papers mentioned in this section
help illuminate the processes that occur in the CAP generation, propagation, detection, and applications, however, the reader may find the five studies just mentioned the most helpful in providing perspective on the experiments presented here.

Mathematical description of the CAP response

This section provides the mathematical groundwork for the analysis presented in Chapters 4 and 5. The analysis may be broken down into three parts; mathematical derivation and description of the acoustic wave; description of the oscillatory optical response; and extraction of material properties from the observed signal. The derivation of the spatial-temporal strain profile is largely based on References (16-18) with more detailed additions from later studies. Special attention is paid to aspects of the analysis important to the data presented in this thesis.

Thomsen, et al., invoked a thermo-mechanical argument to calculate initial stress profiles. One may calculate the temperature rise from a single pulse, considered to be instantaneous, by:

$$\Delta T = \frac{W(z)}{C_v}$$  \[3.1\]

Here \(W(z)\) is the energy deposition profile per pulse and \(C_v\) is the volume specific heat. \(W(z)\) may be written as:

$$W(z) = (1 - r)\frac{Q}{A\delta_{op}} (-z/\delta_{op})$$  \[3.2\]
Here \( r \) is the reflection coefficient at the pump wavelength, \( Q \) is the pulse energy, \( A \) is the spot size, and \( \delta_{op} \) is the optical penetration depth. From the temperature rise, an initial thermal stress profile may be calculated as:

\[
\sigma(z,t=0) = -3B\beta\Delta T(z) \tag{3.3}
\]

\( B \) is the bulk modulus and \( \beta \) is the coefficient of linear thermal expansion. The negative sign corresponds to the thermal expansion which yields a tensile stress at \( t=0 \). Three general relationships governing elasticity then apply: (1) \( F=ma \), (2) \( \sigma_{mn}=C_{mnpq}\eta_{pq} \), where \( C \) is Young’s modulus (or the elastic tensor), and \( \eta \) is strain, and (3) differential lattice strain is equal to a differential atomic displacement, which is a restatement that for a length \( l \), \( \eta=\Delta l/l \). These considerations lead to the set of differential equations governing the travel of the strain:

\[
\sigma_{zz}(z,t) = \rho v_s^2\eta(z,t) - 3B\beta\Delta T(z) \tag{3.4a}
\]

\[
\rho \frac{\partial^2 u(z,t)}{\partial t^2} = \frac{\partial \sigma_{zz}(z,t)}{\partial z} \tag{3.4b}
\]

\[
\eta_{zz} = \frac{\partial u(z,t)}{\partial z} \tag{3.4c}
\]

Here \( v_s \) is the longitudinal speed of sound, \( \rho \) the density, \( u \) the atomic displacement, and the subscript \( z \) refers to the direction normal to the sample surface. These equations yield an analytic solution for the strain \( \eta_{zz} \) as a function of \((z,t)\), with the boundary condition that \( \eta_{zz}=0 \) for \( t=0 \):

\[
\eta(z,t) = (1-r) \frac{Q\beta}{A\delta_{op} C_v} \left[ \frac{1 + v_p}{1 - v_p} \right] \exp \left( -\frac{z}{\delta_{op}} \right) \left[ 1 - \exp \left( -\frac{v_s t}{\delta_{op}} \right) \right] \left[ -\frac{1}{2} \exp \left( -\frac{z - v_s t}{\delta_{op}} \right) \operatorname{sgn}(z - v_s t) \right] \tag{3.5}
\]
Where \( \nu_p \) is Poisson’s ratio. This rather lengthy expression describes a bi-polar strain wave with two components. The first exponential term represents incoherent thermal strain which disappears at long times, while the second term represents a coherent traveling wave.

Turning attention to the actual detection of the strain wave, we consider that the reflection of the probe light from the traveling wave is due to the change in density, and hence complex index of refraction, in the locally strained region. The strength of the signal will then be proportional to:

\[
\Delta n(z,t) = \frac{\partial n(z,t)}{\partial \eta} \eta(z,t) \quad [3.6a]
\]

\[
\Delta k(z,t) = \frac{\partial k(z,t)}{\partial \eta} \eta(z,t) \quad [3.6b]
\]

Here \( n \) and \( k \) are the real and imaginary parts of the complex index of refraction and the subscript \( zz \) has been dropped for convenience. The coefficient of reflection \( R \) at the strain discontinuity may be written as

\[
R = f \int f(z) \eta(z,t) dz \quad [3.7]
\]

Thomsen, et al., used the above considerations to derive a change in reflectivity as:

\[
\Delta R(t) = \int f(z) \eta(z,t) dz \quad [3.8]
\]

Where \( f \) is known as the sensitivity function:

\[
f(z) = f_0 \left( \frac{\partial n}{\partial \eta} \sin \left( \frac{4 \pi n z}{\lambda} - \phi \right) + \frac{\partial k}{\partial \eta} \cos \left( \frac{4 \pi n z}{\lambda} - \phi \right) \right) \exp \left( \frac{-z}{\delta_{op}} \right) \quad [3.9]
\]

and
\[ f_0 = \frac{8 \omega (n^2 (n^2 + k^2 - 1)^2 + k^2 (n^2 + k^2 + 1)^2)^{1/2}}{c ((n + 1)^2 + k^2)^2} \]  

[3.10]

Here \( \lambda \) is the probe wavelength and \( \phi \) is an arbitrary phase factor. In these equations, \( n \) and \( k \) are the real and complex indices of refraction for the unstrained material at the probe wavelength. The derivative terms, \( \partial(n,k)/\partial \eta \), are known as the photoelastic constants, whose values may found in the CRC materials handbook. While a detailed description of the strain profile is not necessary for spectroscopic analysis in general, this result allows insight into how different physical factors influence the optical response. For instance we see from the strain term in the integrand of Eqns. [3.5-8], the strength of \( \Delta R \) is directly proportional to the energy absorbed per pulse and inversely proportional to the specific heat. The spatial extent of the wave will be, neglecting diffusion effects, roughly twice the absorption depth. These considerations based on material properties are straightforward from examination of the above equations, however, a more subtle aspect lies in the derivative (photoelastic) terms. Regardless of the optical absorption or magnitude of \( \eta \) itself, the oscillatory response will be observable only if the photoelastic constants are of sufficient magnitude. Photoelastic constants (\( P_{mn} = \partial(n,k)/\partial E \)) are often given at certain wavelengths away from optical resonances where changes in optical constants as a function of photon energy is nearly zero. On the other hand, many CAP experiments are done with probe wavelengths near electronic features such as the optical band gap, so that certain care must be taken when comparing tabulated values of \( P_{mn} \) to experimental results. Therefore, the contribution of the \( P_{mn} \) to the optical response is unique to each material, but also strongly dependent
on probe wavelength. Figures 3.1(a-d) is taken from Reference (61) and shows how the CAP parameters vary when the wavelength is tuned near an optical resonance (here the GaAs direct band gap). Figures 3.1 (e-f) show the optical response of undoped silicon is shown at probe wavelengths of 400 nm and 800 nm, respectively. Clearly, when the photon energy is tuned near the 3.1 eV direct band gap, the CAP signal becomes observable as the photoelastic response increases. When probed at 800 nm, the photoelastic constant is too small far from any optical resonance, and no CAP response is seen.

It should be kept in mind that in some cases, e.g. transparent materials such as SiO$_2$ or Al$_2$O$_3$ probed at wavelengths in the near IR, although the CAP response may not be observable the strain wave is still generated and propagates throughout the material. In these cases $P_{mn}$ is not of sufficient magnitude to yield a response in $\Delta R(t)$. This sensitivity to probe wavelength is taken advantage of in Chapter 4 and 5 to study variations in the near band gap electronic structure.

**Advantages of the CAP technique**

After considering the technical aspects of CAP, it becomes clear that the technique offers unique flexibility as a materials characterization tool, with depth profiling abilities unlike other current techniques. It has been demonstrated that the picosecond strain waves do not suffer significant attenuation or wave dispersion over length scales up to tens or hundreds of microns. This upper depth limit surpasses most techniques by orders of magnitude (channeling, positron analysis). On the other hand, when used for materials analysis, the lowest “feature size” which
Figure 3.1: The (a) period, (b) amplitude attenuation, (c) amplitude strength, and (d) phase of the CAP response in GaAs as a function of wavelength near the band gap. The CAP response probed at energies of (e) low and (f) high photoelastic responses for silicon.
may be resolved could be argued to be on the scale of one-half wavelength of the optical oscillatory response, roughly 10 nm. This gives CAP a wide range of applicability from small-scale features, to features that may vary over a long distance scale, to features lying very deep (tens of microns) into the sample.

The main consideration in applying the CAP technique to measure subsurface features or depth-dependent material properties is the transparency of the material to the probe light. The material need not be completely transparent, but rather it is sufficient to have an optical penetration depth on the order of the depth at which features are being probed. As this is the only limiting factor in this technique, it implies that it may be applied in a wide variety of different materials. In the case of defect profiling as presented in Chapter 4, defects may be profiled in a variety of different systems, depending on the optical response. The development of tunable optical parametric amplifying systems has opened the possibility of tuning directly to defect absorption lines, an idea developed in Chapter 6 as an extension of the defect profiling experiments.

From a sample damage standpoint, while TEM/STM techniques offer stunning resolution, cross-sectioning samples necessarily destroys them. Here, the low intensity of the strain wave allows it to travel through features or structures without causing noticeable lattice damage. Semiconductors typically have bulk moduli on the order of 10 GPa (33). However, with reference to Fig. 2.5(a), the complete absorption of a 50 µm², 10 nJ pulse (typical of a Ti:sapphire oscillator) will generate a few hundred MPa of tensile thermal stress. This indicates as long as one stays in the low pulse energy/strain intensity regime, no plastic damage will occur to the
crystal lattice as the strain wave passes. This basic mechanical argument demonstrates the non-destructive and non-invasive nature of the technique, which should be contrasted to the destructive nature of cross-sectional microscopy or ion beam analysis, which creates defects through lattice ion collisions. In fact, the damaging nature of ion beam analysis is utilized to create the point defect distributions studied in Chapters 4 and 5.

Finally, from a practical standpoint, pulsed laser systems tend to be much more common than other machines capable of depth-dependent characterization, in the sense that the CAP technique can be easily integrated into existing optical setups. This is opposed to ion beam lines, positron sources, or expensive microscopy equipment and expertise. Ti:sapphire oscillating systems provide femtosecond laser pulses at wavelengths that are adequately transparent in many materials, as well as the limited range of the doubled frequency (roughly 350-450 nm). This makes the CAP technique a more accessible tabletop method of materials characterization.

**Ion irradiation and point defects**

“Damage”, in the context of ion irradiation or implantation, refers to the displacement of atoms that occurs when an energetic ion transfers sufficient energy to a lattice atom during a collision process. The ability of sources to provide highly energetic (~ 10 MeV) ions makes ion radiation an ideal method to reproduce conditions not easily accessible to experiments, such as space or nuclear environments. Ion implantation is also used as a means to produce thin layers of
material with different electrical properties than the bulk, either through doping or creation of charge-trapping defects. Each displacement during the radiation process represents the creation of a point defect. The term “point defect” refers to single atom defects, either atomic vacancies at lattice points, or single atoms being moved from their original lattice position to elsewhere within the crystal. Such defects can alter the electronic properties of the crystal (93, 94), and at sufficient concentrations shift band gaps, and induce disorder effects (93, 95). One of the most important aspects of the study of radiation damage focuses on interactions between point defects and the crystal lattice and the different factors influencing the final damage profile. Implantation species, total dosage, dose rate, ion energy, implantation temperature, and the implanted material all play significant roles in determining the damage profile (8, 94-96). Therefore, a strong motivation exists to develop a technique to accurately identify type and quantity of point defects in samples.

When an ion enters a crystal lattice it interacts either elastically with an atomic nucleus, or inelastically with the electron clouds surrounding each lattice point. In the elastic collisions, part of the ion energy is transferred to the displacement of the atomic nuclei. In semiconductors, an ion will first lose energy through electronic interactions, followed by energy loss through lattice displacement as the ion slows. Each ion induces multiple displacements before finally coming to rest (14, 15). The probability rate of the incoming ion to interact either with the electronic clouds surrounding each lattice point or the atomic nuclei is proportional to the relative scattering cross-sections of each. Collision cascades are statistically straightforward and may be simulated implementing a Monte Carlo approach. Unfortunately, the
accumulation of damage and the final damage profile is not so straightforward due to kinetics of defects during and post-irradiation. Self-healing and defect or ion migration during the irradiation process (95, 97) may occur depending on external conditions, leading to formation of defect complexes which can modify the structural and electronic properties in different ways. The temperature during irradiation is a significant factor as it encourages recombination of vacancy and interstitial defects, reducing the final damage concentration. Recombination effects can selectively retain certain defects based on the diffusion or “hopping” energy for a particular defect type, and many defect types in various materials anneal out over a range of temperatures from 100-1000 K (96, 98). Further complicating matters is the fact that many temperature or rate dependent effects are not gradual, but occur at critical points. For example, medium energy Si irradiation of GaAs induces a sharp transition from relatively low damage to crystal amorphization over a four-degree temperature range (99). Even worse, relative concentrations of defects may act to prevent another defect species from diffusing, increasing the final defect concentration. Predicting the total damage profile attributed to each individual defect type is a complex problem. Typically simulations cannot account for such effects, making quantitative estimations difficult. Still, some rules of thumb apply in general cases. Increasing the ion energy will lead to more damage and push the damage profile deeper into the crystal. Higher ion masses will cause greater number of point defects, but reducing the total dosage can counteract this effect. However even the general rules may not translate between even closely related systems material systems. Diffusion effects and amorphization thresholds for the
III-V arsenides tend to be much higher than in the phosphides (96, 98). In our studies irradiation experiments here were carried out in GaAs wafers, an extremely well studied material. Here, low energy (few hundred keV) helium ions were carried out at low dose rates (less than 1 µA). The total dosages were held between $10^{11}$ and $10^{14}$ cm$^{-2}$. How these values compare with literature is discussed in section 4.4.

Considering the influence of point defects on the lattice properties, there are two major issues relevant to the CAP experiments. The first is the modification of the electronic structure through addition of defect states. Whereas intentional doping produces defect (dopant) states within a few $kT$ of the bottom (top) of the conduction (valence) band edge, vacancy and interstitial defects open states near the middle of the band gap. Most often, these defect states act as charge traps, reducing electrical device performance (100, 101).

In compounds such as GaAs the variety of defects (i.e., their location within the lattice), defect complexes, and defect charge states makes accurate identification of energy levels quite difficult. Often the approach is either through $ab$ initio calculations or linear spectroscopy measurements. Early work demonstrated such high sensitivity to the exact electronic potential at the defect site that many studies yielded contradictory results. Puska (102) calculated the ionization levels of the gallium vacancy ($V_{\text{Ga}}$) were calculated to be on the order of hundreds of meV above the valence band depending on the charge state (similar studies placed the levels nearby, but deeper by a factor of two (103)) while arsenic vacancy ($V_{\text{As}}$) defects were calculated at similar positions below the conduction band (other studies
likewise reported slightly higher energy states (104, 105). Calculations for antisite defects yielded wide ranging in the placement around the Fermi level (almost +/- .5 eV), however, calculations and experiment (106) were in agreement in the separation between ionization levels. More recently, direct scanning tunneling microscopy (STM) measurements have placed As$_{Ga}$ related defects at $E_v+.5$ eV (9, 107). Isolated interstitial defects do not participate in bonding, and therefore do not have ionization energies of the same magnitude as vacancy or antistite defects. Although there is still disagreement about the exact placement of deep defect energy levels inside the band gap, the class of defects considered here certainly lie far enough away from the conduction (valence) band that no significant contribution to the carrier density is seen at room temperature. However, in the context of a pump-probe experiment extraneous absorption by defect ionization is still a significant concern.

The second major modification to the ideal crystal structure is the presence of strain in areas surrounding point defects. The crystal lattice will relax to compensate for the absence or addition of an atom in the crystal, creating a local strain field. In addition to skewing the structural characteristics of the crystal, such strain adds a perturbation to the electronic potentials at lattice points near the defect. Therefore, in these local regions the electronic structure will also be “skewed”, the degree of which depends on the crystal elastic properties, proximity to the defect, etc. This can be detrimental or act to obscure the results of the CAP process, as (a) the propagation of the wave is dependent on local elastic properties, (b) geometrical scattering may occur from anharmonic interactions between aperiodic lattice
points, and (c) the magnitude of the optical response is proportional to certain electronic structure features at specific photon energies. It is therefore important to make some estimate of the "reach" of a single defect via elastic interactions with its neighbor. The most useful direct probe with atomic resolution is STM, which simultaneously measure defect energy levels and distortions in the surrounding lattice. Furthermore, as a microscopy technique STM may be used to reveal the symmetry of certain defects, making identification of defect type more feasible. Hida, *et al.*, employed modulated STM experimental scheme to detect strain fields in LT-GaAs with high (~$10^{20}$ cm$^{-3}$) $A_s$Ga concentrations (108). Direct imaging of the antisite revealed an associated strain field that extended roughly 3 nm (6 nearest neighbors) and had T$_d$ symmetry. Unfortunately such direct measurements of point defects commonly created during ion irradiation are more difficult to come by, though certain aspects may be inferred by studies of similar systems. Feenstra, *et al.*, demonstrated that the effects of an $A_s$Ga defect could be seen via STM out to the 15$^{th}$ nearest neighbor (9, 107), and Capaz, *et al.*, provided calculations supporting this observation (10). However it may be difficult to extrapolate lattice relaxation from observations of the spatial shift in electronic potentials. Much interest has also surrounded characterizing the electronic structure at interfaces. Such studies (9, 109) have shown that structural relaxation occurs over two to three unit cells, although simultaneous STM measurements show electronic structure distortion between six and nine unit cells. This implies that structural relaxation may happen on a shorter spatial scale than electronic relaxation, providing some reconciliation between the STM studies and the strain-specific modulated STM study.
The anisotropic nature of the defect-induced strain makes comparison to previous results difficult. In regions of high defect concentration caused by irradiation, the change in density and elastic constant will be randomized such that negligible change will be seen over short transits. In Chapter 4 we provide experimental evidence that the wave speed $v_s$ remains unaffected through the defect regions. Furthermore, we show that phonon-defect scattering is likewise negligible, owing mainly to the fact that regions of high defect density are relatively narrow spatially ($\sim 100$ nm). Therefore, the main effect of structural lattice distortion in the CAP studies is the secondary effect of a distorted electronic structure. This aspect is investigated in more detail in Chapters 4 and 5 within the framework of defect-induced band tailing.
CHAPTER IV

DEPTH-DEPENDENT DEFECT PROFILING IN HE⁺-IRRADIATED GAAS USING COHERENT ACOUSTIC PHONON SPECTROSCOPY

Introduction

The focus of this dissertation is using coherent acoustic phonon spectroscopy to quantitatively measure defect profiles in crystal. In this Chapter we present data to unequivocally demonstrate that such measurements are possible in a model material system, and that the technique is sensitive to over four orders of magnitude of defect concentration. Further, we show that the profiles generated by the CAP technique compare favorably with Stopping Range of Ions in Matter (SRIM) 2006 simulations in both depth and qualitative form.

We begin with a simple discussion on the use and limitations of the SRIM code, along with general behavior of the residual damage profile expected under a range of different irradiation parameters. We present experimental results showing the effect of depth-dependent damage profile on the CAP response, and demonstrate that the effect is due to the point defect concentrations. By analyzing the oscillation amplitudes of the damaged sample, a Gaussian-like profile is observed with a FWHM almost twice that of the simulated profile. Repeated measurements, along with a high degree of confidence in the efficacy of our simulations, imply that the correspondence between the optical signal and defect concentration is not linear.

The work presented in this Chapter leads to a discussion on the exact nature of the
nonlinear dependence between observed signal and expected defect concentration. This effect, and its implications on how a point defect modifies surrounding lattice structure, is explored in Chapter 5. Ultimately knowledge of the fundamental physics that govern the CAP signal in damaged crystals is necessary to yield quantitative information, however, the data presented in this Chapter provide definite proof that the CAP signal is sensitive to exceedingly low defect concentrations.

Simulation of radiation damage using Stopping Range of Ions in Matter code

Predicting the final damage profile in a material under ion bombardment can be quite complex due to the dependencies on external parameters (temperature, energy, dose rate, material). Still, by considering the various ways that ions lose energy to the lattice during penetration, and the subsequent behavior of the displaced atoms, a reasonably good estimate of the final distribution of damage can be achieved. Typically, Monte Carlo simulations are used based on the statistical nature of the collision process, using the nuclear and electronic cross-sections. One of the most widely used programs to predict implantation-induced damage is Stopping Range of Ions in Matter\textsuperscript{2}. Conceptually, the SRIM simulation tracks an ion as it penetrates the lattice, at each point calculating the amount of energy loss through a variety of different mechanisms. Atoms displaced via ion collisions are also tracked as they travel through the lattice. When the energy of the ions (or displaced atoms) falls below the displacement energy, the ions come to a rest. SRIM

\textsuperscript{2} SRIM may be downloaded for free at http://www.srim.org/
calculates the final stopping range of the ions, and the positions within the lattice of vacancies and displaced atoms are recorded. The profiles are measured in terms of defects/ion/angstrom, so that the results are dose independent. The total defect concentration as a function of depth \( n_d \) can be calculated as:

\[
  n_d \left[ \frac{\text{defects}}{\text{cm}^3} \right] = \left( \text{SRIM} \left[ \frac{\text{defects}}{\text{ion} \cdot \text{angstrom}} \right] \right) \left( \text{dose} \left[ \frac{\text{ion}}{\text{cm}} \right] \right) \left( \frac{10^8 \text{angstroms}}{\text{cm}} \right)
\]  

[4.1]

Simulations are useful for predicting experiments and comparing how different input parameters change the final damage profile. Figure 4.1 shows the predicted damage profiles for a number of light ions commonly used in GaAs implantation experiments. Fig. 4.1(a) shows damage profiles for He\(^+\), Ni\(^+\), Si\(^+\), and Ar\(^+\) at 325 keV. The profiles are clearly strongly dependent on ion mass, with the Ar\(^+\) defect concentrations almost 40x stronger than for He\(^+\). Fig. 4.1(b) shows the total number of defect per ion for the same ion species, for a number of different implant energies. Fig. 4.1(c) shows the damage profiles for a number of different dosages of He\(^+\) at 325 keV, plotted on a semi-log scale. Due to the dose independent SRIM calculations the damage profiles that scale linearly with dose. Fig. 4.1(d) shows profiles calculated for 325 keV He\(^+\) at five different implantation energies. For increasing energy, the ions travel deeper into the crystal before falling below the displacement energy.

For experiments presented here, He\(^+\) ions were used, mainly at 325 keV, and we can expect resulting damage profiles to be similar to Fig. 4.1(b). However it is important to keep in mind kinetic effects such as defect or ion diffusion during or after the irradiation process, recombination of displaced atoms and vacancies, and formation
Figure 4.1: (a) Simulated damage profiles for different ion masses at 325 keV, (b) profiles for He⁺ ions at different energies and (c) doses (note log scale in (c)). Figure (d) shows the total integrated defects created per incident ion for different ion masses and energies. All simulations were done in GaAs.
of defect complexes are not calculated by SRIM. If significant diffusion occurs the experimentally produced damage profile will be different from the simulation, and is discussed in the final section of this chapter. These simulations presented here are used throughout Chapters 4 and 5.

**CAP response in radiation-damaged GaAs**

To recreate the types of damage profiles seen in simulations, GaAs (100) wafers were repeatedly exposed to He⁺ ion bombardment. The helium ions create point defects as they cascade through the lattice, but have little effect on the post-radiation properties, both due to their relatively small size and small concentration compared to the created damage. The GaAs was topped with a 20 nm thick GaSb layer deposited on the polished side of the wafers to act as an efficient absorber for the optical pump pulse. $E_g$ for GaSb is roughly .73 eV while $E_g$ for GaAs is about 1.425 eV, allowing negligible absorption in the GaAs bulk compared to the GaSb layer. The GaSb layers were grown via molecular beam epitaxy at 480°C, where the GaAs substrate was first heated to 600°C to remove oxidation. The process was carried out in a Riber 32 MBE system, equipped with a Veeco SUMO source and a valved cracker source for the Sb, at a rate of approximately 0.8 monolayer/sec. The He⁺ ion beam was generated using a HVE AN-2000 Electrostatic Van de Graaff accelerator with currents near 10-20 nA, and total doses varying between $10^{11}$-$10^{14}$ ions/cm². To reach higher total dosages, the fluence was kept constant while the total accumulated charge was varied, to avoid fluence-dependent annealing effects. The dosages resulted in peak simulated defect concentrations between $10^{18}$-$10^{21}$
defects/cm³. To keep the damage profile within a few microns of the surface, a 2 µm aluminum foil was used to reduce the energy of the incoming ion beam from 1.0 MeV to 300-600 keV. The presence of the Al “layer” was accounted for in the simulation. The reduction in energy to a few hundred keV placed the peak damage range between 1-2 µm beneath the sample surface, and allowed the peak damage range to be easily controlled.

All optical CAP experiments were performed with a 76 Mhz Mira 900 Ti:sapphire laser with a pulse width of 120 fs, used in a standard time-resolved pump-probe setup with typical power ratios of 30:3 mW. The pump-induced signal was measured via lock-in amplification techniques by passing the pump beam through an acousto-optic modulator with modulation frequency of 50 kHz.

The time-resolved reflectivity response ΔR(t) of the damaged wafers was compared with the response of an as-grown sample. Unless otherwise noted the pump and probe photon energies were held at 1.41 eV (880 nm), just below the band gap of GaAs. Fig. 4.2 shows the response of a sample exposed to 5⋅10¹³ ions/cm² with an ion energy of 325 keV, with the probe wavelength varied around 880 nm. Immediately it is clear that the irradiation modifies the CAP response by modulating the oscillatory amplitudes. For 325 keV, the modulation occurs at time delays corresponding to the depths where significant damage is expected. As the probe photon energy is scanned through the approximate region of the GaAs E₉ the behaviors of both the CAP oscillations and the damage-induced modulation change dramatically. For photon energies above E₉ (λ_probe less than 875 nm), strong
Figure 4.2: The oscillatory component of the pump-probe response in an irradiated GaAs wafer. The probe wavelength is scanned around the GaAs bandgap. Near 875-880 nm, strong modulation of the amplitude occurs, corresponding to the damage produced during the irradiation process (200 ps is roughly one micron of pulse propagation).
attenuation of the probe pulse is noticeable and the oscillations damp out quite quickly. For photon energies below $E_g$ ($\lambda_{\text{probe}}$ greater than 875 nm) the oscillations persist throughout the entire time delay. This behavior is attributed to the absorption of the probe light by the GaAs substrate depending on the probe energy relative to $E_g$. Secondly, for $\lambda_{\text{probe}}$ near the band gap, the damage-induced modulation is quite strong (870, 875, 880 nm). When tuned either above or below the band gap (860, 865, 890 nm) the modulation decreases greatly in intensity, even though the CAP signal itself does not decrease in intensity. Therefore we conclude that the ability to observe the damage is wavelength dependent. Noticeably, the peak of the modulation occurs at occurs at $\Delta t=200$ ps for each trace corresponding to roughly 1 $\mu$m below the surface.

To confirm the modulation in the $\Delta R(t)$ traces is caused by radiation damage, the experiment was repeated for increasing ion energies and dosages. Figure 4.3 shows the CAP response for total dosages ranging from $2.75 \cdot 10^{11}$-$1.5 \cdot 10^{14}$ cm$^{-2}$ for probe wavelengths near 880 nm. Modulation of the oscillation amplitude is observable at each dosage above the lowest exposure. Figure 4.4 shows the result of implantations conditions similar to Fig. 4.2 but for increasing energy, resulting in the peak depth moved farther beneath the surface. The number in parenthesis is the ion energy after attenuation by the Al foil. The probe wavelength was held at 880 nm to maximize sensitivity to the damage-induced modulation, according to Fig. 4.2. From Fig. 4.4 it is clear that an increase in the ion energy corresponds to the peak damage range being located deeper into the crystal, about 500 nm for an increase of roughly
Figure 4.3: The oscillatory component of the pump-probe response in an irradiated GaAs wafer for different irradiation dosages between $10^{11}$ and $10^{14}$ ions/cm$^2$. For increasing dose, the amplitude modulation in the damaged region becomes more severe.
Figure 4.4: The oscillatory component of the pump-probe response in an irradiated GaAs wafer for increasing ion energies. Here, the time delay axis has been converted to depth by multiplying by the speed of sound. For increasing energies, the peak amplitude modulation moves deeper into the GaAs crystal.
120 keV. The dashed line represents the expected attenuation of the probe light according to the absorption coefficient for GaAs at 880 nm. These results confirm that the modulation of the oscillation amplitudes is dependent on radiation damage. The shape of the observed modulation recalls the generally expected shape of the simulated damage profiles. The modulation rises, reaches a maximum, and disappears in a roughly “Gaussian” fashion, providing further evidence that the CAP signal is dependent on the crystal damage.

**Measurement of experimental damage profiles**

From the previous section, it is apparent that radiation damage modifies the CAP reflectivity response through changes in the oscillation amplitude. Figure 4.5 shows a direct comparison between the total pump-probe signals of an as-grown sample and a sample exposed to 325 keV He⁺ ions at a total dose of $5 \cdot 10^{13}$ ions/cm². The inset shows the oscillatory component with the initial electronic and long-term thermal background subtracted. The damage-induced amplitude modulation is very clear, and varies strongly as a function of $\Delta t$.

Interestingly, while the amplitude modulation mimics the expected damage profile at early $\Delta t$, for $\Delta t > 350$ ps the amplitude becomes equal in strength to the as-grown sample. The two signals are also in phase, within experimental error. This important observation indicates that the amplitude modulation is not due to changes in the index of refraction. For instance, Eqn. [2.11] shows that if the real part of $\tilde{N}$ was modified by the presence of defects, the period of the damaged sample would not be concurrent with the as-grown after travelling through the
Figure 4.5: The total pump-probe response of as-grown (red) and irradiated (black) GaAs samples at room temperature with the probe wavelength tuned to 880 nm. The oscillatory component is superimposed on top of the initial transient spike associated with electronic excitation.
damaged layer. Likewise, if imaginary part of $\tilde{N}$ were modified through defect absorption, the oscillation amplitudes of the two samples would not be of equal strength for long $\Delta t$. Phonon-defect scattering is negligible here, as the CAP amplitudes after the damaged region are equal to within experimental error. Therefore we conclude that the damage-induced modulation occurs through some secondary effect, beyond direct modification of $\tilde{N}$.

Intuitively, subtracting the amplitudes of as-grown and damaged samples should yield a profile of the damage effects. Figure 4.6(a) shows these profiles for selected irradiation dosages. The result is a broadly peaked distribution, reaching a maximum near 200 ps and going to zero for long $\Delta t$. Please note that the notation has been changed so that $\Delta A$ refers to the absolute oscillation amplitude difference between the damage and undamaged samples, $|A_{\text{damaged}} - A_{\text{as grown}}|$. Increasing the total dose causes the experimental peak to increase, as expected for increasing total residual damage seen in Fig. 4.1.

The experimental profiles have peak depths in agreement with the simulation and have a general Gaussian shape. However comparison with simulations shows that the experimental profiles are almost twice as broad as expected. Fig. 4.6(b) shows the normalized simulation and experimental profile, along with the simulated helium ion profile (enhanced x25). Here the x-axis has been converted to depth by multiplying $\Delta t$ by the longitudinal speed of sound in GaAs ($v_s=4.73$ nm/ps). The discrepancy in width can be attributed either to (a) diffusion of the residual damage during or post irradiation, or (b) a nonlinear dependence of the CAP amplitude modulation on defect concentration. Here we assume that diffusion effects, though
Figure 4.6: (a) Subtracting the oscillation amplitudes of the damaged and as-grown samples, a profile of the effects that irradiation damage has on the optical response can be plotted. (b) Comparison with the simulated defect profiles shows the experimental data to be broader than expected by approximately a factor of two.
almost certainly present to some degree during the irradiation process at 300 K are negligible. This is partly justified by from Fig. 4.1, as the probe wavelength dependence is difficult to explain if the optical response is strictly dependent on the defect concentration, and Fig. 4.3, as the modulation increases with dose at constant ion fluence. However, as SRIM simulations cannot take into effect in situ annealing or Frenkel pair recombination, this is an important possibility to consider.

Therefore we conclude that the primary reason for the difference between simulation and experiment is a nonlinear dependence on defect concentration, which prevents measurement of the damage in a quantitative manner. Without knowing exactly why the amplitude reduces in such a manner versus defect concentration, it is impossible to estimate absolute defect quantities. Still, the above evidence demonstrates that the CAP technique is sensitive to depth-dependent point defect concentrations. To make quantitative estimations of the defect profiles one must understand the underlying nonlinearities and the complex interplay between defect concentration and optical response.

**Discussion**

There are a few limitations to the profiling capabilities of the CAP technique just discussed, namely (a) the lack of a clear theoretical model of the interplay between \( n_d \) and \( \Delta A \), (b) diffusive effects during irradiation not taken into account by SRIM, and (c) the inability to distinguish between specific defect types. While it is practically useful to identify general areas of significant defect population similar to Fig. 4.6(a), it is especially desirable to measure the exact concentration. Kinetics of
the generated defects that occur during the implantation process (or during extended shelf life) are more difficult to identify. In principle, one could obtain a general idea of the residual damage kinetics during and after implantation by comparing our experimental parameters here with other studies regarding light ion bombardment into GaAs, such as N⁺, Li⁺, or electron. Wesch, et al., pointed out that such comparisons can be helpful as long as one stays within the same material system and the ion masses are relatively similar, as opposed to comparisons between He⁺ and heavy metal ions (99). Here the critical parameter becomes the total deposited energy, though we make assumptions that the same conclusion can be arrived at by considering the total number of displacements per ion.

Figure 4.1 shows quick damage calculations using SRIM 2006 code for 325 keV implantation of different light ions. Noticeably, the peak damage for He⁺ radiation is nearly an order of magnitude smaller than Ni⁺ radiation. A threshold of about $10^{14}$ cm⁻² for 100 keV Si ions at room temperature is generally necessary to reach the amorphous limit of GaAs (7). Considering Fig. 4.1, the defect production rate for He⁺ is almost 20x small than for Si⁺, while our maximum dose is $5 \cdot 10^{14}$ cm⁻². Accordingly we can assume that we are strictly in the limit of point defect creation (97), with no blistering effects that occur at low energies but high dosages ($\sim 10^{16}$ cm⁻²) (110), extended defects that occur with energetic heavy ions (111), or complete lattice disorder (96, 98).

The central question becomes how the residual damage profile changes either during or post radiation for our parameters, and therefore how accurately simulations reflect the created damage profiles. Williams, et al. (98, 112), showed
that GaAs irradiated with $10^{14}$ cm$^{-2}$ Ar$^+$ showed strong temperature dependent disorder, with total amorphization at 80 K. When the implantation was done at 300 K, total amorphization was reached, but the depth of the amorphous layer was much more narrow, indicating either temperature or implantation-induced recombination effects. Wesch, et al. (97), showed that for doses of $7 \cdot 10^{13}$ N$^+$, minimum channeling yields were about 20% lower for 300 K than 125 K, again supporting room temperature annealing of the point defects. Therefore, we conclude that while there might be room temperature annealing of our samples, based on small (tens of percent) annealing at damage concentrations exceeding our highest defect concentration by an order of magnitude in previous studies, room temperature annealing does not play a significant role. The consequences of significant diffusion would cause the SRIM simulation to overestimate the defect concentrations measured experimentally, without disqualifying the final conclusion. It is possible that the CAP technique is more sensitive to small defect concentrations due to overestimation by SRIM.

Finally, because we are measuring damage, the sum of all defect types, it is not possible to comment on the relative concentration of different defect species. Therefore it is possible that either during irradiation or high temperature annealing (inset, Fig. 4.7), point defects recombine while more stable defects such as antisites remain. In conclusion, we have demonstrated the ability of CAP spectroscopy to detect and measure depth-dependent defect profiles in damaged GaAs. The experimental profiles show good agreement with simulations, but have full width-half maxes almost double damage profiles from simulation. Modification to the CAP
signal was seen at defect concentrations as low as $10^{18}$ cm$^{-3}$. This technique has a spatial range on the order of tens of micrometers and ~30nm depth resolution throughout the probed range. The upper depth limits achieved here surpass the conventional use of MEIS and ion channeling measurements, which also create similar damage during analysis. Current levels of TEM/STEM provide superior depth resolution, but are not as sensitive in terms of defect concentrations. On the other hand, positron annihilation, one of the most sensitive defect probes, has limited depth resolution. The optical nature of the CAP technique allows it to be used in a wide variety of semiconductor and insulator materials, suggesting the enormous potential of CAP as a robust materials characterization technique.
CHAPTER V

UNDERLYING PHYSICAL MECHANISMS FOR DEFECT PROFILING USING CAP

Introduction

In the previous Chapter a method for detecting subsurface defect concentrations was established. In this chapter we uncover the fundamental physics that cause the CAP oscillations to reduce in regions with significant defect population. This mechanism is directly related to the electronic structure of the GaAs at the probe wavelength, in this case, the near band edge electronic structure. The dependence between the amplitude modulation (ΔA) and defect concentration (n_d) is experimentally established, and this dependence is shown to fit to a simple exponential model. With the quantitative model, we are able to transform the raw data profiles (e.g. Fig. 4.6) into quantitative defect profiles, which show excellent agreement with simulation. With the physical mechanism identified we provide theoretical calculations that demonstrate similar physical phenomena. Finally, we show that how the amplitude varies versus n_d may actually be viewed as how the GaAs electronic structure changes as a function of n_d. We show that changes in the band edge responsible for CAP amplitude modulation actually halt at defect concentrations significantly below lattice amorphization. We discuss this observation within a phenomenological model based on strain-induced electronic structure distortion, and conclude that each point defect distorts the electronic structure of neighboring atoms to a significant degree.
Photoelastic changes as cause of amplitude reduction

In Fig. 4.6 we observed that although the peak depth of the experimental and simulated defect profiles coincided, the experimental profile was almost twice as broad as the simulations. In the absence of diffusion or recombination effects, it must be concluded that the change in CAP amplitude depends on the local defect concentration in a complicated and nonlinear fashion. To determine the root cause of the amplitude modulation we again consider equation [3.9]:

\[
f(z) = f_0 \left( \frac{\partial n}{\partial \eta} \sin \left( \frac{4\pi n z}{\lambda} - \phi \right) + \frac{\partial k}{\partial \eta} \cos \left( \frac{4\pi n z}{\lambda} - \phi \right) \right) \exp \left( \frac{-z}{\delta_{op}} \right)\]  

[5.1 [3.9]]

Where \( f_0 \) is described by equation [3.10] and is dependent only on \( n \) and \( k \). Therefore, the possible underlying mechanisms for the changes in the CAP signal must be due to changes in \( n, k, \) or the derivative photoelastic terms, \( \partial(n,k)/\partial\eta \).

As discussed, by considering the optical response at long delay times after the CAP pulse has passed through the damaged region (inset Fig. 4.5), one sees that the oscillatory signal is equal in both period and amplitude to the undamaged sample. Therefore, through equations [2.11] and [2.12], the observed amplitude modulation cannot be due in part to changes in \( n \) or \( k \). For example, significant change to \( n \) in the damaged region would result in a phase difference at long time delays, while a change in \( k \) would result in decreased amplitude. Because the damaged sample is concurrent with the as grown response at long time delay, it can be concluded that the dominant contribution is from the photoelastic constant of GaAs in the damaged region.
Photoelasticity is the change in the optical properties of a material in response to an applied strain (113). The degree of photoelasticity exhibited by a material is dependent on the bonding characteristics and is a strong function of electromagnetic frequency. To conceptualize the photoelastic response of a material it is helpful to think of the strain as causing a rigid shift in the electronic structure, which is justified in the limit of small strains. In this approximation, the optoelectronic response of a material under strain being probed at photon energy $\hbar \omega_0$ is the equal to the response of the unstrained material being probed at photon energy $\hbar \omega_0 + \partial E / \partial \eta$, where $\partial E / \partial \eta$ is the deformation potential. Therefore, there are two features of the electronic structure that determine the photoelastic response: (a) the magnitude of the change in the optoelectronic response near the photon energy being investigated, and (b) the strength of the deformation potential. One can write the photoelastic constant as:

$$\frac{\partial \tilde{N}}{\partial \eta} = \frac{\partial \tilde{N}}{\partial E} \frac{\partial E}{\partial \eta}$$  \[5.2\]

Here \(\tilde{N}\) refers to the derivative of the complex index of refraction at the energy being investigated. Experimentally one usually measures the real and imaginary coefficients separately, and each may vary with strain independently. Treating $\tilde{N}$ as an imaginary number Eqn. [5.2] can be written as (ignoring the arbitrary phase):

$$\frac{\partial \tilde{N}}{\partial \eta} = \sqrt{\frac{\partial n^2}{\partial E} + \frac{\partial k^2}{\partial E} \frac{\partial E}{\partial \eta}}$$  \[5.3\]

It can be difficult to find a comprehensive database of photoelastic values for different materials, primarily because of the strong dependence on wavelength.
Usually most approaches attempt to calculate the deformation of the electromagnetic fields, atomic polarizability, and transition probabilities under the applied strain. Most studies focus on high symmetry systems such as cubic crystals and focus on simple phenomena such as birefringence. Most theories approximate small strain perturbations resulting in linear changes of the optical response, which do not hold when the photon energy is tuned near an optical resonance. This is illustrated by the values of \( n \) and \( k \) in GaAs near the band gap (\( E \approx 1.43 \text{ eV} \)) at room temperature, shown in Figure 5.1. We see that in relatively flat regions (\( E = 1.1 \text{ eV} \) is chosen arbitrarily in the figure) the derivative terms \( \partial(n, k)/\partial E \) are much lower in magnitude than the same derivative terms at \( E = 1.42 \text{ eV} \). This implies that through Eqn. [5.3], the photoelastic response will be significantly stronger near the GaAs band edge. Incidentally, through eqn. [5.1], this also implies that the oscillation amplitude of the CAP response will be greatly enhanced. With the knowledge that the CAP response is greatly enhanced near the band edge, and having demonstrated experimentally that changes in the damaged sample optical response cannot be due to changes in \( n \) or \( k \), we focus on how the photoelasticity may be modified by the presence of point defects.

As previously mentioned, point defects may affect a semiconducting crystal either electronically, by opening up new states inside the band gap, or structurally, through lattice relaxation around each defect. Most electronic defect states have significant separation (more than a few \( kT \)) from the valence or conduction bands, and would not be expected to contribute to band edge modification. However, the
Figure 5.1: real (n) and imaginary (k) indices of refraction for GaAs at room temperature near the GaAs direct band gap. The dotted (red) line shows the derivative of n or k at E= 1.1 eV and E=1.42 eV, indicated by the dashed (black) line. The derivatives at E=1.42 eV are much greater than those at E=1.1 eV, implying stronger photoelastic response and CAP sensitivity when probed near the band edge.
lattice relaxation has a secondary effect on the electronic structure, as the electron densities around each lattice point also shift in response to the presence of a defect. In areas immediately surrounding the defect the optoelectronic response is perturbed slightly from the ideal crystal response. Therefore, if one were to take the average response of the entire crystal, the contributions from areas with and without point defects would yield a band edge absorption curve that was broadened to a degree dependent on the number of defects present.

In fact, this phenomena has been observed to occur in a variety of semiconducting systems arising from heavy doping (114-116), deep level defects (117), or strain (118). Generally the absorption edge exhibits a tailing behavior commonly described by Urbach’s rule (119), and for this reason is referred to as “band tailing”. The physical mechanisms giving rise to band tails can vary between impurity band overlap in doped semiconductors (119-121), Franz-Keldysch effects from ionized impurities (122), and inhomogeneous strain effects perturbing the density of states (118). As noted, for our experiments where the probe wavelength is tuned in the vicinity of the band edge, electronic contributions from deep level defect states are most likely negligible. Therefore, we conclude that strain associated with structural (lattice and electronic) relaxation around each defect is responsible for a decrease in the terms $\partial(n,k)/\partial E$, and hence the photoelastic constant. The extent of nearest neighbor interactions involved in the relaxation was discussed in Chapter 3. To recap, in GaAs lattice relaxation has been shown to occur over roughly 3-6 nearest neighbors, while the electronic structure may relax over a significantly longer distance. Certain types of more complex defects such as antisite As defects also have
significant lattice distortion associated with them. It should be kept in mind that not all studies focused on the types of defects here, being more concerned with interfacial effects, but still represent a good “starting point” point estimating strain fields associated with defects. Figure 5.2 shows a conceptual diagram of what happens to the band edge when defects are incorporated into the lattice.

In summary, the fundamental physics underlying the CAP amplitude reduction in regions of high defect density has been illuminated. Intrinsic strain associated with point defects tends to broaden the absorption edge near the band gap, which subsequently reduces the photoelastic constant. This in turn causes the CAP oscillation amplitude to decrease through Eqn. [5.2] (or [5.3]). The undamaged and as-grown responses become concurrent at long times, eliminating the possibility of changes in $n$ or $k$ being responsible for the observed amplitude reduction.

The fact that intrinsic defect absorption is not at play offers the unique advantage that features extending a significant depth into the sample may be measured without extra attenuation of the probe signal. The following sections focus on (a) first principle computations of $\partial(n,k)/\partial \eta$ as a function of defect concentration, and (b) using the CAP technique’s sensitive dependence to band tailing effects to observe how the GaAs electronic structure changes as a function of increasing $n_d$. 
Figure 5.2: Conceptual diagram of the absorption near the band edge of a lattice with (a) no defects and (b) some amount of defects. The strain associated with relaxation around each defects skews the density of states and causes the averaged optoelectronic response to ‘tail’ near the absorption edge, thus reducing the photoelastic constant.
Having identified that band tailing effects arising from point defect concentrations are the fundamental cause of the CAP amplitude reduction, we can determine the functional dependence of $\Delta A$ with respect to $n_d$. To do this, a single point on the experimental profile is chosen and correlated with the simulated defect concentration. In principle this should be simple since the time delay pump-probe axis may be very precisely correlated with depth by multiplying by the speed of sound in GaAs. By repeating this procedure for a range of different radiation dosages provides a picture of how $\Delta A$ changes versus $n_d$. While any point pair in the experimental/simulated profile should work, it is intuitive to choose the profile peak. This process is illustrated in Figure 5.3, where the peak change in amplitude ($\Delta A_{\text{max}}$) of the experimental profile is correlated with the peak simulated defect concentration ($n_{d,\text{max}}$) for ten different radiation doses (between $10^{12}$-$10^{14}$ cm$^{-2}$). This quantity is plotted for both absolute change in reflectivity (left axis, open circles) and percentage change in oscillation amplitude (right axis, open squares), that is, by what percentage the amplitude is reduced due to the presence of defects. How each point is chosen is explicitly shown for the profile for a sample exposed to a dose of $7.5\cdot10^{13}$ cm$^{-2}$. The peaks of the simulated and experimental profiles correspond to one point in Figure 5.3. Repeating this procedure for each dose establishes $\Delta A(n_d)$ experimentally. Initially, a small increase in $n_d$ results in a rather large amplitude reduction. At higher values of $n_d$ the change in the CAP amplitude appears to saturate.
Figure 5.3: Plot of the peak change in CAP amplitude as a function of simulated defect concentration. The inset demonstrates how each individual point pair ($\Delta A, n_d$) is chosen.
The data in Fig. 5.3(a) can be fit to a simple model according to

\[ \Delta A = C_0 (1 - \exp(-n_d / \beta)) \]  

[5.4]

The fits are shown by the solid lines in Fig. 5.3(a). Using the values for \( C_0 \) and \( \beta \) determined by the fitting routine, Eqn. [5.4] provides a numerical route to transforming the raw CAP profiles (e.g. the profiles shown in Fig. 4.6(a)) into quantitative defect profiles. For the absolute \( \Delta A_{\text{max}} \) fit, \( C_0=1.16 \cdot 10^{-5} \) and \( \beta=90.96 \text{ cm}^{-3} \), while for \%\( \Delta A_{\text{max}} \) fit and \( \beta=90.96 \text{ cm}^{-3} \) and \( C_0=.74 \). Using these numbers Eqn. [5.4] may be inverted to obtain

\[ n_d(\Delta A) = -\beta \ln \left( 1 - \frac{\Delta A}{C_0} \right) \]  

[5.5]

The ‘raw’ data from the CAP profiles can then be transformed using this equation into quantitative experimental defect profiles. Figure 5.4 shows a quantitative profile for a sample exposed to a dose of \( 1.5 \cdot 10^{13} \text{ cm}^{-2} \). One can see that after accounting for the nonlinear dependence between \( \Delta A \) and \( n_d \) the experimental profile is in excellent agreement with simulations, with slight deviations at the base of the peak. The inset shows the untransformed CAP profile after annealing for 2 hours at 570K. After annealing the profile reduces by nearly 80%. This reduction most likely corresponds to the recombination of vacancy and interstitial defects at elevated temperatures, reducing the total defect concentration.

It should be noted that, as discussed in Chapter four, the data in Fig. 5.3 and the quantitative measurement in Fig. 5.4 are still dependent on defect concentrations estimated by the SRIM code. As SRIM does not take into to account either dynamic annealing or other defect kinetics which may take place during or after the
Figure 5.4: Comparison between SRIM profile (black) and experimental CAP profile (blue) after the CAP profile has been transformed via Eqn. [5.5]. The peaks and widths of both profiles show excellent agreement. The predicted final helium ion distribution is shown (enhanced x25) for comparison. Inset: reduction of CAP profile upon annealing at 570K for 2 hours.
implantation process, it is possible that the $n_d$ values are overestimated to a degree dependent on the amount of defect diffusion that occurs. However, although the absolute defect concentrations may be overestimated Figs. 5.3 and 5.4 demonstrate that the CAP profiles may be transformed into quantitative defect profiles given knowledge of the dependence of $\Delta A$ on $n_d$, and that the CAP technique is capable of noninvasive quantitative measurements of depth-dependent point defect profiles.

**First-principles calculation of near-band edge optical constants**

Figure 5.4 shows experimentally how the CAP oscillation amplitude varies as a function of defect concentration. Since it has been argued that this type of amplitude modulation is reflective of band edge degradation caused by point defects, Fig. 5.4 may be interpreted as the degree of band-tailing present as a function of defect concentration. Still, because experimental evidence is inexorably linked to the accuracy of the SRIM simulations, it is crucial to provide some independent estimate of how the near-band edge optical constants evolve. Ideally, this would be a theoretical model that could accurately predict the how quickly the constants $n$ and $k$ change versus photon energy at the band edge, and would be repeatable for a wide variety of materials. A theoretical approach would eliminate the need to rely on empirical measurements establishing the relationship between defect concentration $n_d$ and amplitude modulation $\Delta A$. The benefits would be two-fold. First, a reliable theoretical model would allow direct quantitative analysis of the defect profiles in the CAP measurement. Secondly, the behavior and effects of point defects have technologically important roles as charge traps and in optical
applications are therefore of fundamental theoretical interest. Since the physical effect responsible for the signal change can be linked to the $\partial(n,k)/\partial E$ parts of the photoelastic constant, our CAP studies may shed light on new aspects of deep level defects.

Our theoretical approach is conceptually described by the modeling of the conduction and valence band wavefunctions of a number of Ga and As atoms arranged in the typical GaAs lattice. To model irradiation damage single atoms are removed, replaced, or placed in interstitial positions to simulate various point defects. The absorption coefficient $k$ is then calculated by determining the transition probabilities through Fermi’s Golden Rule (Eqn. [2.8]). From [2.8] the quantum mechanical matrix element $M$ and the density of states are calculated for the entire crystal. The index of refraction is calculated from the absorption coefficient using the Kramers-Kronig relation. The calculations of $n$ and $k$ are done in a relatively narrow energy range around the band edge. To study the effects of different defect concentrations the calculation is averaged over a random selection of defect types, at multiple defect concentrations. This first principles approach allows computation and investigation of how defect populations modify the optical constants near the band-edge. To compare with CAP results, the derivative of these values are taken with respect to photon energy.

The defect-modified wavefunctions and the optical absorption function were calculated in the $k\cdot p$ framework described by Pan, et al. (123). In this model, the Hamiltonian is the sum of an eight-band $k\cdot p$ GaAs crystal band and a disorder Hamiltonian (124):
\[ H = H_0 + H_D \]  

[5.6]

The radiation-induced disorder Hamiltonian \( H_d \) is summed over the potentials of the randomly distributed defects \((125, 126)\). This model treats the band structure realistically and allowed us to study the effect of impurities in large systems where \textit{ab initio} calculations are not feasible. This approach has been successfully used to calculate the optical properties of semiconductors with defects and impurities \((124-127)\).

Figure 5.5(a) and (b) show the calculated \( n \) and \( k \) values for wavelengths near the band edge. The derivatives are shown in (c) and (d). Both are plotted for different defect concentrations, where the legend shows defect concentration \( x10^{18} \text{ cm}^{-3} \). Notable differences in the near-band edge properties are seen as the defect populations are increased. First, for increasing \( n_d \) the sharpness of the features near the band gap energy for both \( n \) and \( k \) decreases. This results in values of \( n \) and \( k \) that decrease at the band gap, but increase away from the band gap. This implies that in our experiments first order changes are present in regions of the lattice with high defect concentrations. However, as previously pointed out these changes are outside experimental resolution, probably due to the thin \((\sim 100 \text{ nm})\) region with high \( n_d \). This reduction in sharpness is reflected in the derivatives, which decrease dramatically with increasing \( n_d \).

Secondly, one sees that the derivatives decreased dramatically upon incorporation of small levels of defects, but remains similar for concentrations above about \( 10^{19} \text{ cm}^{-3} \).

These results confirm what is observed experimentally. As defects begin to influence the near-band edge optical properties the values of \( \partial(n,k)/\partial E \) decrease,
Figure 5.5: Calculated values for the (a) real and (b) imaginary indices of refraction for GaAs at room temperature near the GaAs direct band gap. (c) and (d) show the respective derivatives. The legend shows the defect concentrations (x10^{18} cm^{-3}).
causing a decrease in the photoelastic response and a reduction of the CAP amplitude. This is seen experimentally by the fact that the CAP amplitude decreases with increasing defect concentration. Additionally, in both theory and experiment the reduction of $\partial(n,k)/\partial E$ seems to halt at higher defect concentrations. This reveals how the electronic structure of GaAs evolves for increasing damage and is discussed at length in the following sections.

The theoretical approach followed here opens an avenue for independent estimations of quantitative defect profiles based on the CAP response. The calculations can be repeated for different semiconductors and different defect types, giving flexibility in application.

Comparisons between theory and experiment

Figure 5.3 shows how $\Delta A$ varies experimentally as a function of $n_d$, while Figure 5.5 shows how the optical constants and their derivatives vary as a function of $n_d$ and wavelength. To compare theory and experimental data a ‘slice’ is taken from Figs. 5.5(c) and (d) at $\lambda=880$ nm. From Eqn. [5.3] the amplitude of the CAP oscillation should be directly proportional to the sum of the squares of the $\partial(n,k)/\partial E$ terms. Figure 5.6 shows this sum for the calculated values of $\partial(n,k)/\partial E$ from Figure 5.5, plotted as a function of defect concentration. The values have been normalized to the values for zero defect concentration, so that the percentage change in the $\partial(n,k)/\partial E$ terms is represented. For the sake of comparison, the inset shows linear absorption measurements of varying irradiation doses. Linear absorption measurements are not particularly helpful in this case, primarily because the
Figure 5.6: Comparison between the change in experimentally observed reduction in CAP amplitude (solid) and the calculated quantity $\Delta A_{\text{max}}/A_0$ (dashed). The lines correspond to fits to Eqn. [5.4]. The inset shows linear absorption measurements for samples irradiated with different dosages.
damaged region is only a few hundred nanometers thick, highlighting the sensitivity of the CAP technique over traditional optical measurements.

Qualitatively, the theoretical and experimental curves show very good agreement in behavior. Both rapidly rise at defect concentrations around $10^{18}$ cm$^{-3}$ and saturate after about a 75% reduction from their initial values. The theoretical model can be fit to Eqn. [5.4] with $C_0=0.73$ and $\beta=10.6$, significantly less than $\beta$ for the experimental data. The difference in $\beta$ causes the theoretical curve to rise much more rapidly, saturating almost an order of magnitude lower than the experimental data. Causes for the discrepancy in the data may be (a) somewhat unphysical aspects in the computational model or (b) overestimation of the defect concentration by SRIM. While the electronic wavefunctions in our computational model relax around each defect placed in the lattice, relaxation of the positive ion core (typical elastic lattice relaxation) is not taken into account. Therefore structural strain is not included. From an experimental standpoint self-annealing of vacancy and interstitial defects may occur. This effect is not taken into account by the SRIM code, implying that the experimental defect concentrations may be significantly lower than predicted. The discrepancy between theory and experiment can be most likely explained by these two considerations. Despite these differences, the good qualitative agreement between the two provides strong evidence that our model of irradiation induced changes in the photoelastic constants, through reduction of the $\partial(n,k)/\partial E$ terms, is essentially correct.
Interpretations of GaAs band edge degradation versus defect concentration

The CAP measurement is sensitive to the relative degree of band tailing as compared to an as-grown GaAs wafer. If it is understood how the band tailing behaves versus defect concentration, then the CAP profiles can be interpreted quantitatively (e.g. Fig. 4.6 can be transformed to Fig. 5.4). However, from a fundamental standpoint, the raw data in Fig. 4.6 reflects the distortion of the electronic structure caused by defects. Unfortunately, the “severity” of band tailing is difficult to quantify, and most experimental studies rely on linear absorption experiments or focus on the tail behavior deep into the band gap. Most theoretical efforts are aimed towards heavy doping scenarios where an impurity band forms and overlaps with the band edge. The precise functional relationship between band tailing and \( n_d \) needed to make quantitative CAP measurements have never been studied in-depth, motivating the type of theoretical study described in the previous section.

However, the data presented in Fig. 5.6 may alternately be viewed as an experimental determination of how the band edge changes as a function of defect concentration. That is, since the CAP technique is extremely sensitive to band tailing, we can use it as a probe to study how radiation effects modify the near band-edge electronic structure. Finally, we are in a position to address why the CAP response has the specific dependence on \( n_d \) shown in Fig. 5.6, namely the rapid rise followed by saturation around \( 2\cdot10^{20} \) cm\(^{-3} \). The most compelling implication of the data shown in Fig. 5.6 is that there is essentially no increase in band tailing between roughly \( n_d=10^{20} \) cm\(^{-3} \) and \( n_d=10^{21} \) cm\(^{-3} \), despite an order of magnitude increase in
defect concentration and the observation that the mechanical properties of the lattice are virtually unchanged.

This somewhat counter-intuitive behavior can be considered within a model where each point defect induces a strain field that extends over a significant number of nearest neighbors. If one approximates each strain field as spherical, each neighboring lattice point falling inside the “zone” will have its density of states slightly altered from the unperturbed crystal lattice. This skewing of the D.O.S. is the fundamental physical effect that manifests as broadened absorption edges when the absorption spectrum is averaged over the entire sample. Therefore a single point defect affects the D.O.S., and therefore causes band tailing of, a number of surrounding lattice points depending on the strength of the nearest neighbor interactions (the size of the “zone”). A vacancy at the [0,0,0] position in the GaAs structure has 8 nearest neighbor atoms (atoms at the [1/4,1/4,1/4] positions) and 6 second nearest neighbor atoms (at the [0,0,0] positions). To a first approximation, for single nearest neighbor interactions, each vacancy would influence 14 lattice points. In reality the number is most likely much higher. For instance, if we consider the defect concentration where saturation behavior becomes dominant (roughly $2.5\cdot10^{20}$ cm$^{-3}$), dividing by the atomic density ($4.42\cdot10^{22}$ cm$^{-3}$), each defect influences roughly 175 neighboring atoms. The size of this zone can be roughly approximated as well as two or three times the coefficient $\beta$ in the curve fitting.

In summary, we have demonstrated that by interpreting the CAP profiles as a measure of electronic structure distortion known as band tailing, the evolution of the GaAs electronic structure versus defect concentration can be measured. The
observed band tailing showed a distinct saturation behavior, orders of magnitude below the expected onset of lattice amorphization. It was concluded that the saturation behavior at low densities is due to the extended strain influence of single point defects altering the density of states of a number of nearest neighbors.

Discussion

In this Chapter we demonstrated that the CAP technique is a sensitive probe of the electronic structure of semiconductors. Its precision in terms of the probe energy, which determines the exact point being observed in the electronic structure, makes it truly unique amongst characterization techniques. Still, questions underlying the studies presented here remain.

First, the dependence of band tailing effects on defect concentration is constructed by correlating the peak change in oscillation amplitude with peak simulated defect concentration. Therefore, the same concerns that were raised over the accuracy of the quantitative defect profiles remain. In the case that significant diffusion occurs during or after the implantation process, the band tailing effects will have a different dependence on $n_d$ than shown in Fig. 5.6. While our experiments are expected to be in a low-dosage, low-dose rate regime where such effects are probably only slightly significant, it is difficult to be certain. If recombination effects occur independent of local defect concentration, i.e. interstitials stay in close proximity to their point of origin, then one would expect a linear decrease of the simulated results. In this case the profile and technique procedure remains the same and the values of $n_d$ would be adjusted accordingly. It is possible, depending on the magnitude of recombination,
that the CAP technique is much more sensitive to low values of $n_d$, which would be an advantage in terms of resolution. On the other hand, if diffusion effects occur such that the profile shape itself is significantly altered the interpretation of the band tailing versus $n_d$ would not be justified.

Another important detail is the discrepancy between the theoretical and experimental band tailing profiles in Fig. 5.6. The main difference is reflected in the fitting parameters. The theoretical result rises much more quickly ($\beta_{\text{th}}=10, \beta_{\text{exp}}=91$). In principle the same diffusive effects could play a role in the observed differences, however, the physical complexity of a crystal lattice can be difficult to reproduce via modeling and can give rise to many different errors. For instance, in order to estimate the size of the strain field around each defect the value of $n_d$ at which saturation behavior became dominant was simply divided by the GaAs atomic density. From this it was estimated that the defect affected roughly 175 atoms, implying an interaction over 2-3 unit cells in each direction (each unit cell has 8 atoms). For comparison, the number of lattice points within the strain field from our calculations is roughly an order of magnitude higher. This suggests that some aspect of the modeling process overestimates the range of influence of a single defect. Because the model does not take into account structural relaxation of the lattice, but does consider relaxation of the electronic wavefunctions, it is possible that the missing structural relaxation counteracts the electronic effects in reality. This would account for the much larger strain fields predicted by theory. Understanding the local physical properties of the lattice surrounding a point defect
is a primary goal of solid-state theory, and this experiment suggests new possible theoretical studies.

Despite the unknowns, it is clear that the CAP technique is sensitive to the exact electronic structure of a material. Because of the flexibility of a pump-probe setup, the band structure of a material, at a specific energy point, could be monitored as a function of external parameters. In our case, the parameter was an invasive introduction of point defect concentrations, however, experiments could just as easily be carried out with external magnetic or electric fields. Many optoelectronic applications rely on the transitions of charge carriers to the conduction band, however, the probability of such a transition rests on the D.O.S. and exact electronic structure at the band edge. In the next Chapter, future experiments are described which would take full effect of the flexibility offered by CAP and pump-probe techniques in general, which would allow CAP to develop into a robust characterization tool.
CHAPTER VI

CONCLUSION

Conclusion

This dissertation explores how the optical response in coherent acoustic phonon spectroscopy experiments change when observed in GaAs crystals exposed to moderate radiation dosages. It was observed that in regions of the crystal with significant point defect concentrations the amplitude of the oscillatory CAP response was reduced. By comparing the response with that of an undamaged crystal, depth-dependent profiles were extracted which peaked at the same depth as simulations of damage carried out by the SRIM code, demonstrating that the CAP technique is a sensitive to point defect concentrations and can be used as a nondestructive probe of depth-dependent radiation damage.

We explore the underlying physics connecting the optical response with the radiation in the damage, specifically why the presence of defects caused the CAP amplitude to reduce. Fundamentally, we demonstrated that each point defect has a strain associated with it that skews the density of states of neighboring atoms. This results in a phenomenon known as band tailing, where the average band edge is broadened out. In turn, this causes a reduction in the photoelastic response at photon energies near the band edge. The CAP amplitude is proportional to the photoelastic constant, so that a reduction in the photoelasticity causes a corresponding reduction in amplitude.
We were able to determine experimentally precisely how the CAP amplitude varies as a function of defect concentration. It was shown that the dependence between ΔA and \( n_d \) was nonlinear, displaying a saturating exponential type behavior. This behavior accounted for the CAP profiles being almost twice as broad as the simulated damage profiles. By curve fitting to the ΔA(\( n_d \)) data, the raw data could be transformed to quantitative depth-dependent defect profiles.

We performed theoretical calculations of the complex index of refraction at energies right around the GaAs band gap. The derivatives were calculated and compared to the experimental data. The theory replicated the exponential-type saturation behavior, although saturating at much lower defect concentrations than the experimental data. The discrepancy between theory and experiment was most likely due to the fact that the computational model did not include structural relaxation.

On the other hand, the untransformed data (Fig. 4.6) is a direct measurement of optoelectronic degradation arising from radiation damage. Therefore, the observed amplitude change versus defect concentration can also be viewed as a how the GaAs band edge changes as a function of defect concentration. The saturation was explained within a model where each point defect skews the electronic potentials of neighboring atoms. Once the local electronic potential is perturbed from the ideal case, further perturbation does not reduce the photoelastic constant further. Therefore, once each lattice point has been affected by the strain of a nearby point defect, further radiation damage does not increase the band tailing and the CAP amplitude no longer reduces.
The data presented here provides strong evidence that the CAP technique is capable of nondestructive, noninvasive depth-dependent defect profiling. Furthermore, it is a sensitive probe of the optoelectronic changes that occur when semiconductors are exposed to ion radiation.


