UNDERSTANDING CHARGE CARRIER RELAXATION PROCESSES IN TERBIUM ARSENIDE NANOPARTICLES USING TRANSIENT ABSORPTION SPECTROSCOPY

by

Laura R. Vanderhoef

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

Summer 2015

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Laura R. Vanderhoef

Approved: _

Edmund R. Nowak, Ph.D. Chair of the Department of Physics and Astronomy

Approved: _

George H. Watson, Ph.D. Dean of the College of Arts and Sciences

Approved: _____

James G. Richards, Ph.D. Vice Provost for Graduate and Professional Education I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: _____

Matthew F. Doty, Ph.D. Professor in charge of dissertation

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: _

Matthew F. DeCamp, Ph.D. Member of dissertation committee

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Signed: _

Yi Ji, Ph.D. Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

Lars Gundlach, Ph.D. Member of dissertation committee I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: _____

D. Bruce Chase, Ph.D. Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: _

Joshua M. O. Zide, Ph.D. Member of dissertation committee

ACKNOWLEDGEMENTS

First and foremost, I would like to thank my PhD advisor Dr. Matthew Doty. He took a chance in taking me on as his student at a time when others were not willing to do so, and he has never since stopped believing in me. Dr. Doty has taught me many things about spatially confined semiconductor materials and ultrafast optics, but the greatest lessons have been how to read and analyze scientific papers, how to question myself and others, and how to be a more thorough scientist. He has also showed me through example how to balance a career in science with a rich family life, and could not have been more supportive when I began a family of my own.

Dr. Bruce Chase has been an amazing mentor to me. When something in the laser system broke yet again, it was his office I went running to. He imparted on me a wealth of knowledge in laser alignment and repair, as well as a healthy dose of humor. Many thanks to my close collaborators, Dr. Joshua Zide and Cory Bomberger, for introducing me to the world of rare-earth nanoinclusions and having patience with me as I caught up on the literature. I also want to express gratitude to all of my group mates past and present for their assistance in the lab and invaluable discussions: Dr. Darry Liu, William Reid, Dr. Xinran Zhou, Dr. Chelsea Haughn, Anagha Kulkarni, Dr. Diane Sellers, Eric Chen, and Xiangyu Ma. I am also grateful for Evan Kimberly, Katharine Mulrey, Cesar Caro, Roy Murray, Brian Kelly, Seth Meiselman, Dr. Inci Ruzybayev, and Jeff Tessein. Together we somehow made it through 800-level Physics courses and the dreaded written candidacy exam, and we even had some fun along the way! In that vein, thanks to all of my friends from the Philadelphia Area Disc Alliance and from That Medieval Thing for helping me maintain perspective outside of the Ivory Tower and keeping me sane all these years! On a more personal note, I have been so fortunate to be part of an incredible circle of women during my graduate school years. Anagha Kulkarni, Nandita Bhagwat, Dr. Chelsea Haughn, and Dr. Nicole Kotulak are some of the strongest and most intelligent women I know. When the world started caving in, these are the people who offered support without hesitation.

I also am incredibly lucky to be part of a large and close knit family. Shout-out to all of the Barclays and Kannaleys by name or by marriage! Thanks as well to the Goffs and the Vanderhoefs for welcoming me into your families. My sister Erin has always been an inspiration to me through her intelligence, drive, amazing mothering skills, and general ability to always have her "stuff" together. My father kindled my interest in science and learning from a young age, as well as given me the patience needed for success. My mother has given me the gifts of creativity and willingness to stand up for what I believe in, even if the person I need to fight for is myself. Together they have been the best parents anyone could ever hope for. Thank you as well to Grandma Barclay, who has instilled in all of us the importance of family and supporting each other through every endeavour.

Last and most important, I cannot even begin to express how thankful I am for my husband Jesse. I would have quit my PhD years ago if not for his support, love, and encouragement. I have never met a person in my life with such a large capacity for patience, empathy, and understanding. Every day I am amazed that I am the lucky woman he chose to marry.

This manuscript is dedicated to my son, James Rohan Vanderhoef. He is my little ray of sunshine and has made the last year of my PhD the most joyful one of all.

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ABSTRACT

Erbium arsenide nanoparticles epitaxially grown within III-V semiconductors have been shown to improve the performance of devices for applications ranging from thermoelectrics to THz pulse generation. The small size of rare-earth nanoparticles suggests that interesting electronic properties might emerge as a result of both spatial confinement and surface states. However, ErAs nanoparticles do not exhibit any signs of quantum confinement or an emergent bandgap, and these experimental observations are understood from theory. The incorporation of other rare-earth monopnictide nanoparticles into III-V hosts is a likely path to engineering carrier excitation, relaxation and transport dynamics for optoelectronic device applications. However, the electronic structure of these other rare-earth monopnictide nanoparticles remains poorly understood. The objective of this research is to explore the electronic structure and optical properties of III-V materials containing novel rare-earth monopnictides.

We use ultrafast pump-probe spectroscopy to investigate the electronic structure of TbAs nanoparticles in III-V hosts. We start with TbAs:GaAs, which was expected to be similar to ErAs:GaAs. We study the dynamics of carrier relaxation into the TbAs states using optical pump terahertz probe transient absorption spectroscopy. By analyzing how the carrier relaxation rates depend on pump fluence and sample temperature, we conclude that the TbAs states are saturable. Saturable traps suggest the existence of a bandgap for TbAs nanoparticles, in sharp contrast with previous results for ErAs. We then apply the same experimental technique to two samples of TbAs nanoparticles in InGaAs with different concentrations of TbAs. We observe similar relaxation dynamics associated with trap saturation, though the ability to resolve these processes is contingent upon a high enough TbAs concentration in the sample. We have also constructed an optical pump optical probe transient absorption spectroscopy system to allow complimentary measurements to be taken on these materials in the near future.

Chapter 1 INTRODUCTION

Modern optoelectronic devices are constructed from semiconductor materials. Semiconductors with the right electronic properties are capable of providing us with sources of clean and renewable energy, higher speed wireless communication, and noninvasive methods of medical imaging. The development of new materials with these properties requires a deep understanding of the electronic structure, optical properties and carrier dynamics. This dissertation explores the electronic structure of terbium arsenide nanoparticles embedded in III-V host materials. Ultrafast transient absorption spectroscopy measurements reveal the charge carrier dynamics that will determine the device possibilities for these new materials. Listed in this chapter are several specific examples of new device technology that can be built on materials with optimal electronic and carrier dynamic properties. Detail will be given about the properties that would be desirable for these applications, which motivates their exploration in new semiconductor materials.

1.1 THz Applications

Throughout this work I will primarily focus on one class of new optoelectronic applications applications which make use of terahertz (THz) radiation. THz radiation is the name assigned to the portion of the electromagnetic spectrum within the band of frequencies from 0.3 to 3 THz (wavelengths in the range from 1 mm to 0.1 mm) known as the terahertz gap. The THz gap is called such because in this region, the frequency of electromagnetic radiation is too high to be measured digitally with electronics, but the frequency is lower than the optical spectrum (Fig. 1.1). This issue will be discussed further in section 1.2. At this time it is worth noting that because the frequency of



Terahertz – between radio and light

Figure 1.1: The frequency range of THz radiation is between radio and optical frequencies on the electromagnetic spectrum.[41]

THz radiation falls between infrared and microwave radiation in the electromagnetic spectrum, it shares some properties with each of these. THz radiation travels in a line of sight and is non-ionizing. THz radiation penetrates clothing, paper, cardboard, wood, masonry, plastic and ceramics, but it is absorbed by metals and water. Due to its shallow penetration depth in materials containing water, THz radiation would be ill-suited for long-range communication or imaging applications deep within the human body.[21]

1.1.1 Communication

THz band (0.110 THz) communication holds great potential for addressing the increasing demand for higher speed wireless communication. Currently, wireless capabilities are limited by a scarcity of available bandwidth. THz band communication offers the opportunity of tapping into an unused portion of the electromagnetic spectrum, allowing for ultra-high data transfer rates. Some of the exciting new possibilities include 5G cellular networks capable of ultra-high-definition multimedia streaming and video conferencing, and ultra-high-speed data transfer between mobile devices. Ultra-broadband communication would also be useful to the military. THz band frequencies are only capable of traveling effectively over a very limited distance, offering

a secure form of communication in the field. Terabit Wireless Local Area Networks (T-WLAN) would allow for personal wireless devices to run as fast as ultra-high-speed wired networks, allowing for complete, seamless integration. Applications such as high-definition holographic video conferencing (Fig. 1.2) would theoretically be possible with a T-WLAN network.[5]



Figure 1.2: Holographic video conferencing requires a broadband network capable of seamless data transfer between wireless personal devices and ultra-high-speed wired networks. A T-WLAN network has the potential to provide this environment.[31]

In order to generate and detect radiation at such a high frequency, the size of THz antennas and transceivers is typically on the order of tens of microns. The inherently small size of these antennas and transceivers could open the door to novel nanoscale communication applications. In one such example, nanosensors could be distributed throughout the human body in order to monitor cholesterol and glucose levels, cancer biomarkers, or possibly the presence of infectious diseases. This information could then be wirelessly sent to a patients cell phone in order to be forwarded to a healthcare provider.[5]

1.1.2 Medical Imaging

In the field of dentistry, x-ray imaging is the standard method of detecting tooth decay. The damage to a tooth can occur below the surface, in the layer known as the dentine, without leaving any visible cavity on the surface. Routine x-ray imaging is commonly employed in order to catch cavities in the early stages of development. However, x-rays only reveal the problem at a relatively late stage, when drilling and filling is the only available remedy. Current THz imaging systems are able to distinguish between the different types of tissue in an excised tooth. In the future, in vivo imaging would allow for earlier detection of enamel erosion and tooth decay (Fig. 1.3). If detected early enough, it is possible to reverse the decay process by the use of either fissure sealing or remineralization.^[2]



Figure 1.3: An internal cavity in a tooth is not detectable with a visible image (left). Time of flight THz data can be used to image enamel and dentine, which have different refractive indices (center). Plotting the peak THz electric field of the transmitted pulse at each pixel shows strong THz absorption in the pulp cavity, indicating tooth decay in this area (right).[47]

Differences in the absorption coefficient of THz radiation can reveal cancerous tissue in addition to tooth decay. Increased THz absorption occurs in tissue with higher water content and with certain structural changes, such as increased cell and protein density.[87] When completing surgical removal procedures, the aim is to excise the tumor with an adequate margin of normal tissue to prevent regrowth, while minimizing the amount of normal tissue removed. In the case of non-melanoma skin cancer, the technique with the highest 5-year cure rate (97-99.8%) is Mohs micrographic surgery.[56] During the surgery, tissue is removed and then examined for cancer cells while the patient waits. The results determine whether or not additional tissue should be removed. The process is repeated until all of the margins of the removed tissue are clear. The technique requires highly trained personnel and is very time intensive, so very few dermatology units are able to perform this surgery. Mohs surgery would be cheaper and faster if accurate delineation of the cancer cells were imaged with THz spectroscopy prior to surgery. This reasoning led Wallace et al.[87] to image normal skin cells and basal cell carcinoma using THz spectroscopy, showing that the two could easily be differentiated. In the case of breast cancer, Mohs surgery is not even an option. A second operation is required if the margins are not clean enough, leading to higher costs and higher risk for the patient. THz spectroscopy studies of mastectomy specimens have shown promising results[32] for being able to determine cancer margins in vivo.

1.1.3 Security

Companies such as TeraView Ltd, headquartered in the UK, have been supplying various entities (including the US Navy) with THz imaging systems for the purposes of homeland security and defense. TeraView's systems are capable of quickly and non-invasively detecting concealed weapons and explosives through many layers of clothing (Fig. 1.4). By viewing the reflection spectrum of THz light incident on the passenger, the system can differentiate between clothing which does not absorb light in the THz range, and explosives, which absorb various THz frequencies to different degrees. Because the known THz absorption spectrum for a variety of explosives has been pre-programmed, complicated spectroscopy images do not need to be interpreted by an operator. THz radiation is non-ionizing and completely safe, unlike the full-body scanners currently in use in airports around the US.[1]



Figure 1.4: Unlike x-ray imaging, THz imaging can detect a ceramic knife hidden in a shoe, as well as explosives hidden under several layers of clothing.[1]

1.2 THz Radiation Generation and Detection

One of the most frequently used methods of generating THz radiation is the excitation of a photoconductive antenna via an optical laser pulse. The antenna consists of a semiconductor substrate patterned with two metal electrodes separated by a small gap. A bias voltage is applied across the metal electrodes. In the absence of a laser pulse the semiconducting substrate does not conduct the electrons from one electrode to the other, so the electric energy is stored in the gap area. When a laser pulse is focused on the antenna, the incident photons generate electron-hole pairs within the semiconducting substrate, and the electric energy is released. In essence, the substrate acts as an insulator until a laser pulse generates the charge carriers and enables it to act as a conductor, completing the circuit across the electrodes. This configuration is referred to as an optoelectronic switch (Fig. 1.5). The THz electromagnetic radiation arises from two processes- the acceleration of the photogenerated carriers under the bias

voltage and the rapid change of the carrier density via femtosecond laser pumping. The bandwidth of the THz pulse is defined by the fourier transform of the carrier lifetime.[28]



Figure 1.5: THz radiation can be generated through the use of an optoelectronic switch. When charge carriers are generated in a semiconductor material, the circuit between the electrodes is completed and current flows. Once the material relaxes to its pre-illuminated state, the current stops flowing.

Due to a smaller effective mass, electrons usually have much higher mobility than holes. The contribution of holes to the current density can be ignored in most cases. Therefore the current density is

$$J(t) = N(t)e\mu E_b \tag{1.1}$$

where N is density of photogenerated charge carriers, e is the elementary charge, μ is the electron mobility, and E_b is the bias electric field. The charge carrier density N is determined by the laser pulse intensity and the carrier lifetime, and varies in time. The energy of the THz pulse is supplied by the bias voltage rather than the optical pulse energy. However, the optical pulse acts as a transient switch that allows the energy stored across the electrode gap to be released into THz radiation. As more charge carriers are generated, more stored energy is converted into THz radiation. This linear relationship plateaus when the laser fluence is high enough that there is an excess of charge carriers. Likewise, the energy of the THz pulse is linearly proportional to the bias voltage until excess voltage causes dielectric breakdown in the substrate.[95]



Figure 1.6: In a THz detection scheme, the electric field strength of a THz pulse can be sampled by short carrier liefetimes generated by an optical pulse.

A photoconductive antenna can be used as a THz detector as well as an emitter. In order to be used as a detector, the two electrodes of the antenna are connected to a current sensor rather than a power supply. Now the bias electric field across the electrode gap is provided by the incoming THz pulse (Fig. 1.6). A laser pulse is incident on the detector, creating charge carriers with short lifetimes in the semiconductor substrate. The detector will produce a different current depending on whether the laser pulse arrives when the electric field of the THz pulse is low or high. Because of the short charge carrier lifetimes, the THz electric field strength is only sampled for a small portion of the entire waveform. An optical delay line is used to vary the timing of the laser pulse, so that different portions of subsequent identical THz waveforms can be sampled, and a complete depiction of the waveform can be constructed.[95]

In order to optimize the performance of a photoconductive antenna, the semiconducting substrate material, geometry of the electrode gap, and the optical laser pulse characteristics should be considered. Materials with a short carrier lifetime, such as low temperature grown GaAs, are necessary to detect THz pulses containing high frequency components. THz waves are more efficiently generated if the substrate exhibits a high carrier mobility and the charge carriers can easily reach the electrodes. Finally, a high dark resistance is required for a detector in order to have a good signal to noise ratio. [95]

1.3 Additional Optoelectronic Applications

Semiconductor materials for optoelectronic applications have many different properties, including different energy bandgaps, carrier lifetimes, carrier mobility, and resistivity. This section will provide a description of how various combinations of these performance metrics lead to the creation of materials best suited for very different purposes. For each optoelectronic application, a statement of the desirable properties will be given. The optimal properties for THz generation and detection have already been discussed, so here the focus will be on multi-junction solar cells, thermoelectrics, and saturable absorbers.

1.3.1 Multi-junction Solar Cells

The efficiency with which a single junction solar cell can convert solar energy to electrical energy has an inherent limit, known as the Shockley Queisser limit. Only photons with an energy equal to or higher than the bandgap of the junction will be absorbed, while lower energy photons will pass through the device unused. Any energy of the photons that is in excess of the energy needed to excite a valence electron into the conduction band will be wasted as heat.[77] In a multi-junction cell, a series of single junction cells tailored to optimally absorb different portions of the solar spectrum are combined into a single device that is able to overcome the Shockley Queisser limit. In 2012 Solar Junction revealed a multi-junction solar cell capable of converting 44% of incident highly concentrated sunlight into electrical energy.[3] Depicted in Fig. 1.7, the top layer has the largest bandgap and absorbs the highest energy photons, while the lower energy photons pass through to be collected by the lower layers with smaller bandgaps.

An ideal tunnel junction would exhibit a low resistance and a large peak current density. The carrier recombination across a tunnel junction can be increased by the addition of gap states such as those provided by ErAs metallic inclusions. The



Figure 1.7: In a multijunction solar cell, the energy bandgaps are tailored to optimally absorb different portions of the solar spectrum with minimal energy waste through thermalization.[3]

increased tunneling current results from electrons tunneling into the metal particles from the conduction band and then out of the particles into the valence band.[66] The performance of a multi-junction solar cell is also limited by the losses that occur within the tunnel junction interconnects. ErAs particles placed at pn junctions reduce the voltage lost between cells.[98] Understanding of growth parameters, such as temperature and amount of ErAs deposited, has led to further enhancements in tunnel junction conductivity.[57]

1.3.2 Thermoelectric Materials

When there is a temperature gradient in a thermoelectric material, an electric potential is generated via the Seebeck effect. In a metal, we can assume a gas of free electrons. The density of free electrons will be higher at the colder end of the wire because electrons on the hot end will have higher thermal velocities and diffuse more quickly to the cold side. If the thermal gradient across the wire is maintained and the electrons are allowed to build up on the cold end, the separation of charge creates a potential difference capable of driving a circuit. The potential difference created per degree of temperature gradient across the material is called the Seebeck coefficient (S). Although the free-electron model is not valid for semiconductors, their conductive properties do exhibit a temperature dependence, and likewise they can also exhibit the Seebeck effect.[83] Thermoelectric materials are rated by a figure of merit ZT, where a higher ZT translates to higher efficiency:

$$ZT = S2\sigma T/\kappa \tag{1.2}$$

Where σ is electrical conductivity, T is the temperature, and κ is thermal conductivity. A good thermoelectric material has a value of ZT < 1.[53]

Ideally, a thermoelectric material would have high electrical conductivity and low thermal conductivity. Optimizing these properties simultaneously is difficult because mechanisms that scatter phonons also tend to scatter electrons.[38] One way to decouple these properties is to employ small ErAs particles within an InGaAs matrix. The ErAs particles scatter medium wavelength phonons, rendering the thermal conductivity sufficiently low. Meanwhile, because the Fermi level of the ErAs particles lies near the conduction band of InGaAs, the particles donate electrons to the InGaAs matrix.[27] The InGaAs material between the ErAs particles supplies conduction paths around the phonon scattering centers so that high electrical conductivity is maintained.[97]

1.3.3 Saturable Absorbers

Saturable absorption occurs when the absorption of light decreases with increasing light intensity. The drop in absorption is caused by charge carriers in the ground state of a saturable absorber material becoming excited into an upper energy state at a high rate. If the intensity of the light is high enough that the charge carriers do not have sufficient time to decay back to the ground state before the ground state becomes depleted, the absorption saturates. The relaxation rate of the charge carriers determines the dynamic response of the saturable absorber. Although many materials exhibit a small degree of saturable absorption, they often saturate close to the optical damage threshold. Applications such as Q-switched laser cavities, especially compact resonator designs for high repetition rates, require materials with a lower saturation intensity. Semiconductor saturable absorbers can be designed to provide an optimal wavelength range and dynamic response through the choice of material composition and band structure engineering.[45]

1.4 Optoelectronic Properties

Advances in growth techniques now allow the synthesis of new nanocomposite materials that are likely to have interesting combinations of optoelectronic properties and charge carrier dynamics. Once the properties are understood for these new materials, they can be tailored for specific device applications. This work aims to establish the carrier relaxation dynamics in TbAs nanoparticles in InGaAs and GaAs host materials.

Chapter 2 REVIEW OF NANOCOMPOSITES

Chapter 2 provides a basic understanding of the general class of materials investigated here. The chapter begins by defining the term "nanocomposite" before moving on to specifically discuss III-V nanocomposites. I will review the consequences of spatial confinement with a brief summary of quantum dots. Rare earth nanoinclusions will be surveyed at length, which is necessary in order to understand how the following chapters fit within the current body of knowledge. I will conclude with a summary of the open questions regarding TbAs nanoinclusions, which are the focus of the work presented in subsequent chapters.

2.1 General Properties of Heterostructures

A heterostructure is a semiconductor made from two or more different solid state materials. The composition of a heterostructure is varied in order to control the generation, recombination and transport of electrons and holes for various optoelectronic applications. This section aims to provide a short review of some of the concepts associated with heterostructures that will be discussed later in this thesis.

2.1.1 Growth Method: Molecular Beam Epitaxy

In order for a heterostructure to perform well, the interfaces need to be of high quality. Molecular beam epitaxy (MBE) is a method that enables the growth of clean interfaces with minimal contaminants, and provides the opportunity to change the composition of layers from one monolayer to another.[22]

In an MBE machine (Fig. 2.1), the chamber is pumped down to an ultrahigh vacuum, usually 5×10^{-11} mbar or less (in comparison, atmospheric pressure is 1000)


Figure 2.1: Schematic of an MBE machine showing four effusion cells, the sample in a heated rotating holder, and a screen for viewing RHEED.[91]

mbar). At such a low pressure, the mean free path of molecules between collisions is much larger than the width of the MBE chamber. Therefore, when elements are vaporized in furnaces, they form a molecular beam rather than diffusing as they would at high pressure. To grow a heterostructure, the elements that will comprise the final product are heated in effusion cells. When the shutter on an effusion cell opens, the molecules travel in a straight line until they are incident on a substrate. The flux of the element can be controlled by the temperature of the furnace. The substrate is mounted on a heated holder that rotates to ensure uniform deposition. The temperature of the sample must be optimized because if the temperature is too low, defects will arise from the atoms being disordered, but if the temperature is too high, diffusion will blur the interfaces.[22]

Many problems can arise during the growth procedure. The starting materials must be very pure, the background pressure must be kept sufficiently low, and the temperature of both the effusion cells and the substrate must be carefully controlled. Because MBE grows a heterostructure at about 1 monolayer per second (1 micron per hour), it is extremely beneficial to be able to monitor and adjust the process as it is taking place. As an observation method, MBE machines use a technique called reflected high-energy diffraction (RHEED). A beam of electrons is incident on the surface of the sample at nearly grazing incidence. The reflected diffraction pattern is observed on a fluorescent screen. The structure of the surface can be inferred from the intensity and pattern of the RHEED signal.[22]

2.1.2 Band Engineering

Heterostructures are grown with the intention of controlling the motion of electrons and holes for various applications. This is achieved through band engineering. There are three different classifications of band alignments shown in Fig. 2.2, all of which lead to interesting consequences for charge carriers. In a Type I arrangement, the narrower bandgap is enclosed within the wider bandgap. This is referred to as a straddling alignment. An example is the bandgap of GaAs being sandwiched between the bandgap of AlGaAs. Type II alignment is called a staggered alignment. An example is InP and InAlAs, where electrons tend to settle in InP but InAlAs tends to have more holes. In a Type III band alignment, the bandgaps do not overlap at all. Thus this is called a broken gap alignment. In InAs:GaSb, a Type III alignment, the conduction band of InAs overlaps the valence band of GaSb. Electrons and holes transfer from one material to the other until enough like charges build up to repel additional carriers from transferring.[22]



Figure 2.2: An energy diagram of the three types of band alignments of semiconductor heterostructures[90]

2.1.3 Relaxation and Recombination Processes

The recombination of electrons and holes can happen through various mechanisms. Any recombination process must conserve energy and momentum. In order to conserve momentum, often the recombination process involves the vibrating crystal lattice of the material.

2.1.3.1 Radiative Recombination

In a direct bandgap semiconductor, charge carriers can recombine through spontaneous emission. The energy released from the recombination is emitted in the form of a photon. Radiative recombination can also occur when photons are incident on the semiconductor, through stimulated emission.

2.1.3.2 Nonradiative Relaxation and Recombination

Nonradiative relaxation, also referred to as Shockley-Read-Hall (SRH) relaxation, can occur in the presence of trap states provided by misfit dislocations, impurities, or nanoinclusions. The localized energy state provided by a trap enables the requirement of momentum conservation to be satisfied. When an electron with a localized wavefunction relaxes into this localized trap state, it exerts a force on the surrounding atoms. This force deforms the lattice and induces lattice vibrations, referred to as phonons (Fig. 2.3). If the electron recombines with a hole nonradiatively during this process, the localized trap state can absorb differences in momentum between the



Figure 2.3: When an electron with a localized wavefunction relaxes into this localized trap state, it exerts a force on the surrounding atoms. This force deforms the lattice and induces lattice vibrations, referred to as phonons.

carriers. SRH recombination tends to be the dominant process in indirect bandgap materials, but it can also play a major part in direct bandgap materials in the low injection regime.^[76]

2.1.3.3 Auger Recombination

In the high injection regime there is an abundance of free charge carriers. In this case, it is possible for the relaxation energy to be transferred to a third charge carrier instead of being emitted as a photon. The third carrier is excited to a higher energy level, and then typically loses the extra energy in the form of thermal vibrations.

2.1.4 Surface Plasmon Resonance

A resonant oscillation of conduction electrons at the surface of a material can be stimulated by incident light of a specific frequency. When the frequency of the incident light is the same as the frequency of the surface electrons oscillating from the electromagnetic force of positively charged nuclei, a surface plasmon resonance can occur. Because the phenomenon requires the existence of an interface between a material with negative permittivity and one with positive permittivity, surface plasmon resonances occur most frequently on the surface of metals in a dielectric such as air or water.

2.2 Definition of Nanocomposites

Composite materials are made from two or more fundamentally dissimilar materials that, when combined, create a product with characteristics that are different from the individual constituents. The individual constituents remain separate and distinct within the final structure. A nanocomposite is a composite material in which at least one of the constituents has one, two or three dimensions of less than 100 nm, referred to as a nanoparticle or nanoinclusion. The small size of nanoinclusions leads to unique electronic, optical, magnetic, chemical, and mechanical properties in relation to the bulk material. [50] In addition to nanocomposites being found in naturally occurring materials such as human bone, they have also been purposely created for thousands of years. For example, recent characterization of ancient Mayan paintings has revealed that the pigments are actually a matrix of clay and organic colorant molecules. The paints also contained metal and oxide nanoinclusions in an amorphous silicate substrate, which were formed from impurities in the clay during heat treatment. The size of the nanoinclusions affected the optical properties of the paint. [4]. Modern nanocomposites offer many exciting possibilities in device applications, but many of them remain poorly understood.

2.3 Rare Earth Nanoinclusions

The vast majority of this work focuses on TbAs nanoinclusions. Therefore, in this section we will discuss the current knowledge of the electronic structure of TbAs and closely related ErAs nanoinclusions with an emphasis on crystal and band structure, formation of the nanoinclusions, the effect of spatial confinement on band structure, placement of the Fermi level, and the opportunity to create more complex core-shell structures.

2.3.1 Bulk Properties of TbAs, ErAs, GaAs, and InGaAs

Before focusing on the structure of TbAs, ErAs, and GaAs when they are grown into nanocomposites, it may be helpful to review their properties in bulk form. The following chart (Table 2.1) summarizes the relevant properties of bulk GaAs and InGaAs[42] at 300 K, and the known properties of bulk TbAs and ErAs.[11] Note that the band structure of TbAs is currently unknown.

| Material Name | Crystal Structure | Lattice Constant (Å) | Energy Gap (eV) | Material Type |
|------------------|----------------------|-------------------------|--------------------|------------------|
| TbAs | rock salt | 5.813 | | |
| ErAs | rock salt | 5.732 | indirect gap | semi-metal |
| GaAs | zinc blende | 5.653 | 1.424 | semiconductor |
| InGaAs | zinc blende | 5.869 | 0.740 | semiconductor |

 Table 2.1: A summary of the bulk properties of revelant semiconductors and semimetals.

Below are figures depicting the band structure of GaAs 2.4 and ErAs. 2.5 Again, an energy band diagram for TbAs is not available.

2.3.2 Structure of ErAs and TbAs in Arsenic Zinc Blende Semiconductors

The following subsections present a brief history of the growth of ErAs and TbAs in GaAs and InGaAs, as well as some of the structural and material characteristics that were determined as growth techniques were refined.

2.3.2.1 ErAs Epitaxially Grown on GaAs

In the late 1980's the ability to bury metal structures within semiconductors was being investigated in the hope of creating new device applications. The metal and semiconductor blendes of the time were aluminum, silver, iron, and body-centered cubic cobalt epitaxially grown on GaAs.[17, 54, 86, 69] These heterostructures are not thermodynamically stable, preferring to form metal-As and metal-Ga compounds. This led Palmstrøm et al[62] to epitaxially grow ErAs on top of GaAs. Er can be evaporated from a conventional MBE effusion cell. ErAs has a high melting point, has a rock salt crystal structure, and a lattice constant of $a_0 = 5.7427$ Å, which is similar to the lattice



Figure 2.4: Band structure of bulk GaAs. Bulk GaAs is a direct bandgap semiconductor.[58]

constant of GaAs. Palmstrøm noted that GaAs did not wet the surface of the ErAs, and so the lack of overgrowth of GaAs led to island formation.

2.3.2.2 Er Doped GaAs

The atomic 4f optical transition in trivalent erbium (Er3+) occurs at 1.54 mm, which is within the low-loss region of optical silica fibers used in telecommunications.[38] Motivated by the desire to take advantage of this transition, some groups began to investigate GaAs doped with Er. In 1992 Poole et al.[67] used elemental erbium to dope gallium arsenide grown by molecular beam epitaxy. In the range of 540-630 °C the ability of the Er to be incorporated into the substrate had no dependence on the temperature of the GaAs. However, transmission electron microscopy (TEM) results showed the existence of a solubility limit of about 7×10^{17} cm⁻³. Samples with a higher concentration of Er in GaAs displayed a formation of ErAs precipitates. The TEM images indicated a rock salt structure for the precipitates, consistent with ErAs



Figure 2.5: Band structure of bulk ErAs. Bulk ErAs is a semimetal. [23]

crystal structure. The creation of ErAs precipitates was a plausible outcome because ErAs has a lattice constant of $a_0 = 5.732$ Å, which is easily accommodated by GaAs with a lattice constant of $a_0 = 5.653$ Å, when the precipitates are small. The size of the ErAs precipitates increased with increasing GaAs substrate temperature. The growth size could be well controlled in the range of 10-20 Å. An activation energy of 0.63 eV was attributed to erbium transport on the surface during growth. When the substrate temperature reached 630 °C, the epilayers containing erbium began to display misfit dislocations, and the ErAs precipitates were no longer spherical. The following year, Gupta et al.[37] measured carrier lifetimes for GaAs doped with ErAs. Gupta observed a gradual reduction in the lifetime with increased concentration of Er. For a doping concentration greater than 5×10^{19} cm⁻³, the carrier lifetime is around 1 ps.

2.3.2.3 ErAs Nanoinclusions in GaAs and InGaAs

By 1999, Kadow et al. [43] began growing self-assembled ErAs islands embedded in GaAs by molecular beam epitaxy. Kadow showed that the nucleation of ErAs on GaAs occurs in an island growth mode, leading to the formation of nanometer-sized islands. Layers of these ErAs islands separated by GaAs were stacked on top of each other to form a superlattice (Fig. 2.6), which was confirmed via x-ray diffraction. Timeresolved differential reflectance measurements revealed that the carrier capture times corresponded to the period of the superlattice, yielding capture times as short as 120 fs (Fig. 2.6c). These results suggested a future possibility of engineering the response time of the material for device applications by simply varying the superlattice period. Moreover, the size, shape, and density of the ErAs nanoinclusions could be controlled more easily through growth conditions than Er precipitates in Er doped GaAs.[38]



Figure 2.6: a) Schematic cross-section of layers of ErAs nano-islands forming a superlattice in GaAs. b) TEM showing the ErAs nano-islands. c) The time constant $\tau 1$ of the initial transient decay as a function of the superlattice period L.[43]

Rather than using GaAs for the host material, in 2001 Driscoll et al.[27] incorporated ErAs into an InGaAs host and showed via Hall measurements that the resultant nanocomposite is n-type. The free electron concentration increases with increasing ErAs nanoinclusions size. In 2005 Klenov et al.[48] continued work on ErAs:InGaAs using high-angle annular dark-field imaging in scanning transmission electron microscopy (HAADF-STEM) and verified that similar to ErAs:GaAs, the crystal structure of ErAs nanoinclusions in InGaAs is rock salt. He also demonstrated that increasing deposition amounts of Er leads to larger ErAs nanoinclusions due to island coalescence. Klenov pointed out that ErAs nanoinclusion size depends on deposition conditions such as temperature and lattice mismatch.



Figure 2.7: Schematic of the two proposed possible models for the interfaces in $ErAs:In_{0.53}Ga_{0.47}As$ and ErAs:GaAs. Schematics (a)-(c) represent the chain model and (d)-(f) represent the shadow model. The schematics in (b) and (e) view the interfaces along the [110] direction. The schematics in (c) and (f) view the interface along the [110] direction. The spacing labeled d marks the spacing between the last InGa column and the As column in the first ErAs layer.[49]

Later that year Klenov and Zide et al.[49] published another paper, this time focusing on the interface atomic structure of ErAs layers epitaxially grown on both GaAs and InGaAs. Two possible models had previously been proposed[82] for the structure of a rock salt/zinc blende interface. The III-V zinc blende can either end with a layer of As called the "shadow" model, or a layer of Ga or InGa called the "chain" model. The two models are schematically depicted in Fig. 2.7 for ErAs:InGaAs.

HAADF-STEM images along [110] and $[1\overline{10}]$ produced images for ErAs:GaAs



Figure 2.8: HAADF/STEM images of a) ErAs:InGaAs and b) ErAs:GaAs viewed along the [110] direction. The blue dots represent As atoms, and red and yellow dots represent Er and Ga. The configuration of the atoms at the interface for both samples is consistent with the chain model, shown in Fig. 2.7b.[49]

and ErAs:InGaAs that were consistent with the chain model (Fig. 2.8). At the interface for both samples, Klenov observed an increase in Ga and As lattice spacing in order to accommodate the Er atoms in the first monolayer of ErAs.

2.3.2.4 TbAs Nanoinclusions in GaAs

Encouraged by the successes of ErAs III-V zinc blende materials in the world of thermoelectrics, in 2011 Cassels et al.[15] codeposited terbium with gallium arsenide by molecular beam epitaxy and characterized the resulting nanocomposite. Formation of TbAs nanoparticles was confirmed using HAADF STEM (Fig. 2.9). Randomly distributed particles of about 1.5 nm diameter were measured. Cassels observed that the TbAs nanoparticles formed a rock salt structure with a continuous As sublattice between the nanoparticles and the GaAs host matrix.

Optical absorption spectroscopy (OAS) revealed an absorption peak around 1 eV that could be attributed to a plasmon resonance, consistent with previous results for ErAs:GaAs.[75] The absorption peak was unaffected by varying the polarization



Figure 2.9: HAADF STEM plan-view images of 1.5 nm in diameter TbAs nanoparticles in GaAs viewed along the $[00\overline{1}]$ direction. The layer concentration of TbAs is about 1.8%.[15]

of the light, suggesting that the nanoparticles were isotropic in shape and distribution (Fig. 2.10). Resistivity measurements were somewhat inconclusive, since the nanocomposite had a higher resistivity than the range of the equipment, which had a maximum of $2 \times 10^8 \Omega$. Results from time domain thermoreflectance (TDTR) showed that in a sample with a TbAs concentration of around 1.6% the nanoinclusions were able to scatter phonons, reducing the thermal conductivity by around fivefold in comparison to a GaAs control sample. Photoluminescence (PL) measurements were performed on a TbAs:GaAs sample with a TbAs concentration of 1.8% (Fig. 2.11). The addition of the TbAs nanoinclusions quenched the PL, suggesting that the dominant recombination process of free carriers is nonradiative for this nanocomposite. Cassels commented that a lack of PL could suggest that the TbAs states are deep within the GaAs bandgap and a possible metal-like behavior for the nanoparticles.

The next year Cassels published a study of TbAs nanoinclusions in an InGaAs host under her new name Clinger.[18] Although Clinger's work primarily focused on the nanocomposite's potential for thermoelectric applications, this paper is extremely relevant for discussions about the electronic structure of TbAs nanoinclusions. TbAs



Figure 2.10: a) Optical absorption spectra from 1.6% and 1.8% TbAs:GaAs samples display a plasmon resonance peaks near 1 eV. b) For the 1.8\$ TbAs sample the plasmon resonance peak is polarization invariant, suggesting that the nanoparticles are isotropic in shape and distribution.[15]

nanoinclusions were expected to behave very similarly to ErAs nanoinclusions. Instead, Clinger observed the first instance of an electronic difference between them. Although trends in the room temperature thermoelectric measurements of TbAs:InGaAs mirrored those found in ErAs:InGaAs, the peak values in carrier concentration and electrical conductivity occurred at different concentrations for the two nanocomposites. Also, the thermoelectric figure of merit (ZT) was enhanced in TbAs:InGaAs mostly because of its higher Seebeck coefficient, while for ErAs:InGaAs the higher conductivity was the deciding factor (refer to section 1.3.2 for details on thermoelectrics).

2.3.3 Formation of the ErAs or TbAs Nanoinclusions

Epitaxial thin films grow on crystal surfaces in one of three possible modes, determined by the interaction strength between the deposited atoms and the crystal surface. In Volmer-Weber growth (Fig. 2.12a), the interactions of the deposited atoms are stronger amongst each other than between the atoms and the surface. This leads to the formation of 3D islands, so Volmer-Weber growth is also called the "island" growth mode. This is the growth mode through which ErAs and TbAs nanoinclusions are formed. In contrast, in the Frank-van der Merwe growth mode (Fig. 2.12b) the



Figure 2.11: When compared with a GaAs wafer, the photoluminescence intensity from the 1.8% TbAs:GaAs sample is quenched.[15]

deposited atoms interact strongly with the surface. This leads to smooth, fully formed 2D layers. The third growth mode, Stranski-Krastanov growth (Fig. 2.12c), is a mix between the first two modes involving both 2D layer and 3D island growth. Transition from the layer-by-layer 2D growth to the island-based 3D growth occurs at a critical layer thickness which depends on the surface energies and lattice parameters of the substrate and deposited atoms.[60] InAs quantum dots epitaxially grown in a GaAs host form through the Stranski-Krastanov growth mode.

2.3.4 Band Structure of Spatially Confined Rare Earth Nanoinclusions

Although TbAs and ErAs are both semimetallic in bulk form, there has been much debate as to whether they remain semimetals when spatially confined. When the size of at least one of the dimensions of the nanoinclusions is smaller than the size of an exciton, quantum effects can lead to changes in the chemical and electrical properties. In addition, the increasing surface-to-volume ratio of the nanoparticles plays a role in these changes. When sufficiently spatially confined, it is possible that the electronic properties of a nanocomposite will be dominated by the effects of strain from the surrounding matrix rather than the intrinsic properties of the constituents.



Figure 2.12: For three different amounts of surface coverage Θ, Cross-section views of the three primary modes of thin-film growth are shown: a) Volmer-Weber (island formation), b) Frank-van der Merwe (layer-by-layer), and c) Stranski-Krastanov (layer-plus-island).[92]

Strain can cause the band energy levels to shift, conceivably causing a band gap to open and thereby converting a semimetal to a semiconductor.^[75] Zhang et al.^[96] observed just such a transition in ultrafine single-crystalline Bi nanowire arrays embedded in a dielectric matrix. As the diameter of the nanowires decreased, a reversal in the temperature dependence of the magnetoresistance was observed, signaling a semimetal to semiconductor transition.

Another good example of band energy levels shifting as a result of spatial confinement can be seen in a paper by Rogach et al.[71] Rogach explains that bulk HgTe has a negative indirect bandgap of around 0.15 eV at room temperature and therefore acts as a semimetal. However, quantum confinement in HgTe quantum dots should increase their effective bandgap, giving rise to photoluminescence (PL) in the infrared region. Rogach grew colloidal HgTe quantum dots about 3-6 nm in size. As predicted, the quantum dots exhibited PL covering the spectral region from 800 to 1400 nm with a maximum located at 1080 nm, confirming a transition from a semimetal to a semiconductor.

2.3.4.1 ErAs Nanoinclusion Band Structure

By the mid 1990's there had already been some debate as to whether or not spatial confinement in ErAs would lead to a semimetal to semiconductor transition. A simple effective mass model predicts the opening of a bandgap for three monolayers of ErAs buried in GaAs,[6] but tight binding calculations for similar structures (GdAs/GaAs superlattices) predict a crossing of the conduction and valence bands at the X point.[93] A density functional calculation of the bulk band structure of ErAs shows that including quasiparticle energy corrections in the calculation shifts the d states of the ErAs upward, which removes the X crossing.[64] Said et al.[73] then completely reworked the calculation using first principles and concluded that there would indeed remain a crossing. In short, there was no consensus or universally accepted position on the probability of a semimetal to semiconductor transition for spatially confined ErAs.

Said's paper [73] is worth a closer look for the purposes of this thesis. Using density functional theory in the local density approximation, he employs the Linear Muffin Tin Orbital (LMTO) method in the Atomic Sphere Approximation (ASA). He sets up the model for two cases for three monolayers of ErAs embedded in a GaAs host and for a single monolayer of ErAs in GaAs. The model is specified to have an As plane at each interface in the GaAs boundary. This means that the f.c.c. structure of the As sublattice is uninterrupted, which is consistent with the geometry favored by other experiments. [51, 80, 36]

For the case of three monolayers of ErAs in GaAs (Fig. 2.13a), the model shows that the energy bands are not simply the superposition of the ErAs and GaAs bulk bands. Said draws attention to the band shown in blue and the two bands shown in red in Fig. 2.13a. The blue band originates mostly from the d-shell electrons of the Er. The two red bands are mostly from the p-shell electrons of the As atoms at the interface, and they clearly cross the Fermi level and into the blue band, showing that the material is acting as a semimetal. These interface As atoms have dangling bonds which give rise to interface states that pin the Fermi level but have nothing to do with



Figure 2.13: Color added to original figure for clarity. According to an LMTO simulation a) three monolayers of ErAs in GaAs results in the band structure of a semimetal and b) a single monolayer also results in a semimetal due to the overlap of interface states. The red bands are mostly from the p-shell electrons of the As atoms at the interface and the blue band originates from the d-shell electrons of the Er.[73]

the confinement of the ErAs particles. In the case of a single monolayer of ErAs in GaAs (Fig. 2.13b), the increased level of spatial confinement resulted in a pronounced minimum, but it did not result in a semimetal to semiconductor transition either. The interface states have not changed, because the interface geometry has not changed. However, inducing a transition to a semiconductor in the model could be possible by either taking interface relaxation and strain effects into account or changing the lattice registry at the interface. A discussion on shifting the Fermi level to induce a transition will be discussed in section 2.3.5.

In 2008 Scarpulla et al. [75] proposed that quantum confinement can indeed lift the semimetallic band overlap in ErAs nanoparticles for diameters less than 3 nm. Layers of GaAs with embedded epitaxial ErAs nanoparticles were grown at three different deposition temperatures, yielding nanoinclusions of 1.7, 1.8, and 2.0 nm diameter. The samples displayed a strong absorption feature that could be changed in magnitude and peak energy by varying the size and fraction of the ErAs nanoinclusions. Scarpulla reasoned that quantum confinement in the ErAs nanoparticles resulting in the opening of an energy gap could account for the variation of the absorption peak with nanoinclusion size. He then created an effective mass model of a simple hard-walled potential indicating a semimetal-semiconductor transition, which was consistent with the observed absorption feature.

The results of Scarpulla's paper were somewhat controversial. A simple effective mass model such as the one proposed by Allen et al.[6] in 1990 had already been shown to not be sufficient. Also, an alternative explanation for the absorption peak could be found in a 2003 paper from Brown et al.[12] Brown observed an absorption peak in ErAs nanoparticles that increased with ErAs density, which he successfully modeled as a surface-plasmon resonance using a Maxwell-Garnett formulation and semiclassical transport theory that treated the ErAs nanoinclusions as semimetallic. Free-carrier optical effects and quantum-size effects were considered, but Brown stated that the most accurate mechanism was the free-carrier effects, which can be quite strong in semimetallic particles when plasmon resonances occur.

The debate as to whether or not spatially confined ErAs in GaAs displays a semimetal to semiconductor transition was finally laid to rest by Kawasaki et al.[46] in 2011. Although the question had been exhaustively studied via modeling, Kawasaki's paper presented the first direct measurements of the electronic structure of ErAs nanoparticles embedded within a GaAs matrix. Cross sectional scanning tunneling microscopy (XSTM) and spectroscopy (XSTS) revealed that the local density of states (LDOS) of the ErAs particles had a sharp but finite minimum at the Fermi level, indicating that the particles were semimetallic (Fig. 2.14). Kawasaki's results strongly suggest that even though Scarpullas particles were smaller than Brown's, the optical absorption feature he observed was due to surface plasmon resonances as Brown proposed.



Figure 2.14: a) Normalized dI/dV curves (differential conductance spectra) from XSTS measurements on protruding ErAs nanoparticles and the GaAs matrix. GaAs shows a distinct bandgap where dI/dV drops to zero, but ErAs does not. b) Individual differential conductance spectra at varying points directly on top of a particle (0 nm) and moving in steps of 1.3 nm into the GaAs matrix (3.9 nm). ErAs displays a minimum but dI/dV never drops to zero. [46]

Kawasaki also observed a state at 0.2 eV above the Fermi level that decayed with distance across the ErAs:GaAs interface, which he attributed to an interface state. These interface states may be responsible for preventing the opening of a band gap in ErAs. Interestingly, Kawasakis interface and metallic screening model predicts that ErAs films should remain semimetallic down to a critical thickness of 0.15 nm. This 0.15 nm thickness is smaller than a single monolayer (0.287 nm), meaning that it would be physically impossible for an ErAs thin film in GaAs to ever become a semiconductor. He concluded that a simple hard-walled potential model does not provide an accurate description of quantum confinement for embedded ErAs nanoparticles. Interface states must be taken into consideration, as Said had concluded in 1996.

2.3.4.2 TbAs Nanoinclusion Band Structure

The band structure of TbAs is currently unknown. One of the aims of this thesis is to gain insight as to whether or not spatially confined TbAs could possibly exhibit a semimetal to semiconductor transition. Based on Kawasaki's results for ErAs, a transition for TbAs in GaAs seems unlikely. Delaney et al.[23] presented a rigorous theoretical study of the effects of strain on the electronic structure of bulk ErAs, with a comparison of first principles density-functional theory and many-body methods in 2008. Based on this study, we believe TbAs nanoinclusions should behave similarly to ErAs.



Figure 2.15: When the 4f states of Er are treated as band-like states without taking into account the strong Coulomb interactions, these states strongly perturb the band structure, resulting in a model that clearly does not accurately describe the electronic structure of ErAs shown in Fig. 2.5[65]

As discussed earlier (section 2.3.4.1) in relation to Said's work, the valence band

of bulk ErAs is predominantly composed of As p-shell states and the conduction band is mostly Er d-shell states. Delaney explains that the Er f-shell electrons are highly localized and are far from the Fermi energy. They do not hybridize with other states. Therefore Delaney makes use of a frozen core approximation, in which the incompletely filled f-shell of Er is treated as atomic core states instead of band-like states. This treatment avoids the issue of having too high of a density of states at the Fermi surface in the model. Petukhov et al.[65] showed why the frozen core approximation is preferable for the treatment of rare-earth monopnictides. When the 4f states of Er are treated as band-like states without taking into account the strong Coulomb interactions (Fig. 2.15), these states strongly perturb the band structure, resulting in a model that clearly does not accurately describe the electronic structure of ErAs (Fig. 2.5). On the other hand, using the frozen core approximation yields results that are consistent with the known band structure of bulk ErAs.

The only difference between terbium and erbium is that terbium has three fewer f-shell electrons, which should be treated as core electrons that would not affect the opening of a bandgap. Therefore we predict that TbAs will not exhibit a semimetal to semiconductor transition when spatially confined in GaAs.

2.3.5 Placement of the Fermi level

Placement of the Fermi level can be a very important consideration when choosing materials for device applications. As discussed in section 2.3.4.1. Said et al.[73] mentioned that a transition from a semimetal to a semiconductor is conceivable if the interface of the two materials is changed or if the Fermi level is shifted. As another example, current state of the art THz detectors and generators are made from low-temperature grown GaAs[55]or radiation damaged silicon on sapphire.[52] By design, these materials contain a large number of defect states, which leads to problems with low mobility and low dark resistance. This can be solved by instead using ErAs:GaAs, which pins the Fermi level mid-gap resulting in high dark resistance. ErAs has a short lifetime, and the matrix material can be of high quality resulting in high mobility.[44, 61] The main issue with using ErAs:GaAs is that the bandgap of GaAs is inconveniently large. In order to generate THz radiation, the charge carriers must be excited by an optical pulse, which until recently, required a large expensive optical table and highly trained personnel to align it. TeraView, the company mentioned in chapter 1 that is constructing THz systems for medical imaging and security applications, currently uses LT-GaAs that requires an 800 nm modelocked Ti:Sapphire laser.[2] The system is larger and more cumbersome than desired (Fig. 2.16). Although compact, low cost, simple to operate fiber laser are now available with an output of 800 nm, ideally the THz device would operate with 1550 nm light in order to seamlessly interface with the already established 1.5 micron communications infrastructure.



Figure 2.16: TeraView, the company mentioned in chapter 1 that is constructing THz systems for medical imaging and security applications, currently uses LT-GaAs that requires an 800 nm modelocked Ti:Sapphire laser[1]

Changing the host material would in theory be a simple way to change the excitation wavelength needed. Absorbing at wavelengths up to 1.67 μ m, InGaAs latticematched to InP is a tempting choice. In this case though, the metallic ErAs inclusions in InGaAs no longer pin the Fermi level in the middle of the bulk bandgap (Fig. 2.17), instead causing an unfortunate n-type background doping of the surrounding narrow gap InGaAs. The resulting material needs to be compensated with p-type dopants in order to suppress the dark current to a usable level.[35] In the past, ErAs nanoislands



Figure 2.17: Metallic ErAs inclusions in InGaAs no longer pin the Fermi level in the middle of the bulk bandgap, as they do in a GaAs host.[14]

codeposited with Be-compensated InGaAs on an InP:Fe substrate has yielded a 3.2 ps carrier lifetime in optical-pump terahertz-probe experiments, which is a promising result for THz communications.[8] However, an alternative route would be to change the host matrix to a material with the desired bandgap, and then purposely shift the Fermi level so that it is pinned within the host bandgap.

2.3.5.1 Controlling the Fermi Level

One of the possible ways to shift the Fermi level of a nanocomposite is by varying the material used for the nanoinclusions. This will be discussed in the next section. Another method is to vary the amount of material deposited for the nanoinclusions. Driscoll et al.[27] successfully implemented this method using layers of ErAs islands embedded in an InGaAs/InAlAs matrix. As the amount of deposited ErAs is increased, the calculated value of the Fermi level decreases from 0.008 eV above the InGaAs conduction-band edge to 0.14 eV below the InGaAs conduction-band edge (Fig. 2.18). As mentioned earlier, interface states can greatly influence the electronic structure. It is possible that as the size and shape of the ErAs particles change, the density and distribution of interface states change as well. Changing the band offset between ErAs and InGaAs interface states at the ErAs:InGaAs boundaries could then affect the Fermi



Figure 2.18: Observed activation energy E_a and the InGaAs conduction band edge energy E_{CB} minus the calculated Fermi level E_F plotted vs ErAs deposition. The temperature dependence of $E_{CB} - E_F$ for each sample is shown.[27]

level.

2.3.5.2 Prediction of the Fermi Level in TbAs Nanoinclusions

As discussed earlier, the most accurate models of band structure for rare earth monopnictides employ a core-shell approximation, in which the f-shell electrons of the rare earth nanoinclusions are considered core-shell electrons far away from the Fermi level.[65] Therefore we follow the computational predictions for strained ErAs completed by Delaney et al.[23] in order to predict the placement of the Fermi level in TbAs nanocomposites. Applying Delaney's results, we expect the tensile strain caused by the presence of the TbAs nanoinclusions to raise the Fermi level to an energy above a universal donor level. Meanwhile we expect that compressive strain will lower the Fermi level of the matrix down below the universal donor level, toward the valence band. We estimate that the 3% compressive strain of TbAs in GaAs will pin the Fermi level near midgap, while the 0.9% tensile strain of TbAs in InGaAs will pin the Fermi level of TbAs:InGaAs near the conduction band edge(Fig. 2.19).[15, 18]



Figure 2.19: Cassels estimates that the 3% compressive strain of TbAs in GaAs will pin the Fermi level near midgap, while the 0.9% tensile strain of TbAs in InGaAs will pin the Fermi level of TbAs:InGaAs near the conduction band edge.[14]

Resistivity measurements of TbAs:GaAs yielded no reportable values because the resistance was greater than the equipments maximum capability of $2 \times 10^8 \Omega$. If TbAs nanoinclusions pin the Fermi level deep within the GaAs bandgap, they could act as Shockley Read Hall combination centers. This would be a plausible explanation for a nanocomposite that exhibits very poor electron conductivity.[15] Clinger et al.[18] measured the electrical and thermal transport properties of TbAs:InGaAs nanocomposites of various TbAs concentrations for possible use in thermoelectric applications. Clinger reasoned that ErAs nanoinclusions in InGaAs pin the Fermi level above the conduction band,[98] but TbAs nanoinclusions would pin the Fermi level below the conduction band due to the smaller lattice mismatch and accordingly smaller tensile strain. This difference in the band structure was presumed to lead to improved thermoelectric performance. Clinger observed that TbAs:InGaAs displays a large Seebeck coefficient with good electrical conductivity, consistent with the prediction that TbAs:InGaAs would pin the Fermi level just below the conduction band.

2.3.6 Core Shell Structures

When choosing materials for device applications, there is often no single "best" choice. Instead, the decision must balance the advantages and drawbacks that each material can provide. Consider the current materials available for THz applications. Low-temperature grown GaAs provides the fast carrier trapping time needed for THz generation and detection, but because the response time and dark resistance are both controlled by growth and annealing temperature, they cannot be independently tuned. [26] ErAs nanoinclusions in GaAs allows these two properties to be decoupled, but GaAs-based materials cannot be excited with 1.55 micron photons- the primary wavelength for fiber optic lasers. [61] Devices incorporating ErAs nanoinclusions in InGaAs can operate in a convenient wavelength range, but the ErAs nanoinclusions pin the Fermi level above the conduction band. This is undesirable in applications requiring a high dark resistance. [98, 38]

In this thesis, we explore the electronic properties of TbAs nanoinclusions in GaAs and InGaAs, which may exhibit desirable characteristics as previously discussed. If TbAs does not provide the fast relaxation rates needed for applications like THz generation, it is possible that a core-shell nanoparticle made of ErAs and TbAs might be of use. When both Er and Tb are co-deposited to InGaAs nominally lattice-matched to InP, a core-shell nanoparticle forms through a strain-driven process. The resulting core-shell structure is comprised of a core mix of ErAs and TbAs, with a TbAs shell surrounding it.[26] We postulate that the TbAs shell could pin the Fermi level below the conduction band as discussed in section 2.3.5.2., resulting in a high dark resistance. Meanwhile, the ErAs in the core could provide the short carrier lifetimes needed for THz applications.

2.4 Open Questions for TbAs Nanoinclusions

Nanocomposites made with TbAs nanoinclusions are a largely unstudied class of materials with promising device applications. TbAs nanoinclusions have been successfully grown in both GaAs and InGaAs.[15, 18] TbAs:GaAs most likely pins the Fermi level mid-gap and has displayed evidence of a possible indirect bandgap, but a verification of this would be helpful. It is unknown if TbAs will exhibit a semimetal to semiconductor transition when spatially confined. We also do not have any knowledge of the relaxation dynamics of the charge carriers, and consequently whether or not TbAs nanoinclusions will provide the fast relaxation rates needed for THz applications. TbAs:InGaAs displays a large Seebeck coefficient with good electrical conductivity, consistent with a Fermi level that is pinned just below the conduction band. Again, more research is needed in order to unambiguously describe the electronic structure. A new and exciting material can be grown by forming a core-shell structure with TbAs and ErAs in an InGaAs host.[26] The electronic structure of this material is entirely unknown at present. The objective of this thesis is to use ultrafast optical spectroscopy methods to probe the electronic and optical properties of TbAs:GaAs and TbAs:InGaAs, and to use these experimental results to infer the underlying electronic structure of the materials.

Chapter 3

OPTICAL PUMP TERAHERTZ PROBE TRANSIENT ABSORPTION SPECTROSCOPY

3.1 Pump Probe Spectroscopy

Pump probe spectroscopy's purpose in characterizing materials is twofold. First, the ability to use ultrashort pulses allows for the probing of charge carrier relaxation processes on sub ps timescales. Second, pump probe spectroscopy uses a change in probe pulse absorption to investigate charge carrier dynamics, which offers a more flexible approach than techniques that rely on photoluminescence (Fig. 3.1). Timeresolved photoluminescence (TRPL) for example, can determine lifetimes for carriers that radiatively recombine. In a TRPL experiment, a laser pulse generates and/or excites charge carriers. These carriers will relax quickly to the band edge or lowest energy state and then recombine and emit a photon. The photons emitted from the sample are collected over a period of time after the optical excitation. A histogram of photon counts per unit time is built up from the collected photons, and an exponential decay curve can be fit to the histogram in order to extract a recombination rate. In contrast, transient absorption spectroscopy can probe the relaxation of charge carriers from higher energy levels within a discrete density of states. The presence of charge carriers in the valence and conduction bands limits the number of available states, and subsequently the number of optical transitions that would lead to a change in probe absorption. As a result, the relaxation dynamics can be viewed regardless of whether or not a photon is emitted, allowing nonradiative relaxation and carrier recombination to be studied.

A well-cited example that demonstrates the usefulness of transient absorption spectroscopy is the investigation of the carrier dynamics in graphene. Graphene is a



Figure 3.1: a) In a time resolved photoluminescence experiment, electrons are excited across the bandgap (1) and then quickly relax to the lowest energy level (2). Electrons recombine radiatively with holes in the valence band and emit a photon (3), which is collected and counted. b) In a transient absorption spectroscopy experiment, processes (1) and (2) are unchanged, but rather than counting photons, the absorption of a probe beam (3) is analyzed to extract relaxation dynamics.

two-dimensional sheet of carbon atoms that are arranged in a hexagonal lattice, which results in a zero-gap semiconductor (Fig. 3.2a). In order to understand the nonequilibrium carrier dynamics as well as the rate at which electron-hole recombination occurs, pump probe spectroscopy was employed. Optical pump optical probe (OPOP) spectroscopy yielded insight into the intraband relaxation dynamics of photogenerated electrons and holes,[81] probing the time evolution of the carrier occupation at specific energies in the conduction band. Optical pump THz probe (OPTHzP) spectroscopy revealed the interband carrier recombination dynamics,[34] which is affected by the carrier density and material disorder. Fig. 3.2b shows a schematic representation of the intra and interband relaxation processes of graphene.

In a transient absorption spectroscopy experiment, a fraction of the electrons in a material are optically promoted to an excited state through an incident laser pump pulse.[9] In semiconductor materials, electrons and holes are generated in the conduction and valence bands, respectively. A probe pulse is directed through the sample with a delay τ with respect to the pump pulse. The intensity of the probe pulse



Figure 3.2: a) An OPTHzP experiment can probe the carrier recombination across the zero-bandgap in semiconducting graphene. b) Optically excited, nonequilibrium electron and hole distributions approach equilibrium. After excitation, the distribution rapidly thermalizes. The hot thermally distributed carriers are then cooled further due to intraband phonon scattering, studied with OPOP spectroscopy. OPTHzP spectroscopy reveals the final relaxation process, where electrons and holes recombine until the equilibrium distribution is restored.[34]

is selected to be of low enough intensity that multiphoton processes are suppressed. A difference absorption spectrum ΔA is then calculated using the absorption spectrum from the excited sample and the sample in the ground/relaxed state. Varying the time delay between the pump and the probe pulses and recording a ΔA spectrum at each time delay results in a ΔA spectrum as a function of time τ and wavelength λ .

Depending on the energy of the pump and probe pulses and the energy structure of a semiconductor material, the probe pulse can exhibit a transient absorption or a transient bleach (Fig. 3.3). In both cases it is the change of absorption of the probe pulse that is measured. For a transient bleach, the pump beam generates charge carriers that fill available states. Due to the decrease in available states, the probe beam will experience a small dip in absorption, referred to as a bleach. There is a significant absorption of the probe regardless of the presence or absence of the pump pulse because the probe can excite carriers across the gap. Thus the $\Delta/background$ due to the presence of the pump is very small. In contrast, the energy of the probe pulse in a transient absorption experiment is smaller than the energy required to generate charge carriers and separate them across the bandgap. No probe absorption is possible without pump-generated carriers, thus the $\Delta/background$ is much larger.



Figure 3.3: A probe beam that is set to an energy that is just above the bandgap will exhibit a transient bleach (top). A probe beam with an energy that is lower than the bandgap will only be absorbed after the pump beam generates charge carriers in the conduction and valance bands, and will exhibit a transient absorption (bottom).

3.2 Ultrafast Lasers

In order to successfully perform a pump probe experiment, several laser requirements must be met. In all of the experiments performed in this thesis, ultrashort pulses around 60-100 fs were used in order to gain short time resolution in the measurements. Every experiment relied on second order optical effects for the creation of the probe beam, and so the laser pulses needed to have a high enough intensity to achieve the desired spectrum. A 1 kHz repetition rate balanced the need for high energy pulses with the need for a timely collection of data. This section details the performance of the oscillator and regenerative amplifier used in all three experiments.

3.2.1 Tsunami Oscillator

The purpose of the Tsunami oscillator is to produce a train of laser pulses from a continuous wave (CW) laser source. This process is referred to as "mode-locking".

The two defining features of the Tsunami are the titanium doped sapphire (Ti:sapph) gain medium and the optical cavity. The Ti:sapph solid-state gain medium is pumped by a a Verdi laser, a diode-pumped solid state (Nd:YVO₄), frequency doubled laser that supplies a 532 nm continuous wave seed beam. The Verdi output creates a population inversion in the ti:sapph, which then lases with a center wave-length around 800 nm. The optical cavity is constructed from two plane mirrors on either side of the ti:sapph, in a Fabry-Pérot configuration. The 800 nm light produced by the gain medium reflects off of the end mirrors of the cavity and produces standing waves. The only frequencies of light that are not suppressed by destructive interference are the longitudinal modes of the optical cavity. The longitudinal modes (ν) are defined by the distance between the end mirrors (L), such that

$$\nu = nc/2L \tag{3.1}$$

where n is an integer and c is the speed of light.[72]

In CW mode, each of these longitudinal modes oscillates independently with no fixed relationship between each other. The output intensity of the Tsunami varies in time, with the time distribution depending on the phase relation between the different modes. As shown in Fig. 3.4a the oscillation in intensity of a single mode is small. The oscillation in intensity is larger when a second mode with the same phase is added (Fig. 3.4b). If eight modes of different phases are added together (Fig. 3.4c), the resultant time distribution of intensity varies randomly. When eight modes travel in phase together, the result is a periodically appearing wave packet or pulse train, forming from constructive interference. These modes are said to be mode-locked.[72]



Figure 3.4: A single mode (a) results in a low, constant intensity. Two modes in phase (b) result in a small oscillation in intensity. Eight modes with random phases (c) result in a random distribution of maxima. Eight modes with the same phase (d) produce a periodic repetition of a wave packet.[72]

The pulsewidth of each wave packet is inversely proportional to the number of modes traveling in phase with each other. If there are N modes locked with a frequency separation $\Delta \nu$, the bandwidth will be $N\Delta \nu$. A wider bandwidth will yield a shorter pulse duration, in keeping with the time-energy uncertainty principle $\Delta t\Delta \omega \geq 1/2$.

The Tsunami passively modelocks the 800 nm light using a nonlinear effect called Kerr lens mode-locking. In order to be passively modelocked, the following conditions must be met: 1) Pulsed mode must be favored over CW mode. 2) The system must shorten the pulses. 3) Something must begin the mode-locking process.[72]. For sufficiently high intensities, the ti:sapph gain medium exhibits a refractive index that varies with laser intensity (I). The refractive index is given by

$$n(\omega, I) = n_0(\omega) + n_2(\omega)I \tag{3.2}$$

where $n_0(\omega)$ is the refractive index under low intensities and $n_2(\omega) \ll n_0(\omega)$. The intensity dependence in equation 3.2 arises from the electric field of the laser inducing a nonlinear polarization of the atomic electron shells of the ti:sapph, called the Kerr effect. For ti:sapph $n_2(\omega)$ is positive, meaning that the higher intensity portion of the laser will experience a stronger refraction. When a laser beam with a Gaussian radial intensity profile passes through the ti:sapph gain medium, the ti:sapph will act like a converging lens, with the focal length depending on the laser intensity. This phenomenon is called self focusing.[25]

Because the strong intensity portion of the laser is more strongly focused and reduced in diameter, it is less subject to losses inside the cavity. In this way, strong intensity maxima are favored at the expense of weak ones,[72] which satisfies condition (1). A sharp aperture can be placed in the beam path in such a way that only the tighter focused high intensity portion of the laser is let through the slit, while the lower intensity portion is attenuated. On every round trip inside the cavity, the pulse duration is shortened,[25] satisfying condition (2). This process is illustrated in Fig. 3.5.



Figure 3.5: Kerr lens modelocking is used for ti:sapphire lasers. This technique combines the effect of self-focusing with an aperture. The beam diameter of the pulsed mode is smaller than the diameter of the CW mode due to self focusing inside the gain medium.

To begin the pulsed mode a quick jolt is given to the optical path, which creates a pulse of higher intensity. This higher intensity mode is favored over the others, so the other modes are attenuated, thus satisfying condition (3).

A simplified schematic of the Tsunami oscillator is depicted in Fig 3.6. The design essentially follows the concept first described by Spence, Kean, and Sibbett in 1991.[79] The ti:sapph is pumped by a 532 nm CW laser through Mirror 1, which is a dichroic mirror that is transparent at 532 nm but reflects the 800 nm emission wavelength of the ti:sapph. The two prisms compensate for the dispersion of the group velocity (see Chapter 6 for more details on group velocity dispersion) inside the cavity. The aperture assists in the mode-locking as described earlier. The result is a train of pulses between 60 and 100 fs in duration with a center wavelength of 800 nm. The power output of the Tsunami is usually somewhere between 365 and 400 mW and the bandwidth around 40 nm FWHM.



Figure 3.6: Most lasers use concave mirrors instead of lenses for Kerr lens modelocking. Prisms are used for dispersion compensation.

Note that the cavity alignment for max CW power is not the optimum alignment for mode-locked operation. An important aspect of Kerr lens mode-locking is the difference in cavity alignment, which enhances the preference for mode-locked operation. The reason for this arises from the Kerr effect looking like a slight positive lens. During pulsed mode, the end mirrors of the cavity should be brought slightly closer together to collimate the pulsed beam. In CW mode, this alignment would result in a slightly diverging beam and a degraded power output. [13]



3.2.2 Spitfire Regenerative Amplifier

Figure 3.7: In chirped pulse amplification, a short laser pulse is expanded in pulsewidth via a grating pair, amplified to an intensity that is below the amplifier damage threshold, and then compressed in pulsewidth to produce a short, high intensity pulse.[84]

Whether the transient absorption experiment makes use of a THz probe or an optical probe, the probe generation requires a high intensity pulse. The Tsunami output supplies pulses with a sufficiently short duration to probe with the desired time resolution, but the intensity of the pulses is not high enough to change the pulse spectrum to the desired wavelengths. The Tsunami output can be amplified using another ti:sapph crystal, but pulse intensities occuring within the gain medium can grow too high due to nonlinear processes such as self focusing. These intensities are higher than the damage threshold of the ti:sapph. The issue can be circumvented using chirped pulse amplification, described in Fig 3.7. Before amplification, the pulse is first
stretched using a grating and mirror pair. With a reduced peak power, the pulse can now safely be amplified using the ti:sapph gain medium. After amplification the pulse is compressed back to its original pulse duration. The Spitfire regenerative amplifier makes use of this technique, with a 1 kHz repetition rate.



Figure 3.8: Diagram of the beam paths inside the Spitfire regenerative amplifier in Dr. Matthew Doty's laboratory. Pulses are first expanded in pulsewidth in the stretcher, gain energy in the oscillator cavity and amplifier, and finally are compressed.

A schematic of the Spitfire regenerative amplifier in Dr. Doty's laboratory is shown in Fig 3.8. This particular Spitfire was custom-built by SpectraPhysics to allow for amplification of ps pulse durations as well as fs. Although we presently make use of the fs amplification capability, the existence of the set of ps amplification optics alters the beam path layout a bit from the standard Spitfire design. The regenerative amplifiers used in Chapters 4, 5, and 7 are both of the standard Spitfire design, but the amplification process is essentially the same as seen here. The seed beam from the Tsunami enters the regen in the top left corner of Fig 3.8, where the stretcher lengthens the pulse duration to several hundred ps.[72] The stretched beam enters the oscillator cavity (bottom right), where the pulses are regeneratively amplified. Once the pulses are released from the cavity, they enter the amplifier (center of the diagram), which uses the concept of multipass amplification. Finally the pulses pass through the compressor (top right) where the pulses are shortened to their original pulse duration of 60-100 fs.



Figure 3.9: Schematic of a stretcher made with a grating pair. The longer wavelengths travel a shorter distance, which adds positive dispersion to the pulse. The output is a pulse with a positive chirp.[89]

The first stage of the regenerative amplifier, referred to as the "stretcher", is designed like a grating pair (Fig 3.9). In reality, there is only one grating (optic 11 in Fig 3.8) and a mirror (optic 12 in Fig 3.8) placed at the focal plane is used to reflect the beam onto the same grating twice. Also, a large gold spherical mirror (optic 13 in Fig 3.8) is used to collimate the beam instead of a lens. However, the concept is the same. The longer wavelengths of the seed beam pulse are reflected off of the first grating at a smaller angle than the shorter wavelengths, causing the pulse to diverge according to wavelength. When the pulse is spectrally spread out in space, it is reflected off of the shorter wavelengths, so the longer wavelengths emerge from the grating before the shorter ones. In this way, the pulse duration is stretched and given a positive chirp.[13] The

pulse train that leaves the stretcher via mirror (optic 14 in Fig 3.8) has a repetition rate of about 82 MHz.

The stretched seed pulse enters the oscillator cavity, where it is trapped in a laser resonator. Inside the cavity, a ti:sapphire crystal (optic 17 in Fig 3.8) acts as the gain medium for the seed beam. The ti:sapph is pumped by about 3/5 of the power from a 20 W continuous wave Evolution laser. The Evolution is a diode-pumped, intracavity, frequency doubled Nd:YLF laser that contains two acousto-optic Q-switches. The Evolution output has a center wavelength of 532 nm (shown in green in Fig 3.8), and creates a population inversion in the same manner as in the Tsunami. In this case, however, the seed pulse initiates a stimulated emission process within the pumped ti:sapph and picks up the emitted photons. The pulse makes several passes through the ti:sapph, each time stimulating the emission of more photons until it has extracted all of the energy stored in the gain medium.

The pulse is let into and out of the oscillator cavity using Pockels cells and broadband polarizers. The first Pockels cell (optic 33 in Fig 3.8) is initially set to be equivalent to a quarter-wave plate. The first cell allows each seed pulse to enter the cavity and make one round trip. Before the evolution pulse is incident on the ti:saph rod, none of these seed pulses is amplified. The first pulse that arrives after the arrival of the evolution pulse is amplified. At this time, the voltage across the Pockels cell is switched, flipping the polarization to a half-wave plate so that none of the next few seed pulses are allowed to pass through the gain medium. While the pulse is making several round trips, the second Pockels cell (optic 38 in Fig 3.8) is set to also be a halfwave plate. On each round trip, the pulse is transmitted through a Brewster window (optic 36). When the pulse has reached its maximum energy, the polarization of the second Pockels cell is flipped and it becomes a quarter-wave plate. Now the pulse is reflected off of the Brewster window and is dumped out of the cavity to optic 40 in Fig 3.8. After this stage the energy is about 1.5 mJ/pulse and the repetition rate is 1 kHz.

The pulse then enters the amplifier stage, where the power is boosted by another

0.5 mJ/pulse. In this stage, the remaining 2/5 of the power from the Evolution laser pumps another ti:sapph crystal (optic 43 in Fig 3.8) in what is known as a multipass or bowtie configuration. This amplifier works on the same principle as regenerative amplification, making use of a population inversion and stimulated emission, except that in this case the different passes in the amplifier are separated geometrically.[72] The pulse completes two passes through this ti:sapph before entering the compressor.



Figure 3.10: Schematic of a compressor made with a grating pair. The shorter wavelengths travel a shorter distance, which adds negative dispersion to the pulse. The output is a beam that has been dispersion compensated.[89]

The compressor stage of the regen compensates for the dispersion introduced by the stretcher. The process is schematically represented in Fig 3.10, but as in the case of the stretcher, the pulses in the regen make two passes on a single grating (optic 53 in Fig 3.8) instead of traveling through a grating pair since gratings are expensive. Again, the process is conceptually the same as shown here. After amplification, the positively chirped beam enters the compressor. Now it is the shorter wavelengths that travel a shorter distance, which adds negative chirp to the pulse. The result is a dispersion compensated, high intensity pulse with a pulsewidth between 60 and 100 fs and a 1 kHz repeition rate.

3.3 Experimental Design

The optical pump THz probe transient absorption spectroscopy data presented in Chapters 4 and 5 was taken in collaboration with Los Alamos National Laboratory. I flew out to Los Alamos to direct the data collection on their equipment, which has the capability of producing a THz probe. The Los Alamos system begins in the same manner as our system. The output of a Tsunami oscillator is fed into a standard 1 kHz repetition rate Spitfire regenerative amplifier, resulting in an output of 800 nm center wavelength, 60 fs pulses with an energy of at least 2 mJ/pulse.



Figure 3.11: Overall design of the optical pump THz probe transient absorption spectroscopy experiment at Los Alamos National Laboratory.

The output is then split into the pump and probe beams, as shown in Fig 3.11. The probe beam passes through a zinc telluride (ZnTe) crystal, which generates THz radiation through optical rectification.[68] The result is a 0.1-2.75 THz probe beam with a power of around a hundred nW. The pump beam is taken directly from the regen, and so it remains 800 nm with a power of several hundred mW. The pump beam passes over a mechanical delay stage, which shortens the path of the pump with respect to the probe beam. This difference in path length causes a variation in the time delay between when the sample is excited by the pump beam and when the probe beam passes through the sample. The delay stage is capable of producing a time delay of up to 400 ps. The sample is mounted in a helium cooled cryostat capable

of lowering the sample temperature to 4.5 K. Reflection measurements of the probe beam are made with a bolometer. The signal to noise ratio is improved with the use of lock-in detection.

3.3.1 THz Probe Generation

The generation of THz fs pulses depends on the creation of a polarization P(t) that varies on a short timescale. When viewed from far away, the emitted electric field from a point source is proportional to the second time derivative of the induced polarization.[72] This transient polarization can be generated in a couple of different ways. Photoconductive switching was discussed in Chapter 1, and is one of the opto-electronic applications for which TbAs is being investigated. The THz probe used in the following experiments is generated from optical rectification, sometimes referred to as the electro-optic effect.

The induced polarization in a material can be written as a Taylor expansion of the incident electric field. If we keep only the first two terms, the induced polarization can be written as

$$P(t) = \chi^{(1)} E(t) + \chi^{(2)} E(t)^2.$$
(3.3)

 χ is known as the susceptibility. If the material is excited by the electric field from an incident laser pulse, the electric field is given as

$$E(t) = A(t)\cos(\omega_0 t) \tag{3.4}$$

where A(t) is the pulse envelope and ω_0 is the frequency. For a nonlinear material, the polarization will not be equal for the two opposite directions of the pulse's electric field, and the $\chi^{(2)}$ term of the induced polarization (Eq. 3.3) will not vanish. The nonlinear polarization can be split into two terms:

$$P^{(2)}(t) = \chi^{(2)} E(t)^2 = 1/2\chi^{(2)} A(t)^2 + 1/2\chi^{(2)} A(t)^2 \cos(2\omega_0 t).$$
(3.5)

The second term of 3.5 is responsible for second harmonic generation, which is covered in Chapter 6. The first term represents the average of the induced polarization over a single optical cycle. Because the material is nonlinear, this term will never be zero and will always point in the same direction. For a short laser pulse, this optical rectification results in the generation of a transient polarization that follows the form of the pulse intensity in time.^[72]

When selecting a nonlinear material for THz fs pulse generation, three considerations are the nonlinearity of the material, absorption of both optical and THz waves in the material, and the coherence length of the optical rectification process. ZnTe crystal is currently considered to be the most favorable material to generate THz waves excited by 800 nm fs laser pulses.[95] Thus, ZnTe was chosen for the generation of the THz probe.

It might seem strange to investigate a new material for constructing an optoelectronic device for THz generation when there are already materials in existence that are capable of instantaneously producing THz radiation through optical rectification. It is therefore worth noting that although optical rectification can produce frequencies up to 50 THz, the process relies on existing nonlinear coefficients and is not very efficient. In a photoconducting switch, a large voltage can be switched by the laser pulse, resulting in a much higher efficiency.[72]

3.3.2 Lock-in Detection

In a transient absorption experiment, the value of ΔA is often very tiny in comparison to the overall intensity of the probe beam. In addition, the intensity of the probe beam is not perfectly stable due to fluctuations in the laser output. One way to dramatically improve the signal to noise ratio is to utilize a method called lock-in detection. In this data collection scheme, the bolometer used to collect the reflected or transmitted probe beam is paired with a lock-in amplifier. The concept behind a lock-in amplifier is that even when the signal is not distinguishable from the underlying noise in the time domain, the signal can be separated from the noise in the frequency domain if the signal has a definite frequency band. Therefore the ΔA signal is modulated using a chopper wheel placed in the pump beam path. The lock-in amplifier is then referenced to the frequency of the chopper wheel. The frequency of the chopper wheel is carefully selected to avoid the frequency of ambient laboratory lighting and electronics, and any higher order harmonics from them as well.

Chapter 4

TERBIUM ARSENIDE NANOPARTICLES IN GALLIUM ARSENIDE

4.1 Introduction

Carrier relaxation and transport dynamics in semiconductors are extremely sensitive to the electronic structure of traps, dopants or nanoparticles. Control over these carrier dynamics is often essential for development of new optoelectronic devices, as discussed in Chapter 1. For example, THz sources generating radiation via optoelectronic switches require materials with fast carrier relaxation times, but thermoelectrics require materials that minimize carrier relaxation. Embedding rare-earth nanoparticles in III-V semiconductors can drastically alter the carrier dynamics. Previous work on ErAs nanoparticles demonstrates that it is possible to precisely control carrier dynamics by varying the size, composition and spacing between layers of the particles.[43, 7, 16, 61, 68]

TbAs nanoparticles are in the same class of materials as ErAs and may provide another opportunity for tunable control of carrier dynamics. TbAs has a lattice constant of 5.815 Å while ErAs has a lattice constant of 5.734 Å.[11] Therefore the lattice mismatch in TbAs:InGaAs is smaller than for ErAs:InGaAs when the InGaAs is lattice matched to InP (lattice constant 5.87 Å). The smaller mismatch and consequently reduced strain could lead to more favorable electronic properties for certain types of applications. As mentioned in Chapter 2, ErAs nanoparticles reduce the thermal conductivity of GaAs by scattering phonons, increase the Seebeck coefficient through energy-dependent electron scattering, and increase electrical conductivity by donating electrons to the conduction band.[97, 98] TbAs may offer similar possibilities.[15]

In order to control the electronic properties of TbAs nanoparticles in III-V semiconductors, the electronic structure of the particles must first be understood. One of the fundamental questions concerns the relaxation time of charge carriers within a TbAs nanocomposite. In this chapter we describe a study of the electronic structure of TbAs nanoparticles epitaxially grown within GaAs using an analysis of the ultrafast relaxation processes of optically excited carriers. Ultrafast pump probe experiments have been used extensively to investigate charge carrier dynamics in semiconductors, particularly for materials with potential optoelectronic applications. [59, 8] Trapping and relaxation processes, which typically occur on ps timescales, are of particular importance in devices where recombination via trap states may limit the device performance or the repetition rate at which the devices can operate. A high fluence optical pump optical probe experiment has been previously used to investigate trap saturation and Auger recombination in low temperature grown GaAs. [78] Optical pump THz probe techniques have also been used to measure short carrier relaxation times and high effective mobilities in radiation-damaged silicon on sapphire. [52] Pump probe studies of ErAs:GaAs have shown sub-picosecond relaxation times, with fast recombination through the ErAs nanoparticles enabling the nanocomposite to return to a pre-illuminated state in only a few picoseconds. Encouragingly, these recovery times vary with superlattice period and pump fluence. [68] Building on these techniques, this experiment uses a fluence dependent optical pump THz probe method to probe the dynamics of carrier relaxation in TbAs:GaAs.

4.2 Experimental Design

The concept of pump probe spectroscopy is covered extensively in Chapter 3, which also offers an in-depth explanation of the ultrafast laser systems used in this experiment. The experimental practices that are unique to a THz probe system are also explained in Chapter 3. The sample was grown by Cory Bomberger at the University of Delaware. I traveled to Los Alamos National Laboratory in order to collect THz probe data on our TbAs:GaAs sample via a collaboration with the Center for Integrated Nanotechnology (CINT), a Department of Energy Basic Energy Science user facility.

4.2.1 Sample Fabrication

A TbAs:GaAs sample was grown on a (001) undoped GaAs substrate with a 50nm thick GaAs buffer layer. The growth was completed using an OSEMI NextGEN solid-source molecular beam epitaxy (MBE) system, equipped with effusion cells for Ga and Tb, and a two-zone valved cracker source for As. The substrate temperature was 490°C measured by band edge thermometry. Terbium was codeposited with gallium and arsenic, with the amount of terbium being in excess of the solid solubility limit of Tb in GaAs (Fig. 4.1). TbAs precipitated out of solution, resulting in nanoparticles of an estimated size of 1.1 nm. No capping layer was grown on top of the TbAs:GaAs layer. Growth and thermal desorption of oxides were monitored with reflection highenergy electron diffraction (RHEED). A GaAs growth rate of 1μ m/hr was used for an expected film thickness of $1\mu m$. Measured by beam equivalent pressure (BEP) using an ionization gauge, an arsenic-to-gallium BEP ratio of about 26:1 was used. Due to the low vapor pressure of Tb, it is very difficult to measure the flux of Tb from BEP measurements. Thus, TbAs concentration was calibrated by matching the RBS measured concentration to the Tb effusion cell temperature. For this sample, a Tb source temperature of 1345°C was used, resulting in a TbAs concentration of 2.12%. Based on these growth conditions and using an average nanoparticle diameter of 1.1 nm, measured from samples of similar growths, [15] a TbAs nanoinclusion density of $3.2 \times 10^{19} cm^{-3}$ was calculated.

4.2.2 THz Probe Transient Absorption Spectroscopy

Optical pump THz probe experiments were performed using a regeneratively amplified Ti:sapphire laser system producing 3.2 mJ, 35 fs pulses centered on 800 nm at a 1 kHz repetition rate. A portion of the amplifier output is used to generate and detect the terahertz pulses through optical rectification in ZnTe, and the rest of the power is used to optically pump the sample. The probe is a broadband THz pulse spanning 0.1-2.75 THz. The delay stage is capable of taking data with a delay between pump and probe pulses as long as approximately 400 ps. See Chapter 3 for additional



Figure 4.1: A cross-sectional schematic showing TbAs nanoparticles within a GaAs host matrix, formed by codepositing terbium, gallium, and arsenic.[85]

experimental details of the optical pump THz probe spectroscopy system. Incident pump fluences of $2\mu J/cm^2$ through $200\mu J/cm^2$ were used to excite the samples. The temperature dependence study was completed using a liquid helium cooled cryostat capable of reaching temperatures as low as 4.5 K.

In the absence of a pump beam, there are no carriers in the conduction or valence bands of the GaAs and the THz probe cannot be absorbed. The 800 nm pump beam excites carriers across the bandgap, leading to a population of electrons in the conduction band and holes in the valence band. Because of the large number of available energy states in the conduction and valence bands, these electrons and holes are both able to absorb low energy photons from the THz probe beam. The absorption of the optical pump and THz probe are depicted in the energy diagram of Fig. 4.2.



Figure 4.2: Optical pump creates electron hole pairs. The low energy THz probe is absorbed only when electrons are in the conduction band or holes are in the valence band, where an abundance of closely spaced energy levels provide optically allowed transitions.[85]

Electrons and holes generated by the optical pump will relax down to the GaAs band edge in less than 100 fs.[44, 29] The initial relaxation due to thermalization is too fast to be resolved by this experiment, which is limited by the pulse duration of the probe (approximately 700 fs). Carriers at the band edge can relax by radiative or nonradiative recombination across the GaAs band gap, or by relaxation into states associated with the TbAs nanoinclusions. We can investigate these carrier relaxation mechanisms by analyzing the decay rates of the carrier population, which are evident in the decay of the THz absorption.

Transient absorption data is collected for delay times between 0 and 400 ps using a delay stage step size of 0.3333 ps/step. By averaging ten complete data runs for each pump fluence and temperature, we improve the signal to noise ratio enough to resolve the dynamics happening on timescales down to a few ps. We fit the data to an exponential decay using a linear least squares method with a Levenberg-Marquardt algorithm in order to determine the relaxation rates of the charge carriers.

4.2.3 Data Analysis and Physical Model

Fig. 4.3a and Fig. 4.3b show the average intensity of the THz probe beam after it passes through the sample as a function of the delay between the optical pump and the THz probe. The data displayed is the average of ten data runs at room temperature for a pump fluence of 6μ W/cm². Averaging ten runs is necessary in order to improve the signal to noise to a sufficient level. When fitting a decay curve, more exponentials can always be added to the fit and the χ^2 value will continue to improve. However, there is a limit to the number of exponentials that represent a physical relaxation process for a given decay curve. In order to determine the correct number of exponentials required to describe the data, we systematically fit an increasing number of exponentials and analyzed their validity. Beginning with a single-exponential curve (solid blue curve in Fig. 4.3a), we see that a single exponential does not accurately describe the relaxation dynamics seen over the full 400 ps range of delay times.

We find that a bi-exponential curve, displayed as a red dashed line in Fig. 4.3a, fits the data well on a long timescale, but does not accurately capture the relaxation dynamics happening during the first 10 ps after photoexcitation. In Fig. 4.3b we compare a bi-exponential curve (red dashed line) and a tri-exponential curve (green dash-dotted curve) over the first 20 ps after photoexcitation. Fig. 4.3b reveals the discrepancy of the bi-exponential fit for short delay times and confirms that a triexponential fit is necessary to capture these fast relaxation dynamics.

Using a four-exponential fit does not improve the adjusted R^2 value relative to the values obtained with a tri-exponential equation. Moreover, the four-exponential fit is completely indistinguishable from the tri-exponential fit in both the visual repesentation of the fit overlaying the data points and in a plot of the residuals. We therefore conclude that the relaxation dynamics in this sample are described by a tri-exponential model for absorption (I) of the THz probe as a function of the delay time (t) between



Figure 4.3: a) For larger delay times (50-400 ps), both a bi (green line) and a triexponential equation (red line) fit the data with good agreement. b) For shorter delay times (0-50 ps), a bi-exponential equation does not accurately reflect the relaxation dynamics.[85]

the optical pump and the THz probe:

$$I = Aexp(\frac{-t}{\tau 0}) + Bexp(\frac{-t}{\tau 1}) + Cexp(\frac{-t}{\tau 2})$$

$$(4.1)$$

The three relaxation time constants returned by the tri-exponential fits are statistically distinct. $\tau 0$ has an average value of 5.4 ps for the various pump fluences and temperatures studied, $\tau 1$ ranges from 65-135 ps, and $\tau 2$ from 500-3700 ps. The amplitude coefficients A, B, and C provide information about the fraction of carriers participating in each relaxation process and will be discussed along with the relaxation rates.



Figure 4.4: Charge carriers can relax via three processes- relaxation into the TbAs trap states ($\tau 0$), relaxation out of the trap states ($\tau 1$), or radiative recombination across the bulk GaAs bandgap ($\tau 2$).[85]

Fig. 4.4 schematically depicts our assignment of the three exponential decay time constants to distinct physical relaxation processes. We will justify these assignments in the next sections with a systematic analysis of our experimental data and then use the results to draw conclusions about the electronic structure of the TbAs nanoinclusions. The shortest time constant, $\tau 0$, is assigned to the relaxation of carriers from the conduction and valence bands into the TbAs trap states.[16] The second shortest time constant, $\tau 1$, is assigned to the emptying of the trap states, which allows additional electrons to quickly relax from the conduction band into the newly available trap states. The longest time constant, $\tau 2$, is assigned to the relaxation of electrons across the GaAs bulk bandgap. The observation of these three distinct relaxation processes, along with their observed dependence on laser fluence and temperature, suggests the existence of saturable trap states associated with the TbAs nanoinclusions, and thus the existence of a bandgap for the TbAs nanoinclusions.

4.3 **Results and Discussion**

4.3.1 Fluence Dependence Measurements

To understand the electronic structure of the TbAs nanoinclusions, we investigate the carrier decay as a function of both temperature and the intensity of the optical pump. The temperature was varied from 4.5 to 296 K at an optical pump fluence of $2\mu W/cm^2$ and the optical pump fluence was varied between 2 to $200\mu W/cm^2$ at room temperature. We consider both the relaxation time constants ($\tau 0$, $\tau 1$, and $\tau 2$) and the relative amplitudes of each decay process (A, B, and C) returned by the tri-exponential fit to each data set. As we show below, these amplitude coefficients provide insight into the fraction of charge carriers participating in each relaxation process as well as evidence for trap state saturation when the intensity of the optical pump is increased.

We consider first the dependence of the relaxation rates and amplitude coefficients on optical pump fluence. The parameters returned by our tri-exponential fit are plotted in Fig. 4.5 as a function of the pump fluence. As shown in Fig. 4.5a, the relaxation time constant for carriers relaxing into the traps ($\tau 0$) does not show any statistically significant dependence on pump fluence and has an average value of 5.4 ps. As noted previously,[29] the photon energy absorbed by electrons in the conduction band is similar to the photon energy absorbed by holes in the valence band. As a result, it is not possible to distinguish which portion of the probe beam is absorbed by the electrons and which is absorbed by the holes. Therefore we only observe the overall effect of these two processes

$$\tau 0 = \left(\frac{1}{\tau 0_e} + \frac{1}{\tau 0_h}\right)^{-1} \tag{4.2}$$

where $\tau 0_e$ reflects the relaxation of electrons into trap states, and $\tau 0_h$ is the relaxation of holes. The difference in the rates of electrons and holes relaxing into the TbAs states is dependent on the location of the TbAs states within the bandgap. Unfortunately the difference is not distinguishable by this experimental technique.

Although $\tau 0$ is independent of pump fluence, the fraction of carriers participating in this relaxation process, calculated by the amplitude ratio A/(A + B + C), does exhibit a strong dependence on pump fluence. As shown in Fig. 4.5b, the fraction of carriers participating in this fastest relaxation process decreases quickly with increasing pump fluence and drops to near zero when the pump fluence reaches $20\mu W/cm^2$. This evidence indicates that the rate of charge carrier capture does not change with pump fluence, but the number of carriers that can relax into the TbAs trap states is finite. As the pump fluence increases, the additional optically generated charge carriers are unable to relax into the TbAs trap states and must relax by a different physical process. The dependence on pump intensity of the amplitude fraction for the fastest decay process suggests that the TbAs trap states are saturable.

The second decay constant, $\tau 1$, which ranges from approximately 65 to 135 ps, is attributed to trap emptying. As the traps empty, carriers at the band edge can relax into the newly-empty trap states, thus reducing the THz absorption. The rate of relaxation from the band edge into the trap states is fast, around 5.4 ps, and thus the rate limiting step for this carrier relaxation process is the trap emptying lifetime $\tau 1$. The fraction of charge carriers whose relaxation dynamics are governed by trap emptying B/(A+B+C) decreases with increasing pump fluence as shown in Fig. 4.5d. This result is consistent with the observed change in the fraction of carriers initially relaxing into the traps A/(A + B + C) because both processes are limited by the saturation of trap states.

In addition to recombination processes, carrier ejection from the trap states is possible. However, carriers that are ejected from the trap states would re-enter the conduction or valence bands and the vacancies left behind in the traps would quickly refill with another carrier via the $\tau 0$ relaxation process. Because the net carrier population in both the trap states and the conduction and valence bands would remain the same, this trap ejection and refilling process would not result in a change in THz probe absorption. $\tau 1$ therefore cannot reflect this process. In addition, the high resistivity of GaAs containing TbAs nanoinclusions suggests that the trap states are deep within the GaAs bandgap,[15] which makes carrier ejection to the conduction and valence bands unlikely. Following the argument that carrier ejection is not responsible for any change in THz probe absorption, there are two possible trap emptying pathways: radiative and nonradiative recombination. Radiative relaxation is unlikely to be the dominant trap emptying pathway for two reasons. First, radiative lifetimes for nanostructures are typically on the order of 1 ns,[19] which is significantly longer than the lifetimes observed for $\tau 1$. Second, spectrophotometry and FTIR measurements out to 12μ m reveal only one absorption peak for TbAs:GaAs, at 750 meV.[15] However, we do not observe any photoluminescence associated with this absorption peak, suggesting that this peak could not be associated with a direct band gap. In the absence of a direct bandgap, the probability of radiative recombination is negligible. The combination of these factors leads us to believe that nonradiative recombination is likely the dominant trap emptying process responsible for $\tau 1$.

Thermal relaxation through metallic-like states of the TbAs nanoinclusions would provide an efficient pathway for nonradiative recombination. However, rapid thermalization of electrons and holes through the continuous density of states of a metal would lead to extremely fast trap emptying. As stated earlier, samples containing semimetallic ErAs nanoparticles return to a pre-illuminated energy state in only a few ps. 68 In this experiment even at the maximum delay time of 400 ps after the pump pulse, the sample is not even remotely close to relaxing to a pre-illuminated state. We also observe that the fraction of carriers relaxing into the traps A/(A + B + C)decreases rapidly with increasing pump fluence, which indicates trap saturation. Trap state saturation is incompatible with rapid trap emptying via thermalization, which leads us to conclude that the TbAs states are not metallic-like. We believe nonradiative recombination of trapped electrons and holes is the likely relaxation pathway. A similar mechanism was proposed to explain the multi-exponential recovery, including a 30 ps component, observed in transient absorption experiments that studied electron relaxation via trap states in aqueous CdS colloids [94] and quantum-size crystallites of ZnCdS in an aqueous colloidal solution.[30]

The exact nature of the electron-hole nonradiative recombination process cannot

be incontestably determined from this data. Possible mechanisms include 1) phonon mediated nonradiative recombination across an indirect bandgap, 2) Auger recombination involving excitation of carriers confined within the TbAs nanoinclusions and 3) recombination of free electrons or holes in the conduction or valence band with oppositely charged carriers confined within the nanoinclusions. Phonon mediated recombination across an indirect bandgap is improbable due to the temperature dependent measurements discussed below. Auger recombination typically results in increased relaxation rates (decreased lifetimes) as increasing fluence increases the number of carriers confined in a nanostructure and thus increases the probability that Auger recombination takes place.[70] We do not observe a decrease in the lifetime associated with $\tau 1$, the trap emptying rate, as the laser fluence is increased. We therefore believe Auger processes involving carriers confined within the TbAs nanoinclusions are not a dominant trap emptying process.

We observe that the relaxation time constant attributed to trap emptying ($\tau 1$) increases from 65 to 135 ps with increasing fluence, as shown in Fig. 4.5c. Notably, the time constant continues to increase with increasing pump fluence well past $20\mu W/cm^2$, the point at which the data for $\tau 0$ suggest that the traps are saturated (Fig. 4.5b). If the traps are saturated, increasing pump fluence can only result in additional carriers occupying the conduction and valence bands. The dependence of $\tau 1$ on increasing occupation of the conduction and valence bands suggests that recombination between carriers in the conduction and valence bands of the GaAs matrix and those in the conduction and valence bands of the TbAs nanoinclusions is a significant nonradiative recombination pathway. The existence of this mechanism is supported by the observation that the fraction of carriers participating in the trap emptying process decreases more slowly with increasing fluence (Fig. 4.5d) than the fraction of carriers participating in the direct trapping process (Fig. 4.5b).

The fraction of charge carriers relaxing across the bulk bandgap C/(A+B+C)increases with increasing fluence and slowly approaches unity, as shown in Fig. 4.5f. This result is consistent with the decrease in the fraction of charge carriers participating in the fastest relaxation pathways discussed above. If there are a finite number of saturable traps, there are a finite number of carriers that can participate in the fast relaxation processes enabled by the traps. At high pump fluences the carrier population exceeds the saturation threshold and all additional carriers must relax via bulk radiative decay. We observe that the relaxation time constant for charge carriers relaxing across the bulk bandgap ($\tau 2$) increases with increasing pump fluence, as shown in Fig. 4.5e. This result is consistent with our previous work on trap saturation: higher pump fluences saturate the traps and lead to a bulk radiative lifetime that becomes longer and approaches the normal radiative lifetime of GaAs without any nanoinclusions or traps.[39]

4.3.2 Temperature Dependence Measurements

In addition to the fluence dependence study, we also investigated the dependence of carrier relaxation dynamics on temperature. As shown in Fig. 4.6, the fraction of charge carriers relaxing directly into trap states A/(A + B + C) and the fraction whose relaxation dynamics are dominated by the trap emptying process B/(A + B + C) are not dependent on temperature. Similarly, $\tau 0$, $\tau 1$, $\tau 2$ and C/(A + B + C) do not show a statistically significant temperature dependence over the temperature range 4.5 K to 296 K (data not shown). If phonon related recombination was a significant relaxation process, the trap states would display increasing lifetimes with lower temperatures. The absence of a temperature dependence for the relaxation times is consistent with previous optical pump THz probe experiments completed on ErAs[68] and supports two conclusions: 1) the trap states are relatively deep and 2) phonon-mediated nonradiative recombination across an indirect bandgap is unlikely to be a dominant trap emptying pathway.

4.3.3 Comparison to Theoretical Calculations

As discussed in Chapter 2, studies have shown the possibility of a semimetal to semiconductor transition when some materials are sufficiently spatially confined. [96, 71]

ErAs nanoinclusions however do not show evidence of such a transition. ErAs nanoinclusions remain semimetallic, even with a high degree of spatial confinement.[73, 12, 46] It was expected that TbAs, which is in the same class of materials as ErAs, would also fail to exhibit a semimetal to semiconductor transition when spatially confined. When considering the effects of interface states[24] and strain[23] on the Fermi level, and subsequently the possible transition from a semimetallic material to a semiconductor, the f-shell electrons of ErAs can be dealt with by the frozen core approximation. Therefore it is reasonable to assume that the small differences in the number of f-shell electrons contained by ErAs and TbAs would cause minimal changes in their electronic properties. Our evidence of trap saturation in TbAs nanoinclusions indicates a surprising transition to semiconductor behavior and suggests a more sophisticated theoretical treatment may be necessary to understand the electronic structure of TbAs nanoinclusions.

4.4 Conclusions

We have investigated carrier relaxation processes in GaAs samples containing embedded TbAs nanoinclusions on a GaAs substrate using an optical-pump THz-probe transient absorption spectroscopy experiment. Fitting the data to a triple exponential decay yields numerical values for the carrier relaxation lifetimes as well as the fraction of carriers participating in each relaxation process. We observe a pump fluence dependence of the fraction of carriers participating in fast relaxation processes, as well as the bulk lifetime. These dependences suggest that the TbAs states are saturable, ruling out the existence of metallic states that would allow fast thermalization of carriers and therefore prohibit saturation. Absorption spectra and the evidence for trap state saturation point to the existence of a bandgap. The absence of photoluminescence associated with the only optical absorption peak allows us to rule out the existence of a direct bandgap. The data therefore suggest that spatial confinement of TbAs likely results in nanoinclusions with the electronic structure of an indirect gap semiconductor. The trap filling dynamics at low pump fluence are not affected by temperature over the range of 4.5 to 293 K, which suggests that the trap states are deep in the bandgap and that phonon mediated recombination across an indirect bangap is not a dominant trap emptying process. The dependence of trap emptying rate on increasing population of carriers in the conduction and valence bands suggests the existence of important nonradiative recombination pathways involving both free carriers and those confined within the nanoinclusions.



Figure 4.5: The relaxation lifetime $\tau 0$ of carriers into the TbAs traps (a.) shows no statistically significant fluence dependence. The fraction of electrons entering (b.) and exiting (d.) the TbAs traps decreases with increasing pump fluence, indicating trap saturation. The relaxation lifetime $\tau 1$ of carriers out of the TbAs traps (c.) increases with fluence, which suggests that recombination between carriers in the conduction and valence bands of the GaAs matrix and those in the TbAs nanoinclusions is a significant nonradiative recombination pathway. The relaxation lifetime $\tau 2$ of carriers across the bulk bandgap (e.) increases with fluence, consistent with trap saturation. The fraction of electrons relaxing across the bulk bandgap (f.) increases with fluence, which indicates that at high pump fluences the carrier population exceeds the saturation threshold and all additional carriers must relax via bulk radiative decay.[85]



Figure 4.6: For a $2\mu W/cm^2$ pump fluence, the fraction of carriers entering the TbAs traps (A/(A+B+C), black squares) and the fraction leaving the traps (B/(A+B+C), red circles) do not show any statistically significant dependence on temperature.[85]

Chapter 5

TERBIUM ARSENIDE NANOINCLUSIONS IN INDIUM GALLIUM ARSENIDE

5.1 Introduction

In Chapter 2 I discussed the importance of the material bandgap for THz generation. When a semiconducting material is being used as an optoelectronic switch, the bandgap of the material determines the minimum energy (longest possible wavelength) of light needed to excite charge carriers into the conduction band. InGaAs has a bandgap of 0.74 eV,[42] which corresponds to an excitation wavelength of about 1.67 μ m. Therefore, using InGaAs as a host material would allow the optoelectronic switch to be conveniently operated with 1.55 μ m light- the wavelength for which an infrastructure in communications already exists.

ErAs nanoparticles in GaAs have already been shown to exhibit the fast carrier excitation and relaxation processes necessary for THz generation.[37, 43, 44, 35, 68, 16] However the bandgap of GaAs is 1.424 eV,[42] corresponding to an excitation wavelength of about 870 nm- an inconveniently high energy. ErAs nanoparticles in InGaAs have also been studied.[35, 8, 98] Although a short carrier relaxation time of about 3.2 ps was observed by Azad et al. for a codeposited sample lattice matched to InP,[8] the ErAs nanoparticles pin the Fermi level above the InGaAs conduction band, resulting in an undesirable n-type background.[98] In order to increase the dark resistance, Azad had to dope the InGaAs with beryllium.

We initially considered TbAs:InGaAs to be a candidate for THz generation using 1.55 μ m light due to the similarities between Er and Tb. We believed that because TbAs has a larger lattice constant than ErAs, the TbAs nanoparticles would pin the Fermi level below the bandgap of InGaAs, leading to a higher dark resistance. In fact,



Figure 5.1: A cross-sectional schematic of (a) a mixed core of Er/Tb atoms in an InGaAs host matrix and (b) a mixed core of Er/Tb atoms surrounded by a shell of Tb atoms.[26]

the results of our study of TbAs:GaAs reveal that TbAs nanoparticles are most likely semiconducting and do not give rise to the fast carrier dynamics required for THz generation unless the excitation energy is prohibitively low.[85] However, advances in growth have made is possible to use a core-shell structure, in which a core containing both TbAs and ErAs is surrounded with a shell of TbAs, and the entire nanoinclusion is embedded in an InGaAs host material lattice matched to InP (Fig. 5.1).[26] We postulate that the ErAs in the core could provide the short carrier lifetimes needed for THz generation, while the TbAs shell could pin the Fermi level below the conduction band, resulting in a high dark resistance. Dongmo et al. have shown that these coreshell nanoparticles can be formed through a strain-driven process,[26] but the electronic structure and carrier dynamics of these materials is unknown.

Before we investigate the core-shell structure's potential for THz generation, we must first understand the electronic structure of TbAs nanoparticles alone in an InGaAs host matrix. In this experiment we investigate how changing the host material to InGaAs affects the relaxation dynamics. We also study the effect of TbAs concentration to further refine our understanding of the electronic structure and carrier dynamics.

5.2 Experimental Design

The samples were grown by Cory Bomberger at the University of Delaware. The optical pump THz probe transient absorption spectroscopy measurements were completed by Dr. Abul Azad at Los Alamos National Laboratory via another collaboration with the Center for Integrated Nanotechnology (CINT). I analyzed the transient absorption pump probe data.

5.2.1 Sample Fabrication

Two TbAs:InGaAs samples with different TbAs concentrations were grown on an InP Fe doped (001) substrate. Our OSEMI NextGEN solid source MBE machine is equipped with effusion cells for indium, gallium, and terbium, and a two-zone valved cracker source for arsenic. The growth was done at 490 °C measured by band edge thermometry, and monitored using reflection high energy electron diffraction (RHEED). For both samples, Tb was co-deposited with the In, Ga and As in excess of the solid solubility limit, yielding TbAs precipitates in an InGaAs matrix. The samples were grown at a rate of 1.27 μ m/h, resulting in a TbAs:InGaAs film thickness of 1 μ m. An indium to gallium flux ratio of about 2.65 was used to obtain a nominally lattice matched film.

| | 1.304% TbAs | 0.84% TbAs |
|---------------------------|--|--|
| Buffer layer | 100nm In _{0.53} Ga _{0.47} As | None |
| As/Tb flux ratio | 10.4 | 11.5 |
| Effusion cell temperature | 1330°C | 1285°C |
| TbAs nanoparticle density | 2.54x10 ¹⁹ cm ⁻³ | 1.59x10 ¹⁹ cm ⁻³ |

Table 5.1: A summary of the two different TbAs:InGaAs samples.

The concentration of terbium was calibrated by matching the Rutherford backscattering spectroscopy (RBS) to the terbium effusion cell temperature. An effusion cell temperature of 1330 °C was used to obtain a TbAs concentration of 1.304% in one sample, and 1285 °C resulted in a TbAs concentration of 0.84% in the other sample. An arsenic to terbium flux ratio of about 10.4 and 11.5 was used for the 1.304% and 0.84% TbAs sample, respectively. The 1.304% TbAs sample was grown on top of a 100 nm $In_{0.53}Ga_{0.47}As$ buffer layer (nominally lattice matched to InP) and the 0.84% TbAs sample had no buffer layer. A TbAs nanoparticle density of 2.54×10^{19} cm⁻³ was calculated for the 1.304% sample and 1.59×10^{19} cm⁻³ for the 0.84% sample, assuming an average nanoparticle size of 1 nm based on previous measurements of similar samples.[18] These growth conditions and sample characteristics are summarized in Table 5.1.

5.2.2 THz Probe Transient Absorption Spectroscopy

The optical pump THz probe transient absorption measurements were taken on the same equipment used to collect the TbAs:GaAs data discussed in Chapter 4. Again, this experimental technique is presented in Chapter 3. Transient data was collected over a 400 ps range. A fluence dependence study was completed for the range of $0.5 \ \mu J/cm^2$ through 200 $\mu J/cm^2$. The confidence intervals were too large for any meaningful conclusions to be drawn for fluences greater than 100 $\mu J/cm^2$, and so these data points are not included in the analysis. All measurements were taken at room temperature.

5.2.3 Data Analysis Technique

The analysis of the two TbAs:InGaAs samples was completed in the same manner as the TbAs:GaAs analysis explored in Chapter 4. The transient absorption data for each pump fluence was fit to an exponential decay function using a Levenberg-Marquardt algorithm, a linear least squares method of curve fitting. Similar to the fitting results for the TbAs:GaAs sample,[85] the transient absorption curves for pump



Figure 5.2: An energy diagram of the three relaxation processes. Charge carriers can relax via three processes- relaxation into the TbAs states $(\tau 1)$, relaxation out of the TbAs states $(\tau 2)$, or radiative recombination across the bulk InGaAs bandgap $(\tau 3)$.

fluences up to $12 \ \mu J/cm^2$ incident on the 1.304% TbAs concentration TbAs:InGaAs are best fit with a triple exponential equation:

$$I = Aexp(\frac{-t}{\tau 1}) + Bexp(\frac{-t}{\tau 2}) + Cexp(\frac{-t}{\tau 3}).$$
(5.1)

The fastest time constant $\tau 1$ is attributed to the fast charge carrier relaxation into the TbAs states. The middle time constant $\tau 2$ describes the emptying process of the TbAs states. The longest time constant $\tau 3$ represents the carrier recombination across the bulk InGaAs bandgap. These three relaxation processes are schematically depicted in Fig. 5.2. Again, this technique cannot differentiate between the relaxation of electrons from the conduction band into the TbAs states $\tau 1_e$ and the relaxation of holes from the valence band $\tau 1_h$. Instead, the change in the probe absorption reveals the combined effect of these two types of carriers entering the TbAs states $\tau 1$ given by

$$\tau 1 = \left(\frac{1}{\tau 1_e} + \frac{1}{\tau 1_h}\right)^{-1}.$$
(5.2)

The amplitude coefficients A, B, and C offer information on the fraction of free charge carriers that are participating in these three relaxation processes.

5.3 Results and Discussion

The fitting results for the two TbAs:InGaAs samples are discussed, and the relaxation dynamics are compared to those found previously for TbAs:GaAs.

5.3.1 Fitting Results for Indium Gallium Arsenide Host Samples

The two samples are identical except for the concentration of TbAs. Sample 1 has a TbAs concentration of 1.304% and Sample 2 has a concentration of 0.84%. These samples exhibited different fitting results, outlined below.

5.3.1.1 Sample 1: TbAs Concentration of 1.304%

The relaxation rate of charge carriers entering the TbAs states $\tau 1$ has an average value of about 4.6 ps for pump fluences between $0.5 - 12 \ \mu \text{J/cm}^2$. For pump fluences between $20 - 50 \ \mu \text{J/cm}^2$, a triple exponential decay fit could not be obtained, and a bi-exponential fit was used instead. The shortest time constant $\tau 1$ does not appear in the transient absorption data for this pump fluence range. The rate of charge carriers leaving the TbAs states $\tau 2$ ranges from 71 - 92 ps for pump fluences between $0.5 - 50 \ \mu \text{J/cm}^2$. The transient absorption collected with the highest fluence $100 \ \mu \text{J/cm}^2$ can only be described by a single exponential decay, corresponding to the $\tau 3$ relaxation process. Over the full range of pump fluences measured $(0.5 - 100 \ \mu \text{J/cm}^2)$, the time constant associated with bulk recombination $\tau 3$ varies from 766 ps to around 44 ns. A few of the pump fluences and their corresponding exponential decay fits are shown in Fig.5.3.

The fitting results for the fluence dependence study completed on the 1.304% TbAs concentration sample are summarized in Fig. 5.4. The relaxation time of carriers into the TbAs energy states $\tau 1$ (Fig. 5.4 a) shows no statistically significant pump fluence dependence. The fraction of free charge carriers relaxing into the TbAs states from the In_{0.53}Ga_{0.47}As band edge A/(A + B + C) (Fig. 5.4 b) and leaving the TbAs states states B/(A + B + C) (Fig. 5.4 d) decrease with increasing pump fluence. If the number of free charge carriers that can enter and exit is finite, then the TbAs states



Figure 5.3: a) For a pump fluence of 100 μ J/cm² a single exponential decay fits the transient absorption data. Two exponentials are needed to properly fit the 50 μ J/cm² pump fluence data. b) A zoomed-in plot (original data was taken over a 400 ps range) shows that a 1 μ J/cm² pump fluence data requires a triple exponential decay fit.

in InGaAs are acting as saturable trap states. For pump fluences above 12 μ J/cm² the fraction of carriers entering the TbAs trap states is so small that any change in the probe absorption from this process is lost within the experimental noise. For this reason, only the τ 2 and τ 3 relaxation processes appear in the transient absorption data collected for pump fluences greater than 12 μ J/cm². Similarly, for a 100 μ J/cm² pump fluence the fraction of carriers leaving the TbAs nanoparticle B/(A + B + C) (Fig. 5.4 d) also becomes too small to measure, leaving only the τ 3 process to appear in the transient absorption data.

The relaxation time for charge carriers across the bandgap of InGaAs $\tau 3$ (Fig. 5.4 e) rises with increasing pump fluence and approaches the natural radiative lifetime of bulk In_{0.53}Ga_{0.47} at room temperature (about 10-100 ns depending on majority carrier density).[40] This result is also consistent with trap saturation.[39] The fraction of free charge carriers recombining across the bulk bandgap C/(A+B+C) (Fig. 5.4 f) reaches unity, indicating that at a 100 μ J/cm² pump fluence the fraction of free charge carriers



Figure 5.4: For the 1.304% TbAs sample the relaxation time of charge carriers into the TbAs states (a) shows no statistically significant fluence dependence. The fraction of carriers entering (b) and leaving the trap states (d) decreases with increasing pump fluence, indicating saturation of the TbAs energy states. The relaxation times of carriers out of the TbAs states (c) initially increases with pump fluence and then seems to remain constant. The relaxation time across the bulk bandgap (e) approaches that of the lifetime of InGaAs and the fraction of carrier relaxation across the bandgap (f) reaches unity at sufficiently high fluences.[10]

that interact at all with the TbAs nanoparticles is too small to be detected with this technique.

The relaxation rate of carriers out of the TbAs states $\tau 2$ (Fig. 5.4 e) increases with pump fluence until around 2 μ J/cm², above which there is no statistically significant difference. Possible explanations for this behavior are screening effects and band banding. Below the saturation threshold for the TbAs trap states, increasing the pump fluence would increase the number of charge carriers in the nanoparticle. If a significant trap emptying mechanism is nonradiative recombination, the presence of extra charge carriers of the same sign (electron-electron or hole-hole interactions) could effectively shield a carrier from recombining with a carrier of the opposite sign (electron-hole interaction). On the other hand, an increased number of carriers in the TbAs states could lead to band bending and increase the energy separation between the holes and electrons in the nanoparticle. If the TbAs energy states are near the band edge of the InGaAs, the band bending could result in either a flat valence band or a flat conduction band. This would result in carriers in the TbAs trap states recombining with carriers in the InGaAs matrix. The amount of band bending required to see a change in carrier lifetime would be small if the energy levels of the TbAs nanoparticle lie close to one of the band edges in InGaAs. In either case, continuing to increase the pump fluence above the saturation level would no longer result in additional charge carriers being added to the TbAs states, and the rate of carriers leaving the TbAs states would remain constant.

5.3.1.2 Sample 2: TbAs Concentration of 0.84%



Figure 5.5: A single exponential decay is sufficient for fitting all of the pump fluence data collected for the 0.84% TbAs sample. The smallest pump fluence data, $0.5 \ \mu J/cm^2$, is shown here as an example.

The transient absorption data collected for all pump fluences for the 0.84% TbAs sample was fit with a single exponential decay, shown in Fig. 5.5. The decay constants are summarized in Fig. 5.6. The relaxation time for this sample ranges from about 1 - 19 ns, which is on the same order of magnitude as the fluence-dependent natural



Figure 5.6: For the 0.84% TbAs sample the decay lifetime increases with increasing pump fluence.[10]

radiative lifetime of bulk $In_{0.53}Ga_{0.47}$ at room temperature (around 10 ns).[40] As such, we attribute this relaxation process to nonradiative recombination across the InGaAs bandgap (τ 3). We believe that the shorter relaxation processes associated with the TbAs trap states τ 1 and τ 2 are not observed because of the low TbAs concentration of this sample. The fraction of free charge carriers that interact within the TbAs nanoparticles is too small to be detected within the signal to noise capabilities of this experiment, even at the lowest pump fluence available. In other words, the TbAs

5.3.2 Comparison of Results for Gallium Arsenide and Indium Gallium Arsenide Host Samples

A comparison of the pump fluence dependence data for the 0.84% TbAs sample and the 1.304% TbAs sample shows that a sample with a smaller concentration of TbAs will saturate at a much lower pump fluence. Our previous fluence dependence study of TbAs in a GaAs host also fits this trend. Specifically, we observed all three relaxation processes in the sample with 2.12% TbAs in a GaAs host even for the highest pump fluence (100 μ J/cm²). We also observe that the rate of carrier relaxation into the TbAs trap states was about the same for both of the 1.304% TbAs:InGaAs and the 2.12%TbAs:GaAs samples. Physically, this corresponds to the fact that the density of TbAs nanoinclusions is sufficiently high in all samples for the rate of carrier relaxation to be dominated by the rate of carrier trapping rather than the rate of carrier diffusion to a TbAs inclusion. Moreover, it implies that the rate of carrier relaxation into the states of the TbAs nanoinclusions is not strongly influenced by either the concentration of TbAs or the energy offset between the host material band gaps and the states of the TbAs. This, in turn, implies that states of the TbAs conduction band or valence band remain confined below the respective band edge of the host material for both GaAs and InGaAs hosts. As long as the concentration of TbAs in a sample is high enough to be able to observe the fastest relaxation dynamics in this experiment, the length of time it takes a charge carrier to relax into a TbAs state is not affected by the concentration of TbAs. This confirms that changing the amount of TbAs deposited in a co-deposited sample primarily changes the number of nanoparticles rather than the nanoparticle size.

5.4 Conclusions

We have investigated carrier relaxation processes in two different In_{0.53}Ga_{0.47}As samples containing embedded TbAs nanoinclusions grown on InP Fe doped substrates. One sample has a TbAs concentration of 1.304% and the other has a concentration of 0.84%. The relaxation time of carriers into the TbAs energy states $\tau 1$ remains constant with increasing pump fluence. The fraction of free charge carriers relaxing into the TbAs states from the In_{0.53}Ga_{0.47}As band edge A/(A + B + C) and leaving the TbAs states B/(A + B + C) decrease with increasing pump fluence. This leads to the conclusion that the TbAs states are saturable, and TbAs:InGaAs acts as a semiconductor in keeping with previous results for TbAs:GaAs. The rate of charge carriers exiting the trap states, $\tau 2$, increases with increasing fluence until about 2 μ J/cm² and then
remains constant, suggesting the possibility of a charge screening effect or band bending. In the case of band bending, this result would suggest that the energy levels of the TbAs trap states lie close to the InGaAs band edge, as expected. If the previous results for 2.12% TbAs concentration TbAs:GaAs are viewed in the context of these two different concentration TbAs:InGaAs samples, we see that a lower concentration of TbAs in a sample leads to saturation of the TbAs trap states at a lower fluence. This result implies that changing the amount of TbAs in a co-deposited sample affects the number of nanoparticles and not the size. The results presented here provide critical information for the deduction of the energy band structure of TbAs:GaAs and TbAs:InGaAs materials. They also provide a baseline for future transient absorption analysis of TbAs ErAs core-shell structures in InGaAs, and set a more concrete groundwork for constructing a possible energy band structure for TbAs:GaAs and TbAs:InGaAs.

Chapter 6

BUILDING AN OPTICAL PUMP OPTICAL PROBE TRANSIENT ABSORPTION SPECTROSCOPY EXPERIMENT

6.1 Introduction

The design of the THz probe experiment described in Chapter 3 and used for the data collection in Chapters 4 and 5 yields temperature and fluence dependent measurements of carriers relaxing from the conduction and valence band edges of the GaAs. The primary limitation of this technique is that the energy states within the TbAs traps themselves cannot be detected. In contrast, an optical probe experiment can probe these energy states directly, as shown in Fig. 6.1. Like the THz probe experiment, optical probes will be absorbed by free carriers in the conduction band of GaAs after the sample is excited by the pump. Optical probe energies are high enough to also be absorbed by charge carriers in the TbAs trap states themselves. Probes of various wavelengths will experience different degrees of absorption depending on the energy structure of the traps. It is also possible for some probe energies to create charge carriers directly in the TbAs nanoinclusions, resulting in a bleach contribution to the transient absorption spectrum.

Having already acquired a Princeton Instruments spectrometer and liquid nitrogen cooled CCD camera, we decided to build an optical pump optical probe system that is capable of multi-channel detection. In such a system, one scan of the delay stage results in three dimensional data showing the relation between probe transmission intensity, delay time, and probe wavelength (Fig. 6.2). This powerful technique would provide ample amounts of data which could then be broken down in post-analysis to reveal the energy structure of the TbAs nanoparticles, as well as numerous other nanocomposites.



Figure 6.1: An optical probe experiment can reveal carrier dynamics related to specific energy levels within the TbAs trap states.

6.2 Experimental Requirements

An optical pump optical probe experiment in its simplest form requires an optical pump, a way to generate a broadband continuum probe, and a measurement method that spectrally resolves the probe transmission. In an effort to build a powerful technique that is versatile enough to study a variety of materials, we expanded on this concept. We use an optical parametric amplifier (OPA) to generate pump pulses that are high enough in intensity to generate charge carriers in the materials being studied, as well as being widely tunable in wavelength. We also designed a data collection scheme for a spectrometer coupled to a CCD camera array in an effort to simultaneously collect time and energy resolved data. The first iteration of our optical pump optical probe experiment is represented in Fig. 6.3. The 800 nm output from the Spitfire regen is split and sent to the optical pump with a tunable wavelength provided by the Topas OPA, and to the broadband optical probe generation system, which uses a sapphire crystal. This technique relies on several different nonlinear optical processes, which are described in detail in the following subsections.



Figure 6.2: A CCD camera is capable of multi-channel detection simultaneously collects probe intensity data over a range of delay times and wavelengths.[88]

6.2.1 Nonlinear Optics

Before delving into the processes involved in generating the broadband continuum probe and the tunable wavelength pump, a short review of nonlinear optics will help put these processes in context. In equation 6.1, the time dependent polarization series is truncated to three terms. The first term involves the linear susceptibility $\chi^{(1)}$ and describes the linear response in a dielectric medium. The second term, which contains $\chi^{(2)}$, is only nonzero for noncentrosymmetric mediums. Almost every instance of a $\chi^{(2)}$ process in this experiment uses β -Barium Borate (BBO) crystals. The only exception is the use of Lithium Borate (LBO) in the Evolution 20 W continuous wave diode laser used to pump the Spitfire regen. Third-order effects arise from the third term, which contains $\chi^{(3)}$. Third-order effects exist in all mediums including sapphire, a centrosymmetric crystal, and glass, which is isotropic.[13]



Figure 6.3: Schematic of the original optical pump optical probe experimental setup. The 800 nm output from the Spitfire regen is split into the optical pump with a tunable wavelength provided by the Topas OPA, and the broadband optical probe generated with a sapphire crystal.

$$P(t) = \epsilon_0 \chi^{(1)} E(t) + \epsilon_0 \chi^{(2)} E^2(t) + \epsilon_0 \chi^{(3)} E^3(t)$$
(6.1)

The second term is responsible for several nonlinear optical effects, including optical rectification mentioned in Chapter 3 in reference to THz probe generation and difference frequency generation discussed later in this chapter in reference to optical parametric amplification. The third term is responsible for the Kerr effect needed for the passive modelocking discussed in Chapter 3 and self phase modulation, which is the primary effect involved in white light continuum probe generation. The effects of these two nonlinear susceptibilities are summarized in the following chart (Table 6.1).

6.2.2 White Light Continuum Probe Generation

The generation of a broadband continuum, or white light continuum (WLC), is a nonlinear optical effect. Like the generation of the THz probe discussed in Chapter 3, WLC arises from the inability of the dipoles in a material to respond to an alternating electric field in a linear fashion.[63] However, the optical rectification needed for THz generation is a $\chi^{(2)}$ process and the self-focusing and self phase modulation

| 2 nd Order Effects | | 3 rd Order Effects | |
|---------------------------------------|----------------------------------|---------------------------------|--------------------------------------|
| Second harmonic generation (SHG) | $\omega + \omega = 2\omega$ | Third harmonic generation (THG) | $\omega + \omega + \omega = 3\omega$ |
| Optical rectification (OR) | $\omega - \omega = 0$ | Self focusing (Kerr lensing) | $n = n_0 + n_2 I$ |
| Sum frequency generation (SFG) | $\omega_1 + \omega_2 = \omega_3$ | Self phase modulation (SPM) | |
| Difference frequency generation (DFG) | $\omega_1 - \omega_2 = \omega_3$ | | |

Table 6.1: A summary of the nonlinear effects arising from the second and third terms of equation 6.1. In the associated equations, n is the index of refraction, Φ_{NL} is the nonlinear portion of the phase, c is the speed of light, z is the displacement in the direction of propagation, and I is intensity. For a pulse with a Gaussian distribution, I is a function of both time and space.

(SPM) needed for WLC generation are $\chi^{(3)}$ processes. The intensity must be at least 10^{13} W/cm² for the pulse to undergo the self-focusing and SPM required for spectral broadening.[72]



Figure 6.4: The optical Kerr effect occurs when a high intensity laser beam with a Gaussian profile passes through a medium and the refractive index shows a radial gradient with the maximum value occurring in the center. The medium acts as a lens and focuses the incident beam.

When the intensity of a pulse is high enough, Kerr lensing can occur. Kerr lensing was discussed in Chapter 3, and the index of refraction was given in equation 3.2 as

$$n(\omega, I) = n_0(\omega) + n_2(\omega)I \tag{6.2}$$

The nonlinear refractive index n_2 depends on the intensity of the pulse. Since the intensity of the laser pulse has a Gaussian distribution, the value of n_2 will be the greatest in the center of the pulse and the medium will act as a positive lens (Fig. 6.4. The phase can be written in terms of time and displacement in the z direction:

$$\Phi(z,t) = \omega_0 t - (n\omega_0/c)z \tag{6.3}$$

When equation 6.2 is inserted for n in equation 6.3, the phase becomes

$$\Phi(z,t) = \Phi_L(z,t) - \Phi_{NL}(z,t) \tag{6.4}$$

where

$$\Phi_L(z,t) = \omega_0 t - (n_0 \omega_0/c) z$$
(6.5)

$$\Phi_{NL}(z,t) = (n_2 \omega_0 / c) I(z,t) z$$
(6.6)

 Φ_L is the linear phase. Φ_{NL} is the nonlinear term of the phase, which is a function of intensity *I*. In other words, the pulse modulates its own phase. This nonlinear effect is called self phase modulation (SPM).[13]

SPM broadens the frequency spectrum when max $\Phi_{NL} < \pi$. When max $\Phi_{NL} = \pi$ the spectrum begins to distort and fine ripples begin to appear in the center. As Φ_{NL} grows with further propagation in the z direction, the spectrum continues to broaden, more ripples form, and the energy concentrates in the spectral wings.[13] The sapphire used to generate WLC is thick enough that positive group velocity dispersion (+GVD) also occurs. This +GVD has the effect of broadening the pulsewidth, and the pulse takes on a positive chirp. Fig. 6.5 shows an example of the broadening of a pulse envelope with increasing displacement z, computed in Matlab.¹ The combined effect of SPM and +GVD is shown² in Fig. 6.6. With increasing z the spectrum broadens

¹ This particular result was calculated for an ultrashort pulse of $\lambda_0 = 0.8$ nm propagating through 500 mm of a single-mode fiber. This optical system is conceptually the same as our 800 nm pulse traveling through sapphire, in that both involve SPM and +GVD

 $^{^2\,}$ Again, this calculation was for a 500 nm single-mode fiber



Figure 6.5: A laser pulse experiences positive group velocity dispersion (+GVD) from traveling through the sapphire. The pulsewidth broadens and the pulse takes on a positive chirp, so the longer wavelengths arrive before the shorter wavelengths. This plot shows the increasing pulse duration of a pulse envelope with increasing distance z from the sapphire.

and ripples form, but with the addition of +GVD the energy no longer concentrates in the spectral wings.[13] Instead the result is a smooth broadband continuum pulse, with the initial pump energy distributed over the entire generated continuum, leading to very low intensities for the wavelengths on the wings of the spectrum, far from the original 800 nm wavelength.[72]

The material that generates the WLC was selected based on the energy structure of the samples being studied. For TbAs nanoparticles grown in GaAs or InGaAs, the highest energy transition we are interested in studying is the bulk bandgap of GaAs. At room temperature the bulk bandgap of GaAs is 1.424 eV,[42] which corresponds to a wavelength of 870 nm. Therefore we chose to use sapphire, which is capable of producing a spectrum that ranges from about 400 nm to 1100 nm, for the continuum generation. Calcium fluoride is another commonly used material for continuum generation, but the most stable wavelengths generated are much too high in energy for probing the energy structure of TbAs:GaAs. Calcium fluoride is also prone to damage



Figure 6.6: As the pulse travels through the sapphire (z direction), the power is not as concentrated in the center of the spectrum but instead begins to distribute across the wavelengths. The pulse itself begins to encompass a wider portion of the spectrum.

and must be mounted on a slowly moving stage to prevent overheating from the focused laser. This is highly inconvenient for an experiment that relies heavily on careful spatial overlap of the pump and probe beams in the sample.

When viewing the spectrum of the WLC probe, it is quickly evident that the majority of the 800 nm that is incident on the sapphire actually passes through the crystal unchanged. For this reason, an 850 nm long-pass (LP) filter is placed in the beam path after the sapphire. The CCD camera is also only capable of viewing wave-lengths up to 1000 nm, and so the usable probe wavelength range for this experiment

is 850-1000 nm.

6.2.3 Optical Parametric Amplification

The second term in equation 6.1 can be expanded to the form presented in equation 3.3 from Chapter 3. We can write the second-order polarization $P^{(2)}$ as

$$P^{(2)}(t) = \chi^{(2)} E(t)^2 = \frac{1}{2} \chi^{(2)} A(t)^2 + \frac{1}{2} \chi^{(2)} A(t)^2 \cos(2\omega_0 t).$$
(6.7)

The first term represents the average of the induced polarization over a single optical cycle and is responsible for optical rectification. This is the term from which the THz probe is generated. Looking at the second term of equation 6.7, we can see that the dipole oscillations constituting the time dependence of the polarization generate electromagnetic radiation of angular frequency 2ω . This doubled frequency is present in the resultant field along with the the much stronger fundamental frequency ω . This is referred to as second harmonic generation (SHG), which appears in Table. 6.1.[63]

When two beams of different frequencies interact within a nonlinear medium, frequency mixing can occur. The resulting electric field can be written as

$$E = E_{01}\cos(\omega_1 t) + E_{02}\cos(\omega_2 t) \tag{6.8}$$

or in exponential form,

$$E = \frac{1}{2}E_{01}(e^{i\omega_1 t} + e^{-i\omega_1 t}) + \frac{1}{2}E_{02}(e^{i\omega_2 t} + e^{-i\omega_2 t}).$$
(6.9)

Second-order polarization depends on E^2 , and from equation 6.9 it is easy to see that the square of E produces harmonics in $2\omega_1$, $2\omega_2$, $\omega_1 - \omega_2$, and $\omega_1 + \omega_2$. One type of frequncy mixing is parametric amplification, where $\omega_3 \rightarrow \omega_1 + \omega_2$. In this case, power flows from a pump wave of frequency ω_3 into signal and idler waves of frequencies ω_1 and ω_2 , respectively. An optical parametric amplifier uses this process by allowing a small signal wave of frequency ω_1 and a powerful pump of frequency ω_3 to interact within a nonlinear medium. An idler frequency $\omega_2 = \omega_3 - \omega_1$ is produced as a beat frequency. The idler frequency then beats with the pump frequency to enhance the signal frequency $\omega_1 = \omega_3 - \omega_2$. In this way, both signal and idler waves are amplified by drawing energy from the pump wave via difference frequency generation (DFG).[63]

Parametric amplification can only occur if two conditions are met:

$$\omega_3 = \omega_1 + \omega_2 \tag{6.10}$$

and

$$\mathbf{k}_3 = \mathbf{k}_1 + \mathbf{k}_2, \tag{6.11}$$

where \mathbf{k}_j are the wave vectors of the three waves. Equation 6.11 is known as the phase matching condition, and can be written as

$$\frac{n_3}{\lambda_3} = \frac{n_1}{\lambda_1} + \frac{n_2}{\lambda_2} \tag{6.12}$$

By adjusting the angle between the optical axis of the birefringent crystal and the direction of wave propogation, the wavelength for which equation 6.12 is satisfied can be changed.[72]

For this experiment we use a Topas optical parametric amplifier (OPA) from SpectraPysics. This OPA has the addition of frequency mixer stages mounted to the output port, which are capable of producing second harmonic generation, fourth harmonic generation, and sum frequency generation, resulting in a laser output that is tunable to any wavelength in the range of 300-1600 nm. Although such a wide range of wavelengths is not needed for pumping the TbAs nanoparticle samples in this thesis, the capabilities of this system will be widely applicable to future projects.

The Topas generates an output beam of a specific wavelength via a three step process. In the first step, a small fraction of the 800 nm input beam is used to produce a white light continuum (WLC) in sapphire. This process is identical to the WLC generation described in the previous section. In the second step, the WLC is focused inside a BBO crystal, along with another portion of the the input beam referred to as the pre-amp beam. The pre-amp beam will parametrically amplify only the wavelength in the WLC that satisfies the phase matching condition in equation 6.12. The wavelength of the resulting signal beam can be tuned by changing the delay of the WLC



Figure 6.7: A simplified schematic of the beam paths inside the TOPAS OPA. White light continuum (WLC) is generated in the sapphire. One wavelength from the WLC is parametrically amplified by the pre-amp beam in the first BBO crystal. This signal beam is then parametrically amplified by the pump beam in the second BBO crystal.

pulse with respect to the pre-amp pulse and adjusting the crystal angle for optimal phase-matching. The pulses are overlapped non-collinearly in order to easily separate out the amplified signal beam. In the third step, the signal beam is parametrically amplified from a pump beam that contains the majority of the energy from the original input beam. This portion of the input beam is split off from the rest using the first beam splitter (BS1 in Fig. 6.7). The signal and pump beams are overlapped collinearly in the second BBO crystal, resulting in collinear and well-collimated signal and idler beams.[20] Filters are screwed onto the Topas output port in order to spectrally filter the idler beam from the output beam.

6.2.4 Spectrometer and CCD Camera

In order to spectrally resolve the transmission of the WLC probe beam through the sample, we use an Acton Research SpectraPro-300i spectrometer coupled to a 400x1340 pixel CCD camera array. The spectrometer has a focal length of 300 mm and spatially separates the wavelengths of the incoming light via a 1200g/mm diffraction



Figure 6.8: A schematic of the Acton SpectraPro spectrometer. The WLC probe is focused onto the entrance slit of the spectrometer with an off-axis parabolic mirror (OAP), and is spectrally separated by the diffraction grating. The spatially separated wavelengths are incident on the CCD.

grating. See Fig. 6.8 for a schematic of the optical components of the spectrometer. The incident probe is focused with an off-axis parabolic mirror (OAP) onto the entrance slit, which is imaged by two spherical mirrors M1 and M2 onto the plane of the CCD array.

The optical grating contains numerous narrow grooves, separated by a distance d. The grooves are covered with a reflective layer. The narrow groove spacing causes the reflected light to have a diffraction-limited angular distribution. The collimated light is incident on the grating with an angle of α with respect to the normal of the grating plane, and is reflected by each of the grooves into an angular cone defined by diffraction.[25] The constructive interference of the reflected partial waves is given by the grating equation

$$d(\sin\alpha + \sin\beta) = m\lambda,\tag{6.13}$$

where the angles α and β are shown in Fig. 6.8.

The spectrally separated light is then incident on a charge-coupled device (CCD) camera. The CCD chip in the camera contains pixels made of p-doped MOS capacitors. Incoming photons are converted into electric charges. These electric charges are shifted between capacitive bins and then converted into a digital value that is sent to the computer for readout. The CCD is cooled with liquid nitrogen to suppress dark counts arising from ambient photons, which are present even when the room lights are turned off.

6.3 Reference Detection Scheme

The first iteration of our optical pump optical probe transient absorption spectroscopy experiment was a simple system, depicted schematically in Fig. 6.3. We excited the sample with our tunable wavelength pump beam and observed the changes in the absorption of the probe beam as a function of delay time. We quickly came to the realization that, with this design, we were not directly observing the change in absorption of the probe. Instead we were observing the change in the transmission of the WLC probe through the sample and making the dangerous assumption that no changes in the transmission were occurring from fluctuations in the WLC probe itself due to optical instabilities. To test the stability of the WLC probe pulses, we viewed the probe pulses without a sample in the holder and with the pump pulses turned off. To reduce the noise as much as possible, we set the spectrometer shutter and CCD camera to the maximum integration time of 7 seconds. We observed that the WLC spectra were not reproducible due to optical fluctuations, and therefore it was not possible for us to attribute changes in transmission to changes in sample absorption.

6.3.1 Optimizing the Stability of the WLC Probe

Our first efforts to remedy the situation revolved around increasing the stability of the WLC probe. After meeting Dr. Jennifer Ogilvie from the University of Michigan Physics Department at an AMO seminar hosted by the University of Delaware, we asked one of her graduate students for advice on constructing our experiment. Franklin Fuller, a fourth year PhD student, emphasized the importance of the beam quality when generating the WLC probe, as well as the stability of the optics used after the WLC generation.^[33] As a result of these conversations, we redesigned our probe beam path.

We began with improving the quality of the 800 nm light used to generate the WLC. In order to not damage the sapphire crystal, we had used a Glan polarizer to attenuate the output power of the Spitfire regen (after the portion that powers the Topas OPA was split off). The use of a Glan polarizer allowed us to adjust the power at will, but resulted in poor spatial mode quality of the beam. The output mode looked like a square. We replaced the Glan polarizer with an 80%/20% pellicle beam splitter, allowing us to significantly attenuate the power without sacrificing the TEM_{00} Gaussian mode of the beam. A variable ND filter wheel placed after the beam splitter provides us the ability to tune the power to the value that yields the most stable WLC. Too little power results in a flickering WLC where occasionally the intensity in the sapphire dips below the third-order regime, but too much power results in a massive instability in WLC generation. The mode quality was further improved with the installation of a pinhole iris after the ND wheel. The iris is closed just enough to cut off the outer fringes of the beam, which tend to fluctuate in time. Finally, the addition of a polarization wheel offers yet another parameter that can be adjusted for optimal WLC generation.

We then turned our attention to improving the stability of the WLC beam, which depends on its collimated width. In order to decrease the width of the collimated beam, we replaced the lens used to focus the 800 nm beam into the sapphire with a longer focal length lens, and replaced the 2" diameter off-axis parabolic mirror (OAP) used to collimate the generated WLC with a 1" diameter OAP. We placed this new 1" OAP on a highly stable kinematic stage offering adjustability in the x, y, and z directions, combined with a mount that allowed us to also adjust the tilt in the x and y directions. The other three OAPs in Fig. 6.3 were replaced with spherical mirrors on stable mounts, which are much easier to align in order to achieve a tight focus in the sample and a well-collimated probe beam after the sample. We also upgraded our sample holder to a sturdy mount designed to hold wafer samples.

All of these improvements resulted in a significantly more stable WLC probe, but unfortunately the power fluctuations in the probe were still too large to be able to extract absorption data. Seven consecutive data runs, each integrated over a 7 second time interval, can be seen in Fig. 6.9. At this time we realized that we would need to redesign our data collection method to use a reference detection scheme. I visited Dr. Oglivie's laboratory at the University of Michigan to observe her experimental setup and learn how to build a similar data collection scheme in our lab. Her experiment had some significant differences from our own, but I was able to learn the basic concept and adapt it to our needs.



WL Noise No Pump, with ND Filter, 7s Integration

Figure 6.9: Seven consecutive data runs observing the WLC probe spectrum with no sample and no pump beam. Each data run was integrated over a 7 second time interval. The WLC probe intensity fluctuates over time.

6.3.2 Reference Detection

By sampling the probe intensity for each pulse via a reference beam, we are able to correct the calculated ΔA spectrum for power fluctuations. In the following derivation,

 $Pu \equiv$ unpumped probe beam transmission intensity,

 $Pp \equiv$ pumped probe beam transmission intensity,

 $R \equiv$ reference beam intensity,

 $G \equiv$ a diagonal matrix of gain factors,

 $\Delta T \equiv$ the change in probe transmission due to absorption in the sample.

Each of these is a two-dimensional matrix of i and j, where the subscript i designates each individual laser shot and j designates each CCD pixel and corresponding wavelength. We would like to calculate a transient absorption spectrum for each wavelength:

$$\Delta A_{i,j} = \frac{\Delta T_{i,j}}{P u_{i,j}} \tag{6.14}$$

For each laser shot, the true value of ΔT for each wavelength is defined as

$$\Delta T_{i,j} = P p_{i,j} - P u_{i,j} \tag{6.15}$$

Unfortunately we cannot directly measure both Pp_j and Pu_j simultaneously for the same laser shot *i*. We can however measure Pp_j and R_j for the same *i*, and as long as we know how to transform $R_{i,j}$ into $Pu_{i,j}$ using a gain factor $G_{i,j}$, we can reconstruct what $Pu_{i,j}$ must have been for a given $Pp_{i,j}$.

It is not surprising that when reconstructing the unpumped probe spectrum $Pu_{i,j}$ from the reference spectrum $R_{i,j}$, there will be a slightly different gain factor $G_{i,j}$ for each wavelength j. The spectral response of the optical elements in the reference and probe beam paths is not uniform for all wavelengths. Therefore each pixel readout of the reference beam will need to be multiplied by a different linear gain factor to obtain an estimate of the probe beam at the corresponding wavelength. It would be tempting to first take a few spectra to find a 1-D matrix for the gain factors given by G_j and then apply it to an entire data set of $R_{i,j}$ taken over the course of i laser shots.

However, Dr. Ogilvie has found that this method is not sufficiently accurate.[33] The gain factors only remain valid for about a minute before they are no longer accurate. However, we can assume that the gain factor will remain constant for two sequential pulses, so that $G_{i,j} \approx G_{i-1,j}$. We therefore estimate that the unpumped probe $Pu_{i,j}$ is roughly equivalent to

$$Pu_{i,j} = G_{i-1,j}R_{i,j} (6.16)$$

for i = 1, 3, 5...n. We implement a data collection scheme in which every other probe pulse (i = 0, 2, 4...n - 1) is incident on the sample without an accompanying pump pulse. The gain factors $G_{i,j}$ are calculated from these pulses, and then applied to the $Pp_{i,j}$ and $R_{i,j}$ collected for i = 1, 3, 5...n. We now obtain a ΔA spectrum for i = 1, 3, 5...n and j = 0, 1, 2, 3...n,

$$\Delta A_{i,j} = \frac{Pp_{i,j} - G_{i,j}R_{i,j}}{G_{i,j}R_{i,j}}$$
(6.17)

where $G_{i,j}$ is given by

$$G_{i,j} = \frac{Pu_{i-1,j}}{R_{i-1,j}}.$$
(6.18)

For each delay time that data is collected for ΔA , the CCD will collect light from two sequential pulses over a range of 1340 pixels corresponding to different wavelengths. The CCD is simultaneously collecting light from the probe and reference beams from both of these two pulses, resulting in a 1340 × 4 matrix of data for each delay time.

6.3.3 Optical Path Design

The reference detection scheme required a new optical layout for the experiment, shown in Fig. 6.10. A 50%/50% beam splitter was installed before the sample, splitting the WLC into a probe beam that is focused in the sample and a reference beam that is routed around the sample. As noted earlier, three of the OAPs were swapped out in favor of spherical mirrors for easier alignment and the availability of affordable stable mounts. Note that unlike OAPs, where the angle between the incident and reflected beam is 90°, the incident and reflected beams for a spherical mirror should be as close



Figure 6.10: The revised optical layout includes a reference beam and chopper wheel for the reference detection scheme. Four spherical mirrors replace the three OAPs that had been used to focus the probe onto the sample, recollimate it, and focus it onto the spectrometer entrance slit. For clarity, this schematic excludes the optical components for improving the WLC generation, as well as the optional ability to image the transmitted pump beam onto the spectrometer.

to on-axis as possible to minimize distortions. This leads to a very different optical path.

The probe and reference beams are split after the first spherical mirror, necessitating the use of a spherical mirror in the reference beam path for collimation. The probe beam and the pump beam are both collimated after the sample with a single spherical mirror, and the reflected beams are picked off using a D-shaped mirror located on either side of the incident beams. The probe and reference beams heading to the spectrometer are nearly parallel and collinear, but not quite. This results in the two beams being imaged onto separate portions of the CCD, offset in the vertical direction. In the pump beam path just before the beam stop, there is a flip mirror which allows the transmitted pump to line up on the reference beam path into the spectrometer, while the reference beam itself is blocked by the back of the flip mirror. This allows the pump to be imaged onto the spectrometer for diagnostic purposes. A chopper wheel was installed in the pump beam path to facilitate the collection of pumped and unpumped probe spectra. The chopper wheel was placed about a foot away from the delay stage to offer a longer lever arm when trying to align the beam onto and off of the delay stage. Any small deviation from a parallel configuration will result in the pump beam "walking off" of the probe beam at the focus spot in the sample as the delay stage moves. In order to temporally overlap the pump and probe pulses in the sample, this extra distance in the pump beam path, along with the three passes made by the pump beam through the Topas OPA, must be compensated for by lengthening the static delay line of the probe. Due to limited space on the optical table, the static delay line wraps back and forth several times.

6.3.4 Creating a Timing Scheme for Data Collection

The benefit of reference detection is that any shot-to-shot power fluctuations in the WLC probe power can be eliminated from the data by using the reference beam to sample each laser shot. However, this means that the data can no longer be collected and integrated over several seconds. Instead, the spectrometer is operated in free-run mode with the shutter left open, and the CCD must be triggered by the laser. The dark time between the pulses themselves become the "shutter" for data collection. A digital delay generator (model DG645) from Stanford Research Systems is triggered by the Pockels cells of the Spitfire regen. The delay generator then creates a signal that triggers the chopper and CCD camera. In addition, two separate regions of interest (ROIs) must be specified on the CCD chip, so that the probe and reference pulses for each laser shot are binned and read out separately from each other. Since the pixels in the x-direction correspond to separate wavelengths, the ROIs were defined to be in different locations in the y-direction.

To make this scheme feasible, the CCD camera chip must be fast enough to bin the pixels in the y-direction for two separate ROIs, read out the data to the computer, and clear the charges from the CCD within the dark time between pulses. The time required for this process is affected by chip size and how many ROIs must be read out. Dr. Ogilvie's Princeton Instruments PIXIS 100 spectrometer and CCD camera is a newer model than ours, and is capable of collecting data for two ROIs on a 1340×100 pixel chip area in less than 2 ms.[33] We experimented with our CCD camera to see how fast we could possibly bin the pixels, read out the data, and clear the chip. Within Labview, we were able to program the chip to only use a portion of our 1340×400 pixel chip. We set the custom chip size to 1340×80 pixels and defined ROI 1 as pixels 1-40 in the y-direction, and ROI 2 as pixels 41-80. Under these conditions, the fastest time we could obtain was 7.89 ms.

Because of the relatively long time required for a single cycle of CCD readout, we needed to lower the repetition rate of our Spitfire regen from 1 kHz down to 125 Hz. At such a low repetition rate, the Spitfire was extremely unstable, increasing the shot-to-shot noise of the experiment. The instability was sufficiently large enough to cause our noise to overcome our signal, rendering this approach untenable. As a result, we decided to switch the data collection scheme to a single-channel scheme using a lock-in detector. We later stumbled across a 2009 paper in *Photosynthesis Research*, a journal in a completely different field from our own, that states,

Under some experimental conditions, detection with a diode array is not possible or appropriate. For instance, for many experiments in the near-IR and the UV, other detector types need to be employed that, in combination with the white-light continuum intensities at those wavelengths, lack the sensitivity required for array detection. In these cases, single wavelength detection is often employed.[9]

This reference validates that our challenges with multi-channel detection in the NIR are not uncommon.

6.4 Lock-in Detection Scheme

To install components for single wavelength detection using a lock-in amplifier. I installed a silicon photodetector from Thorlabs at the exit slit of our spectrometer. The spectrometer diverter mirror was flipped to direct the probe beam to this exit slit rather than to the CCD chip. I then installed a Princeton Applied Research lock-in amplifier and worked on interfacing it with our computer. Eric Chen, another graduate student, was also assigned to this project and completed the installation of both singleand double-modulation lock-in systems. Using the updated single-channel detection scheme, we have recently obtained promising preliminary results, shown in Fig. 6.11. Eric is currently working on rewriting the Labview control software to automatically scan the delay stage for data collection using this new approach. We anticipate using this system to obtain optical pump optical probe data on rare-earth nanoparticles in the extremely near future.



Figure 6.11: Preliminary data taken for TbAs:GaAs with an 860 nm pump and 930 nm probe. The data was collected by manually stepping the delay stage over a 900 ps range, and represents the average of five separate data runs.

Chapter 7 SUMMARY AND CONCLUSIONS

The objective of this research was to investigate the electronic structure and charge carrier dynamics of TbAs nanoparticles in GaAs and InGaAs. Based on the plethora of studies completed on ErAs nanoparticles over the past 20 years, we hypothesized that TbAs nanoparticles would be semimetallic in nature, as is the case for ErAs nanoparticles. TbAs at first glance seems very similar to ErAs. The only difference between them is the addition of two more f-shell electrons, and prior theoretical calculations suggest that F-shell electrons should be treated as core electrons that would not affect the opening of a bandgap.

The results of our optical pump THz probe transient absorption spectroscopy measurements on both TbAs:GaAs and TbAs:InGaAs are not in agreement with our initial hypotheses. We observe three distinct relaxation processes in TbAs:GaAs that correspond to 1) the rate of free charge carriers relaxing into the TbAs states, 2) the rate of carriers exiting the trap states, and 3) the rate of carriers nonradiatively recombining across the bulk GaAs bandgap. Changing optical pump fluence affects these three rates and the fraction of free charge carriers that participate in each process. From this data we conclude that the TbAs states are saturable, and spatially confined TbAs acts as a semiconductor. This result is in stark contrast to ErAs nanoparticles. The lack of a temperature dependence confirms that the TbAs states are deep within the GaAs bandgap.

We see evidence of these same relaxation processes in TbAs:InGaAs, but our ability to observe all three relaxation rates depends on the concentration of TbAs in the sample. In samples with a low concentration of TbAs (e.g. 0.84%), the fraction of free charge carriers relaxing into the TbAs states is too small to be resolved for the range of optical pump fluences available in this experiment. Experiments on a sample with 1.304% TbAs confirm that the TbAs states in InGaAs are also saturable. The fluence dependent data for the 1.304% TbAs concentration sample also suggests that the TbAs states are close to the InGaAs band edge, as expected.

Optical pump optical probe transient absorption spectroscopy is a technique that offers measurements that are complementary to our data collected with a THz probe. To this end, we have spent a great deal of time and effort constructing an optical pump optical probe system in our laboratory. The technique of multichannel detection using a CCD camera is already frequently used to collect energy-resolved transient absorption in the 300-600 nm probe range. We sought to expand this technique to be used in the near infrared probe range for observing charge carrier relaxation processes in solid state materials but ultimately realized that multichannel detection is simply not possible with our current equipment. We have now redirected our efforts to constructing a single channel data collection scheme using a lock-in amplifier. We are currently optimizing this system for data collection in the near future.

Our new understanding of the electronic structure and carrier dynamics in TbAs nanoparticles will impact the design of materials for future optoelectronic devices. Interest in the electronic properties of rare-earth nanocomposites other than ErAs is increasing, [74] and our work pioneers the systematic analysis of electronic structure and carrier dynamics for this new area of nanocomposite research. Our optical pump optical probe transient absorption system will extend the type of measurements that can be done and the range of information that can be extracted.

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Appendix A

OPTIMIZING THE TSUNAMI OSCILLATOR ALIGNMENT

For information on performing a complete realignment of the Tsunami oscillator, refer to the Tsunami user's manual and the helpful tips listed in Dr. Matthew Doty's PhD Thesis appendices. The following is a simple procedure for optimizing the power output of the Tsunami under typical conditions.

1) Turn on the Tsunami as during normal operation and mode-lock it. Allow the Tsunami to warm up for about 20 minutes before proceeding with the alignment.

2) Remove the black lid pieces of the beam covering between the Tsunami and the Regen. Place a power meter at the Tsunami output, checking to make sure that it is set to read 800 nm light. You are aiming for a power reading of around 370 mW.

3) There are four plastic knobs that protrude through the top casing of the Tsunami, two green knobs that control the horizontal adjustment of the end mirrors, and two blue knobs that control the vertical adjustment. These end mirrors are what defines the cavity that causes the laser to modelock. First adjust one of the green knobs to maximize the power. Then adjust the other green knob, followed by the two blue knobs. Repeat this procedure, walking the beam until you no longer see any improvement. Two rounds of this are usually sufficient. Note that there is a slight time lag between adjusting a knob and seeing the effect on the power meter. Be sure to allow the meter to catch up before making the next adjustment.

4) Do not forget to remove the power meter and replace the black lid pieces when you are done.

Appendix B

SPITFIRE REGENERATIVE AMPLIFIER REALIGNMENT

For all of the alignment procedures pertaining to the Spitfire, please refer to the following beam path diagram in Fig. B.1. Please note that the Spitfire in Dr. Doty's lab is a regenerative amplifier from SpectraPhysics that was custom-built to have the capability of amplifying ps laser pulses as well as fs pulses. As a result, the optical layout is a bit different from the beam path published in the Spitfire users manual.



Figure B.1: This diagram depicts the optical beam paths for the Spitfire regenerative amplifier. See the text for a description of each optical component. Note that this beam path differs from the diagram in the Spitfire manual because our system was custom-built to accomidate ps pulse durations as well as fs.

B.1 Making Small Adjustments

On most days, you should be able to simply turn on the laser using the Standard Operating Procedure (SOP) found next to the Regen. If you find that after letting the Regen warm up, you are not getting quite as much power as usual, but the reading is within a few tenths of a Watt, you do not need to do a full realignment. If you are getting less than 1.5 W compressed Regen output and the energy buildup in the cavity looks low or nonexistent, you will need to do a full realignment (see Section B.2). To make small adjustments:

 Place the power meter after optic (51). Make small adjustments to (14) and (16) to optimize the amplitude of the cavity build-up pulses on the oscilloscope, taking care that this does not result in a dip in power on the meter.

2) If you are not satisfied with the output power, try making small adjustments to the end mirrors of the cavity, optics (35) and (39). Again, aim for the maximum cavity build-up as well as the max power reading.

3) Repeat step 1. If you are still not satisfied, consider moving on to the complete realignment procedure.

B.2 Complete Realignment Procedure

Refer to Fig. B.1 for all of the numbered optical components listed.

B.2.1 Stretcher Realignment

1) Begin the alignment procedure with the Tsunami modelocked. The spot will be brighter and easier to see on the irises. After lifting the lid of the Regen, override the safety defeat mechanism (See the user manual if you dont know how to do this) to allow the beam to enter the stretcher. The Tsunami output enters the Regen next to mirror (1). The beam enters a Faraday isolator from Electro-Optics technology (EOT), labeled (3). The Faraday isolator essentially acts as a uni-directional light valve. It is used to protect the laser source from destabilizing feedback or actual damage from back-reflected light. Use the two mirrors outside of the Regen and after the Tsunami
to align the beam through irises (2) and (4). Use the second mirror after the Tsunami output to center the beam on iris (2) and the third mirror (the one closest to the Regen entrance) to center beam on iris (4). Note: You may need to climb onto the optical table to be able to see the irises properly.

2) There is a movable iris that is kept lying on the bottom of the stretcher. Insert this iris into post holder (8). Use mirror (6) to center the beam on this iris. Remove iris and place it in post holder (9). Use mirror (6) to center the beam on this iris. Repeat this step, walking the beam until it passes through the center of the iris placed at either location. Remove the iris and return it to the bottom of the stretcher where it is out of the way.

3) Knock the Tsunami out of modelock by closing the shutter to the Tsunami and opening it again. On grating (11) you should see four dots, all in a vertical line down the center, and all should be evenly spaced. The first dot counting from the top of the grating is where the beam hits the grating for the third time. The second dot is the first time the beam hits, or in other words, the input beam that has just passed through irises (8) and (9). The third dot is from the beams second pass, and the fourth dot is where the beam hits the grating for the fourth and final time. Here is the process in more detail. The beam hits the optics in the following order: $1 \longrightarrow 2 \longrightarrow 3 \longrightarrow 4 \longrightarrow 5 \longrightarrow 6$. The beam passes through optic (7) and over the tops of (8) and (9), assuming the iris has been removed. After optic (6) the beam is incident upon grating (11), which shows up as dot 2. If the Tsunami is modelocked, at this point the beam becomes stretched in time and then travels $11 \longrightarrow 13 \longrightarrow 12 \longrightarrow 13 \longrightarrow 11$. This stretched beam shows up on grating (11) as spot 3, which looks like a line when the Tsunami is modelocked. The beam then travels $11 \longrightarrow 7 \longrightarrow 11$ and shows up on the grating as spot 1, which also looks like a line when modelocked. At this point the beam returns to its original size and travels $11 \longrightarrow 13 \longrightarrow 12 \longrightarrow 13 \longrightarrow 11$ and hits the grating for the final time at spot 4. From here the now temporally stretched pulse reflects off of mirror (14) and leaves the stretcher.

4) If the dots are not spaced evenly in the vertical direction or one is missing,

adjust the vertical knob (the top knob) on the gold mirror (13) until they are. Note that the dots should not move horizontally at all. If they do, check to be sure that gold mirror (13) and its mount are securely attached to the table and are stable. There should be a beam that goes over the top of grating (11) and hits the retro-reflection mirror (12). This beam should hit mirror (12) in the center horizontally and about 3 or 4 mm from the bottom. If the beam is not centered on mirror (12) horizontally, shift mirror (12) in its mount until the beam is centered.

5) Look at the four spots on the grating (11). If dots 2 and 3 are not in a vertical line, use the knob on retro-reflection mirror (12) to adjust them horizontally.

6) If spots 1 and 4 on grating (11) do not line up with spots 2 and 3, use the horizontal adjustment knob on mirror assembly (7) to shift the dots horizontally until all four dots form a vertical line down the center of grating (11). If the dots seem to occasionally shift horizontally on their own or when you cause a disturbance by either shuttering the Tsunami or bumping the table, the Tsunami might be mode-hopping. Try adjusting the wavelength on the Tsunami to find a more stable spot.

7) Check to make sure that there is only one spot that appears on retro-reflection mirror (12). If there are two, use the horizontal axis adjustment of the upper mirror of mirror assembly (7) until the second spot disappears. Check to make sure that the four spots on the grating are still in line with each other.

8) Modelock the Tsunami at this time. You should see two spots on grating (11) and two horizontal lines, as discussed in step 3. Fig. B.2 shows how the grating should appear under normal conditions. If the lines do not look centered on grating (11), do not worry too much. Your eyes might not be sensitive enough to see the entire IR spectrum of the beam. If you would like to make sure that the lines are centered, look at them with the IR viewer.

B.2.2 Oscillator Cavity Realignment

1) Check to make sure that the modelocked output from the stretcher is not being clipped by either periscope (15) or mirror (16) in Fig. B.1. If it is, try to adjust



Figure B.2: The first line counting from the top of the grating is where the beam hits the grating for the third time. The first dot is the first time the beam hits. The second line is from the beams second pass, and the second dot is where the beam hits the grating for the fourth and final time. See Stretcher Realignment step 3 for a more detailed description.

mirror (14) in the stretcher until the beam is no longer clipped. Periscope (15) cannot be adjusted so in the case of a gross misalignment, you may need to try adjusting mirror assembly (7). If you decide to do this, recheck the stretcher alignment to make sure the beam is still being properly stretched. You may need to alternate between these steps several times.

2) Before proceeding to align the seed beam, you should align the pump beam in the oscillator cavity. Block the seed beam before periscope (15). The most convenient way to do this is to find the flip mirror located about where the words Seed Beam are written in Fig. B.1 and flip this mirror to the up position. This mirror is part of the setup for ps amplification and is flipped to the down position during normal fs operation.

3) If a power meter is placed after the oscillator cavity when the regen is in pulsed mode (as it is during regular operation), the beam will burn out the power meter. Therefore in order to use a power meter to optimize the pump power, the oscillator cavity will have to be set to run in continuous wave (CW) mode. In order to do this, use a hex key to loosen 1/4 waveplate (34) enough to be able to rotate it in

its holder. Rotate the waveplate about 45° so that the black dot is closer to optic (30) rather than pointing upward. Tighten with the hex key. Turn off both Pockels cells by hitting the buttons labeled Delay 1 and Delay 2 on the timing box above the Regen. The two square red lights should now be off. Override the safety defeat to allow the pump beam from the Evolution to enter the Regen next to 1/2 waveplate (18). The pump beam is now lasing in the oscillator cavity in CW mode.

4) You should now see the green pump beam hitting the first ti:sapph rod (17) and some faint red lasing making its way around the oscillator cavity. If you don't see this, measure the power before mirror (27) and make sure that the beam has 12 W of power. If the power is low, see the section Evolution Troubleshooting. There is a beam block stored in the section of the Regen for ps amplification. Slide this beam block into the pump beam directly after optic (24) in order to protect your hands from burns in the next several steps.

5) Assuming the power is fine, the issue is most likely that the pump beam is not hitting the rod (17) at the correct angle. Use the horizontal and vertical adjustments on mirrors (27) and (28) to walk the beam on the back face of the rod, the side closer to Pockels cell (33). The beam should hit the rod in the bottom right quarter of the back face.

6) Place a power meter directly after mirror (40) to monitor the CW pump power exiting the oscillator cavity. Take care that the meter is not blocking the beam as it travels from Brewster window (36) to Pockels cell (38).

7) In the next seven steps you will be walking the pump beam to optimize the power. Your goal is to achieve 1.7 W, though anything higher than 1.5 W is high enough to run the experiment. These next steps will take a great deal of patience. Do not attempt if you are tired.

8) Adjust the horizontal and vertical knobs on mirrors (27) through (31), (35), and (39) for maximum power.

9) Since the pump beam must overlap itself several times in the rod, there can be quite a few local maximums in the power. Chances are that even though each mirror has been adjusted for maximum power, the reading is still significantly lower than 1.7 W. To find the true maximum, you will be walking the alignment off just enough to get past the local minimum and then maximizing the power again for each pair of mirrors. Begin by turning the horizontal adjustment of mirror (31) until the power dips about halfway. Turn the horizontal adjustment of mirror (30) and see if you can get the power any higher than it was before this step. If not, return the mirror adjustments to approximately their original settings. Now try this same step again, this time turning the horizontal adjustment of mirror (31) in the opposite direction of what you just tried.

10) Turn the vertical adjustment of mirror (31) until the power dips about halfway. Turn the vertical adjustment of mirror (30) and see if you can get the power any higher than it was before this step. If not, return the mirror adjustments to approximately their original settings. Now try this same step again, this time turning the vertical adjustment of mirror (31) in the opposite direction of what you just tried.

11) Repeat the procedure stated in steps 8 and 9 except this time turn the adjustments of mirror (30) until the power dips to half its value and use mirror (31) to make the power higher.

12) Repeat the procedure stated in steps 8-10 with the next pair of mirrors, (35) and (39).

13) Repeat the procedure stated in steps 8-10 with the pair of mirrors you started with, (27) and (28).

14) Chances are that the power reading is still below 1.7 W. There is a possibility that the 1/4 waveplate is not allowing as much light through as it could. Try loosening it with a hex key and rotating it slightly until the CW power is maximized. If this does not gain you enough power to reach 1.7 W, repeat steps 8-12 again, except this time leave the mirrors in alternate positions than their original positions even if the power is not any higher. At this point, you are just trying various combinations of the horizontal and vertical adjustments of all six mirrors until you find the global max and the power skyrockets.

15) Pinhole irises (32) and (37) are tools to help you overlap the seed beam with the pump beam. Close iris (32) and see where the CW pump beam hits. Note that if you completely block the pump beam with the iris, the rod will stop lasing. This is normal. You need to shift this iris so that the pump beam goes through its center. Be sure to do this extremely carefully, because the tubing that delivers chilled water to rod (17) is very close to this iris, perhaps even touching it. If the chilled water tubing is bumped hard enough, or simply unluckily enough, the rod will slightly shift in its holder, completely undoing the alignment you just completed from steps 4-13. Shift iris (37) until the pump beam goes through its center as well.

16) Assuming that you have successfully completed step 15, use the safety defeat of the Regen to shutter the pump beam. Use a hex key to loosen 1/4 waveplate (34) in its holder and rotate it until the black dot is facing up- its original position. Do not leave this waveplate slightly rotated, even if doing so gives a higher power reading. If this waveplate is at all rotated during normal operation, the timing of the pulses will not be correct, giving rise to extra peaks in the buildup that show up between the true peaks. Tighten this waveplate. Turn on both of the Pockels cells but leave the pump beam shuttered for now. Remove the power meter.

17) You are now going to align the seed beam to overlap the pump beam on the back face of the rod. Unblock the seed beam by returning the flip mirror to the down position. The seed beam should be reflecting off of the front face of the rod, the side closest to Pockels cell (38), and hitting mirror (31) off-center. During normal operation the residual green light from the pump beam will hit mirror (31) on the right side of the front face, and the seed beam hits on the left.

18) Adjust mirror (16) so that the seed beam goes through the center of iris (32). Adjust mirror (14) so that the seed beam goes through the center of iris (37), taking care to not block the beam in the stretcher with your hand. Using the IR viewer will help you to see the seed beam on iris (37) while adjusting mirror (14). Walk these two mirrors until the seed beam goes through the center of both irises at the same time. Open both irises.

19) Remove the beam block after optic (24) and return it to the ps amplification section of the Regen. Override the safety defeat to allow the pump beam to enter the Regen. Hit the reset button on the timing box. You should now see that the oscilloscope is showing some power buildup in the oscillator cavity.

20) There is a small web cam stored on the shelf above the Regen. Plug it into the computer for the Tsunami. Open the icon on the desktop labeled Watcher. I downloaded the trial version for free so the first thing that will pop up is a message urging you to register the product and buy the full version. Click ignore and a small screen displaying what the camera sees will appear. Set up the camera so that the buildup of the cavity displayed on the oscilloscope can also be clearly seen on the computer monitor. Note that the cameras microphone makes a good support to keep it balanced on the shelf. Now you will be able to complete the next step without a partner viewing the oscilloscope for you.

21) Similar to the pump beam, the seed beam can have a series of local maximums in power. Just as you did in steps 9 and 10, look for a global max using the horizontal and vertical adjustments of mirrors (14) and (16) to walk the seed beam, using the buildup on the oscilloscope and computer monitor to view the power in the oscillator cavity.

22) Adjust the timing of the second Pockels cell by turning the knob on the timing box Out 2 Delay so that the Pockels cell releases the pulse right after maximum power buildup. The buildup on the oscilloscope should have the second to last pulse be the tallest pulse. The Pockels cell should not be set to dump the pulse exactly at its max power (tallest peak being the last peak) because this will result in a less stable pulse. Reasonable numbers for timing are:

Out 1 Delay: 89-102 ns Out 2 Delay: 534-744 ns Sync Out Delay: 605 ns Trigger Frequency: 1 kHz

B.2.3 Amplifier Realignment

1) Place the power meter in the beam right before it enters the compressor. Your goal is to get 2.7 W at this location, which is the uncompressed output. However, anything greater than 2.5 W is enough to run the experiment. Because the alignment in the oscillator cavity has completely changed, the beam will not be hitting mirror (42) in the same place or at the same angle as it did before. There is a chance that simply adjusting mirror (40) will fix most of the misalignment. Use iris (41) as a guide for this adjustment. Now try making small adjustments to the horizontal and vertical components of mirrors (42), (44), and (45). If you have at least 2.5 W, you are done with this section. If not, proceed to step 2.

2) Check that the pump beam is roughly going through the center of rod (43). If the pump beam is grossly misaligned, meaning that it is clipping on the side of the crystal or almost clipping, use mirrors (20) and (21) to adjust it. In general, the pump beam should be going through the center of optics (22) through (24). A small hex key may be needed to adjust mirror (21) because of its close proximity to Brewster window (19). Attempting to force a hex key into the adjustment knob hole of mirror (21) may result in accidentally loosening the mirror in its mount, causing the pump beam to drastically change direction. Take care that this does not happen.

3) The beam makes two passes through rod (43), approaching from the right each time. You are now going to set up the ability to measure the power between the first and second passes, so that mirror (42) can be optimized independently from mirrors (44) and (45). Shutter the pump beam to the Regen, using the safety defeat.

4) See Fig. B.3 for the rest of this step. Place power meter behind and to the left of mirror (45). Note, there is a flip mirror used during ps operation behind mirror (45), which is currently turned downward. Flip this mirror up in order to make room for the power meter. Locate the high intensity optics labeled LFS and LBF that are stored in a box in the wooden cabinet closest to our lab. Override the safety defeat and let the pump beam into the Regen. Slide lenses LFS and LBF into the beam at the same time, as shown in Fig. B.3. These two lenses form a telescope that expands

the beam enough that it will not harm the power meter. Adjust the lenses to direct the beam to the left of mirror (45) and onto the power meter. Use mirrors (40) and (42) to achieve the best overlap of the 800 nm beam and the pump beam in rod (43), thereby maximizing the power on the meter.

5) Shutter the pump beam and return the setup to normal by removing the two telescope optics, removing the power meter, and turning down the flip mirror. Adjust iris (41) so that the beam goes through its center, for future reference.

6) Place power meter directly before entrance to the compressor. Walk mirrors (44) and (45) until the beam's second pass through the rod now overlaps with its first pass and the pump beam. If at any time the beam is clipped by periscope (51), adjust mirror (48) to correct this. At this point the power meter should be reading something above 2.5 W, ideally 2.7 W.

7) The beam should enter the compressor with an alignment that allows the beam to leave the Regen and go through the center of the iris directly after the beam splitter that is directly after the autocorrelator. To ensure this, use the IR viewer to look at the beam's placement through optics (49) and (50). Use mirror (47) to align beam through the center of these two optics. Now use mirror (48) to align the beam through the center of the iris after the autocorrelator. Walking mirrors (47) and (48) may be necessary in the case of gross misalignment.

B.2.4 Compressor Realignment

In general, there should be no need for realigning the compressor. If the situation arises where it is necessary, see the appropriate section in the Spitfire users manual.



Figure B.3: In order to expand the beam after the second crystal, the two ultrafast optics lenses should be placed in this orientation.

Appendix C

TOPAS OPTICAL PARAMETRIC AMPLIFIER ALIGNMENT

For any gross misalignment of the Topas, a SpectraPhysics technician should be contacted. The following is a daily alignment procedure to ensure peak power. Refer to the Topas users manual Fig. 8 for the beam diagram.

 Measure the power of the beam entering the Topas. You should have about
W. Open the Topas lid and screw on the safety lock defeat. On the computer, click to open the Topas shutter.

2) There is a pinhole iris mounted to the outside of the Topas directly after mirror BRM2 (not shown in the diagram). Adjust the beam splitter (also not shown) between the autocorrelator and the Topas to center the incoming beam onto the center of this iris. Then open the iris completely.

3) Adjust mirror BRM2 to center the beam on the pinhole iris in L3.

4) Repeat steps 2 and 3 until the beam is simultaneously centered on both irises. Open the L3 iris completely.

5) The MC401 controller is connected to a mechanical stage in the Spitfire stretcher and changes the amount of negative dispersion added to the pulses. Use the (+) and (-) buttons on this controller to find the pulsewidth that causes the generation of the brightest white light from WLG. To do this, place a white card after the WLG and before L4. The best setting for the pulsewidth is when the white light shows completely symmetric rings of color. There will be some filamentation in the rings from the crystal being overly pumped.

6) Slowly close down the iris in L3 until all of the filamentation in the white light disappears.

7) Remove the white card and replace the Topas cover. Observe the Topas output beam with the Ocean Optics 4000 spectrometer. You may want to try adjusting the mirrors in steps 1 and 2 again while viewing the spectrum to optimize the output.

Appendix D

MISCELLANEOUS HELPFUL LAB PROCEDURES

D.1 Evolution Laser Troubleshooting

If the Evolution laser is giving an output that is less than 20 W, there are several things to check when diagnosing the problem:

- 1) Optics are dirty or damaged
- 2) Filter water is dirty and has deposited debris onto the rod
- 3) End mirrors of the Evolution need to be optimized (see users manual)
- 4) Q-switch should be switched to "internal" (this is controlled by the laptop)
- 5) LBO crystal temperature needs to be optimized (see users manual)
- 6) LBO crystal is damaged
- 7) Rod has dissolved a bit and has a slight hourglass shape
- 8) Diodes are aging or dead

D.2 Flushing the Chillers

The two ti:sapph rods in the Spitfire and the ti:sapph rod in the Tsunami are kept cool during operation by the small Lytron chiller in Dr. Doty's laboratory. The large Lytron chiller prevents damage from overheating in the Evolution laser. The large chiller should be flushed once a year as general maintenance. Change the filter in the large chiller before you begin. The filter casing is in the back of the chiller.

1) Drain the chiller. To do this, unscrew the top of the chiller and slide it off. Unscrew the left side of the chiller. Pull out the drainage hose and place a collection bucket underneath it. Unscrew the hose cap and drain the water reservoir in the chiller. Replace the hose cap. 2) Unscrew the cap for the reservoir (on the top of the chiller). Pour 1/2L of distilled white vinegar into the reservoir. Fill the reservoir the rest of the way up with distilled but NOT DEIONIZED water. Run the chiller (with the laser off) for 3-4 hours.

3) Repeat steps 1 and 2.

4) Drain and fill with distilled but NOT DEIONIZED water. Let run for 3-4 hours. Repeat twice.

5) Drain and fill the reservoir with distilled but NOT DEIONIZED water and top it off with one bottle of algae growth inhibitor.

D.3 Spitfire Grating Cleaning Procedure

In order to tell if the grating needs to be cleaned, shine a flashlight at grazing incidence onto the grating. If you are able to see what looks like a film covering the grating everywhere except where it has been burnt off by the laser striking the surface, a cleaning would be beneficial. The cleaning process will improve the reflectivity and the beam profile off of the grating. Be sure to wear gloves during this procedure and never EVER touch the grating surface itself. You will need a glass vessel big enough to swirl the grating around in (A glass vessel can be borrowed from the glass blowing shop in the Chemistry department), deionized water source, dry nitrogen source, and pure liquid dish soap such as Ivory.

1) Thoroughly wash the large glass vessel. Fill it with 1 L of pure DI water.

2) Add 2 drops of the pure liquid dish soap. Swish it around with a gloved hand. The solution will not look very soapy.

3) Before removing the grating from the holder, have a strategy for replacing the grating in the same orientation and close to parallel. I labeled the top of the grating and traced the contour of the holder onto the back of the grating when I performed the cleaning procedure.

4) Carefully remove the grating from its holder with a gloved hand. With the grating side down, gently shake the grating in the soap water solution for 1-2 minutes.

5) Gently rinse the grating (on all sides) with pure DI water copiously for several minutes.

6) Gently dry the grating by blowing pure dry nitrogen (not at full blast) to remove all of the water spots from the grating surface. The sides and back of the grating will still be wet, so wipe them dry with a Kimwipe. Be careful not to touch the grating surface when you do this.

7) Replace the grating into the holder and align to parallelism.

D.4 Using the Autocorrelator

The autocorrelator is located immediately after the Spitfire and provides a method of measuring the pulsewidth. Inside the autocorrelator the beam is split into two beams that are then noncolinearly frequency doubled in a nonlinear crystal. A spatial time delay results in an autocorrelation of the temporal intensity profile. This is read by a CCD and sent to an oscilloscope for observation. Refer to the users manual for a beam diagram and alignment procedure in the case of gross misalignment. Otherwise, the standard operating procedure is as follows:

1) Center the Spitfire output beam into the autocorrelator and connect an oscilloscope.

2) The MC401 controller is connected to a mechanical stage in the Spitfire stretcher and changes the amount of negative dispersion added to the pulses. Use the (+) and (-) buttons on this controller to achieve the highest and most narrow peak on the oscilloscope. Use the silver micrometer dial on the side of the autocorrelator as well.

3) Optimize mirrors M4a and M3 (see the users manual Fig. 2.2 for this) for the best peak.

4) Calibrate the oscilloscope reading to determine the pulsewidth using the following example for a delay stage distance of 100 μ s. Read the micrometer dial of the autocorrelator to determine the distance the delay stage has moved (s). Each tick on the dial is 10 μ s. Note how far the peak has moved on the oscilloscope (t).

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Delay stage distance (s): 100 μ s Optical path length ($l = s \times 2$): 200 μ s Optical delay change ($d = l/(3 \times 10^{14} \mu m/s)$): 665 fs Peak movement on scope (t): 1300 μ s Calibration term (C = d/t): 0.511 fs/ μ s Pulsewidth ($\tau = s \times C$): 51.1 fs