SINGLE PARTICLE SPECTROSCOPY: ULTRAFAST STUDIES AND
ABSORPTION TECHNIQUE DEVELOPMENT

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Abstract

by

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In this thesis, I present topics involved in single particle spectroscopy. Specifically, the topics of ultrafast transient absorption on semiconductor nanowires and the development of a polarization modulation technique are discussed. These two topics demonstrate the advantages of single particle spectroscopy as they pertain to the scientific process of experimentally determining the properties of nanostructures.

The ultrafast transient absorption portion of this thesis describes experiments performed primarily on Cadmium Telluride (CdTe) nanowires and sparingly on Cadmium Selenide (CdSe) nanowires for comparison. The CdTe nanowires demonstrated a fast decay on the order of a several picoseconds. This decay process is attributed to the trapping of charge carriers at surface defects. The characteristics and time constants observed for this trapping process varied from wire to wire. The time constant for a given wire was also observed to change as different parts of the wire were probed. The variations observed were attributed to changes in the trapping energies and/or densities of surface states. The CdSe nanowire displayed no fast time dynamics in
their transient absorption traces. The absence of the fast charge trapping in CdSe is consistent with the higher emission quantum yields observed in CdSe when compared to CdTe. These results demonstrate the information that can be gained from this technique.

The second part of this thesis describes the development of a new single particle spectroscopy extension of the technique called polarization modulation microscopy (PMM). This technique utilizes a photo-elastic modulator (PEM) to rapidly modulate the polarization of a focused laser to study single anisotropic particles. A lock-in amplifier records the signal produced from the polarization modulated laser-particle interaction at twice the fundamental frequency of the PEM, which gives the difference between the extinction cross-sections for light parallel and perpendicular to the optically active axis of the nanostructure. Furthermore, PMM demonstrates the ability to determine the nanoparticle orientation on the sample slide. To demonstrate this PMM technique, studies preformed on gold nanorods are presented. The PMM’s strengths and weaknesses are also compared to the photothermal heterodyne imagining (PHI) technique and the spatial modulation spectroscopy (SMS) technique.
This is dedicated to friends, lab colleagues, family, and Mallory.

May we all find the path in life for which we seek.
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CHAPTER 1:
INTRODUCTION

1.1. Single Particle Spectroscopy

In recent years, the interest in nanoscale materials has become a staple topic in the scientific community. The reason for this interest stems from the many different nanoparticles shown to have different properties than their bulk material parents. Single particle spectroscopy is a classification of experiments that allows for the observation of individual single nanoparticle properties. These single particle techniques explore or reveal properties that are often overlooked or neglected in the ensemble measurements. Ensemble measurements average a signal from over all the particles of all the different shapes and sizes. Averaging the signals arising from a diversity of particles in a diversity of environments and conditions washes out any information about the environmental effect on each particle. In effect, ensemble averaging causes a deficit in the understanding of the properties of nanoparticles. By focusing on single nanostructures, single particle spectroscopy contributed to our understanding by demonstrating that differences in local environment can, and do, affect the properties of different nanomaterials [1-4]. Also, ensemble measurements did not detect the phenomenon of fluorescence intermittency, commonly called “blinking.” Blinking is a process in which single semiconductor quantum dots exhibit assumedly random bouts of dark periods when their emission temporarily stops [5-7]. This blinking phenomenon was not detected
in an ensemble measurement because the multitude of quantum dots being sampled do not “blink” at the same time. From these cases, single particle spectroscopy is demonstrated to be an essential tool to investigate nanomaterial.

1.1.1. Time Resolved Studies of Semiconductor Nanoparticles

The usefulness of single particle spectroscopy is now evident from the prior section. However, the application of single particle spectroscopy to study particular events and samples proves to be challenging. For example, how does one studying semiconductor nanoparticles and their peculiar “blinking?” A technique called time-correlated single photon counting (TCSPC) has been utilized to measure the change in contributions of radiative or nonradiative relaxation to investigate the blinking rates of semiconductor nanoparticles [8-10]. TCSPC works well, but it has a drawback in the limited time scale over which it is effective. The limited time resolution renders it useless when attempting to look at other processes that occur in less than a hundred picoseconds, such as Auger recombination and surface trapping [11,12].

This fast time resolution deficiency was overcome by using laser techniques that utilize the time between two synchronized laser pulses. Ultrafast studies of single semiconductor nanostructures were first reported by Johnson et al. using a time-resolved second harmonic generation (SHG) to study the dynamics of single ZnO nanowires and nanoribbons [13]. This trend continued to catch on when the Leone group used pump-probe spectroscopy [14,15] and fluorescence upconversion [16] on ZnO tetrapods and nanowires. These works focused on exploring the lasing threshold of nanomaterials through characterization of the dynamics of optically excited charge carriers. Evidence for stimulated emission in the ZnO semiconductor nanomaterials were revealed through
an observed decrease in decay times of excited charge carriers as the intensity of the pumping light source increased [13-17]. While the idea of semiconductor nanomaterials lasing is an exciting thought, these studies covered single particles as a whole, without an ability to see the individual parts. This omits any possible investigation into the variations of the structure or signal as the structure progresses in any given direction. However, Gundlach and Piotrowiak performed spatially resolved ultrafast emission measurements of single CdSSe nanobelts utilizing a CCD camera and a Kerr gate [18]. This experiment was successful in resolving spatial images, but it is limited by the emission quantum yields of the material. Near field techniques have also been used to study single particles. The literature has shown that using an ultrafast laser system in conjunction with a near field microscope can give you spatial and temporal resolution over single particles [19]. The key draw back to near field techniques is their experimental difficulty.

The next direction for studies on semiconductor nanomaterial is to utilize a far-field technique that possesses a good spatial resolution in addition to an ultrafast time resolution. Over the rest of this paper, the methods and results of such an experiment will be discussed.

1.1.2. Absorption Measurements

Single particle spectroscopy involves the use of optical techniques to explore the properties of nanoparticles and how they interact with their local environment [20-23]. Common single particle techniques utilized to explore nanostructure properties are collecting emissions for semiconductor nanostructures [20-23] and Rayleigh scattering for metal nanoparticles [4,24,25]. These two techniques have a very powerful benefit of
being very sensitive. They exhibit a “zero-background,” which means that there are no signals originating anywhere else but the studied particles. The experimental strength of these techniques is the sensitivity, but this strength beguiles limitations that prevent them from being the standard for all single particle experimental practices. For example, emission measurements rely on the material’s quantum yield. If your material does not emit photons well, this experiment may not be the best choice to investigate that material. The limitation of Rayleigh scattering is derived from the ability of your particle to scatter. The scattering dependence limits the size of detectable particles to about twenty nanometers or larger due to efficiency of Rayleigh scattering, which is proportional to the volume of the nanoparticle squared [26]. The limitations of Rayleigh scattering and emission studies caused a drive for developing absorption-based techniques for investigation of nanomaterial [26-31]. Absorption techniques work better than Rayleigh scattering for smaller nanoparticles because absorption is proportional to the volume of the nanoparticle, unlike Rayleigh scattering’s proportionality to the nanoparticle’s volume squared [30]. In addition, studies have proven that absorption techniques are able to provide fundamental information about nanoparticle. Examples of this included information on the plasmon resonance for metal materials [32,33] and absolute absorption cross-sections for different nanostructures [29,33-35].

Many types of absorption-based approaches have been use for detecting and probing characteristics of nanoparticles. One of the more sensitive approaches is photothermal heterodyne imaging (PHI) [28,36]. PHI uses a modulated laser beam to heat the nanoparticle, which then dissipates into the surrounding medium. The medium undergoes a change in the refractive index due to the heat, effectively creating a thermal
lens. This thermal lens then changes the propagation of the probe beam. Coupling this (modulated) thermal lensing effect with a lock-in amplifier (synchronized with the modulator apparatus), allows for a sensitive detection scheme. The literature contains records of these measurements detecting particles as small as several nanometers [32].

PHI has been very useful in experimentally determining the absorption cross-sections of single carbon nanotubes [34] and CdSe semiconductor nanowires [35]. The cross-sections from these experiments are determined by comparing the PHI signal from the sample subject (nanotube or nanowire) to the signals from particles with well-known cross-sections, like a dimensionally well-defined gold nanosphere. The mandatory cross-section comparisons demonstrate a drawback of PHI technique as an indirect measurement of absorption cross-section. The PHI technique also possesses an abnormal focus dependency [35]. In a “true” thermal lensing experiment, the probe beam should only be affected by the modulated thermal lens created by the heating beam. The PHI signal, in this case, shows a minimum at the focus point of the heating beam with two maximums on either side of the focus [37,38]. This unintuitive focus dependency is caused from the Gouy phase change of the beam as it passes through a focus [39]. Since the probe beam is affected by more than just the thermal lensing, the two maximum peaks in this focus dependent signal can become distorted [37]. This distortion of the Gouy phase predicted dependency creates an uncertainty in the comparison of the absorption cross-section of two different nanoparticles [35]. Also, heating beams in these types of experiments are typically in the MW/cm² regime [34,35,40]. This fluence exceeds the normal amount used on semiconductors in emission studies, and it is large enough to alter the samples it is meant to study. The effect of this level of fluence leads to photo
brightening in semiconductor nanostructures [41] and renders this technique not ideal for biological imaging [42].

In addition to PHI, spatial modulation spectroscopy (SMS) is another technique used to investigate nanostructures [29,33,43]. SMS utilizes a piezo stage to move the particle in and out of the focus of the beam. The constant moving of the stage creates a modulation in the signal, which is then measured to produce the absorption cross-section for the particle. A huge benefit of this measurement is that it does not require an intense light source like the PHI technique. In fact, SMS has been successfully executed using an incoherent light source [44]. This technique has demonstrated that it can detect 5 nm metal nanoparticles [29]. However, SMS can only be modulated at frequencies approximately .1 to 1 kHz due to the mass of the sample and stage that the piezo motor is required to move. The restriction to low modulation frequencies causes the signals in the experiment to suffer from 1/f noise. PHI does not suffer from this frequency born noise due to the high frequency modulators used to modulate the heating beam [28,36]. Additionally for SMS, particles must be fixed to a surface on the sample, which is not a requirement for PHI. Therefore, PHI could be used for particles in a liquid, which would allow for correlation measurements similar to fluorescence correlation spectroscopy (FCS) [45-47].

1.2. Transient Absorption of Semiconductors

The idea is to utilize a far-field transient absorption technique that possess an ultrafast time resolution in the femtosecond regime and a spatial resolution limited only by the diffraction limit of the wavelength of light to improve the knowledge about fast
time processes in semiconductor nanomaterials. This technique is applied to single particles by focusing its high repetition rate pump and probe through a high numerical aperture objectives onto a sample of interest. These transient absorption experiments have been completed on single metal nanoparticles in the literature [48-50]. Transient absorption is applied to metal nanoparticles in literature because metal nanoparticles have a large absorption cross-sections, causing them to absorb plenty of photons to give a good transient absorption signal [48-50]. The signal arises from changes in the transmitted probe beam on the order of $\Delta I/I \sim 10^{-5}$ [49]. When the technique utilizes a low-noise Ti:Sapphire laser, the signal to noise levels have been reported to be greater than 100 to 1 and a time resolution of subpicoseconds for the many different shapes and sizes of silver and gold nanoparticles studied [48-56]. This experiment has the attribute of recording absorption to probe the particle signal and, therefore, does not rely on materials having a large emission quantum yields required for fluorescence or a noncentrosymmetric crystal structure for second harmonic generation techniques like the previous time resolved techniques discussed [13-18].

Metal nanoparticles have proven to be ideal for single particle transient absorption experiments due to strong resonances and absorption cross-sections that can be larger than $10^{10}$ cm$^2$ [57]. The multitude of elections that contribute to the large absorption cross-section enable the particles can absorb many photons with out suffering saturation [49,50]. However, for studying semiconductor nanostructures with this technique, more caution is required. It is not obvious where saturation effects become important for semiconductor nanoparticles, as they do not necessarily have the large number of
electrons contributing to the optical transitions as do metals [11]. The saturation of the transitions in the single particle would increase the difficulty of obtaining a signal.

Keeping in mind the obstacles of measuring semiconductor nanomaterial, an ideal sample for studying these materials with the transient absorption technique needs to be considered. CdTe and CdSe nanowires are promising materials to investigate due their band gap, structure, and previously acquired information. Also, they are made with two commonly used materials in semiconductor nanostructures [58], which might extend insight and experimental applications into other similar nanostructures. Experiments on these CdTe and CdSe nanowires display the importance of the single particle measurement’s ability to detect differences in the ultrafast response of individual nanostructures. Furthermore, the application of diffraction limited resolution allows for the observation of dynamics at different parts of a given wire, which were seen to vary in the experiment. This variation in dynamics along the wire is attributed to differences in the energy or density of the trap states along the wire.

1.3. Polarization Modulation Microscopy

The goal of designing a new absorption based technique is to develop a technique that can combine the strengths of the single particle absorption techniques discussed previously, while trying to minimize or surmount the associated limitations. All the previous techniques demonstrated the need for modulation of some sort to detect any changes in the transmitted photons. The general idea proposed is the detection of the absorption of single anisotropic nanoparticles (nanorods in this case) through the rapid rotation of the polarization of the investigating beam. This proposed technique is an
extension of polarization modulation microscopy (PMM), applied to the single particle measurements [59-62]. A device known as a photo-elastic modulator (PEM) is used for polarization modulation. The PEM rotates the polarization of light at ~100kHz. This fast modulation allows for the PMM technique to possess an advantage of lower noise than the SMS technique and removes the need to secure the particles to a slide. PMM can be used to measure the extinction cross-section (specifically the difference between the parallel and perpendicular cross-sections for the rods used in this study) of an anisotropic nanoparticle without comparison to a standard calibration particle, like PHI. Unfortunately, the PMM technique lacks the ability to be useful for anything other than anisotropic nanostructures. However, there are plenty of anisotropic materials that would benefit from this technique, such as carbon nanotubes and semiconductor wires.
2.1. Transient Absorption Technique

2.1.1. Experimental Setup

The experimental set up for this transient absorption experiment follows a basic pump and probe set up. The laser source for this experiment is a KMLabs Ti:Sapphire laser with a 89 MHz repetition rate, pumped by a Coherent Verdi V-5 diode pumped solid state laser. The Ti:Sapphire laser’s wavelength range is between 780 and 820 nm. The bandwidth is deliberately narrowed to approximately 20 nm full width at half maximum, to reduce dispersion caused by the optics in the set up and the microscope. The laser beam from the Ti:Sapphire was divided with a 90-10 beamsplitter, and the more intense beam was utilized for the pump beam after it was frequency doubled via a 0.5 mm BBO crystal (Castech). The remaining red beam (weaker beam after the beamsplitter) from the Ti:Sapphire was utilized for the probe beam. As with typical pump and probe experiments, the pump beam in this experiment was modulated by an acousto-optic modulator (Crystal Technologies 5100-35). The acousto-optic modulator device modulated the pump beam at 75 kHz. The modulator was driven by the internal reference of the lock-in amplifier (Stanford Research Systems, SR830), which is also used to collect the signal. After the pump beam was modulated, the pump and probe
beams were adjusted to be collinear and spatially overlapped. The two beams were then focused on to the sample via a 1.35 NA (numerical aperture) oil immersion objective (Olympus, UPlapo100x). After the sample, the beams were recollimated by a 1.30 NA oil immersion objective (Olympus, UPlanFLN100x). The newly recollimated beam had the pump beam contribution removed by a long-pass filter, leaving the probe beam to be detected with an avalanche photodiode (Hamamatsu, C5331-03). The signal from the avalanche photodiode was then passed to the same lock-in amplifier (Stanford Research Systems, SR830) that was driving the acousto-optic modulator.

The intensities of the pump and probe beams were regulated through a combination of neutral density filters and λ/2 waveplate-calcite polarizer pairs. The standard pump intensity of this experiment is 0.1 pJ pulse⁻¹, lower than previously listed metal nanoparticle experiments [48-51], while the probe was adjusted to be much weaker than the pump. The polarization of both the pump and probe were circularly polarized to avoid complications from the strongly anisotropic absorption properties of nanowires [52]. The time resolution was estimated to be 0.5 ps (Gaussian Full width at half maximum), making it broader than the transform limited pulse width of the laser. This discrepancy is attributed to the dispersive effects of the focusing objective. The time delay of the transient absorption technique is controlled by a stepper motor translation stage (Newport UTM100PP.1, with a ESP300 controller). The transient absorption images were a result of raster scanning via a piezoelectric (piezo) stage (Physik Instrumente, P-527.3Cl) with a delay time of 300 ms between each step. Unfortunately, despite many attempts, the pump and probe beams focus in slightly different planes due to the differences in the wavelength. This inconvenience circumvented maximizing the
transient signal, which turned out to be close to the focus of the probe beam. In addition to the transient images acquired, scattered light images were also obtained using epi-illumination by a white light source (ThorLabs, OSL1), after the sample slide was placed on the microscope. A drop of fluorescence free immersion oil (Zeiss, Immersol 518F) was applied to both the top and bottom of the slide. The scattered light images were collected with a CCD camera (QICAM, Quantitative Imaging Corp.) utilizing back reflections in the microscope.

2.1.2. Sample Preparations

The sample was prepared by drop casting a dilute toluene solution of wires onto a flamed coverslip. The CdTe and CdSe nanowires used in this experiment are made and supplied by the Kuno group at the University of Notre Dame. These materials were synthesized by the chemical vapor deposition (CVD), and the procedure can be found in ref [63]. The nanowires produced through CVD are usually straight wires with lengths extending several micrometers. These nanowires present an ideal first study because they possess a wider diameter than other nanowires grown by the more common solution-liquid-solid technique [57,64]. The larger width gives the CVD wires a larger absorption cross-section, which will benefit the signal detection process.
2.2. Polarization Modulation Microscopy

2.2.1. Experimental Setup

The laser source used for the polarization modulation microscopy technique on the sample of gold nanorods was a homebuilt CW Ti:Sapphire oscillator pumped by a DPSS Nd:YAG laser (Spectra Physics Millenia Pro-Vs). The wavelengths required for the excitation of the nanorods ranged from 760 nm to 860 nm (which is similar to the laser output range). The power of the beam produced by the Ti:Sapphire was regulated using neutral density filters and a $\lambda/2$ waveplate/polarizer combination (fluence ~ 150 kW/cm$^2$). Before the laser beam passed through the Photo-elastic Modulator (PEM) (Hinds Instruments, I/FS50), the polarization was aligned to be 45° with respect to the axis of the PEM. The PEM was operated in the $\lambda/2$ retardation mode which causes the polarization of the light beam to oscillate between 45° to -45° polarization at 101 kHz (the intermediate state is circular polarization). After the PEM, the laser beam is directed into an inverted microscope (Olympus IX-71). The beam was brought to a focus on the sample using a 100x, 1.3 NA oil immersion objective and recollimated with a 60x, 0.9 NA oil immersion objective. The collimated light was monitored by a silicon photo detector (Hinds Instruments, DET-100-002).

The photo detector’s output was fed into a lock-in amplifier (Stanford Research Systems, SR830) referenced at two times the fundamental frequency of the PEM controller (Hinds Instruments, PEM-100). The signal from the lock-in corresponds to the difference between the two orthogonal polarizations from the PEM. The data in the paper was recorded with a lock-in time constant of 10 ms and an integration time of 50
ms. In order to control the polarization of the laser beam at the sample, a \( \lambda/2 \) waveplate was positioned after the PEM.

2.2.2. Sample Preparations

The gold nanorods were made by Petrova et. al. and a description of how they were made is outlined in ref. [65]. The average dimensions of the gold nanorods are 51 ± 10 nm in length and 13 ± 2 nm in width. The samples were prepared by spin coating a dilute sample of approximately 1% PVA solution of gold nanowires onto a flamed glass cover slip. The cover slip is placed on top of a piezoelectric (piezo) stage (Physik Instrumente, P-527.3Cl) for fine adjustment and for collecting images through raster scanning. The piezo stage is mounted on a manual X-Y micrometer stage (Semprex) to allow for course adjustment. The step size used in the majority of the recorded images is 0.1 \( \mu m \) unless otherwise stated.
CHAPTER 3:
RESULTS AND DISCUSSION

3.1. Transient Absorption of CdTe

The CdTe nanowires were the major focus of this transient absorption study due primarily to the fact that their band gap (827nm) [66] is close to the center of the wavelength for our Ti Sapphire laser. It has been shown in other ultra fast transient absorption studies of semiconductor nanomaterials that the strongest signals are found near the band edge of the materials [11] and this has also been shown for nanomaterials with a wire shape [66,67]. On the other hand, Cadmium Selenide (CdSe) nanowires have a band gap in the 700nm to 720nm [66] range, which is outside the range of our Ti:Sapphire laser (~780nm to ~820nm). Despite this limitation, transient absorption signals were observed from CdSe nanowires, and the results from these materials are compared to those for CdTe nanowires.
Figure 3.1: (a) and (b) are TEM images of the CdTe nanowires from the stock sample used in the transient absorption experiment. The visible surface roughness (panel a) and the polycrystalline nature (panel b) are displayed. (c) 10 µm x 10 µm transient absorption image of two crossed CdTe nanowires at zero time. (d) A false colored scattered light image cropped to fit the corresponding image of the two nanowires in (c).

To start the analysis, a general feel for the sample must be obtained. In the figure above, Figure 3.1 a and b are TEM images of CdTe wires from the CdTe wire solution used in the transient absorption experiment. In Figure 3.1 a, the rough features of the wires are blatantly evident. This feature is also seen in the zero time transient absorption scan, Figure 3.1 c, and the scattered light image in Figure 3.1 d. Closer inspection of the wires through a higher resolution TEM imaging (Figure 3.1 b) revealed that the wires
themselves, grown by the Kuno group utilizing the technique of Chemical Vapor Deposition (CVD), are composed of a polycrystalline structure. Although not seen in the pictures above, the average diameter of the CdTe nanowires is measured to be $37 \pm 7$ nm from a collection of TEM images [68]. In the CdSe wires, for which there are no TEM images included in this paper, the measured average diameter is $39 \pm 11$ nm [69]. The measured dimensions of the wires allows for the estimation of the absorption cross section for 400nm circularly polarized light of $\sigma \sim 8 \times 10^{-11}$ cm$^2$ µm$^{-1}$ [70] for both the CdTe and CdSe nanowires.

The images in Figures 3.1 c and d are a transient absorption image (at zero time delay) and a scattered light image of the same two, crossed wires, respectively. We can see from the two images that there is good agreement to the shapes and roughness of features seen in both. The transient absorption image displays a good contrast between the wires and their surroundings. This demonstrates that there is very little to no background signal when the spatially overlapped pump and probe beams do not overlap with a wire. Taking the full width at half maximum across the diameter (dfwhm) of the wire images shows that the spatial resolution of our experiment is 0.33 µm. This resolution is remarkably close to the diffraction-limited spot size of the probe beam (~0.30 µm). The spatial resolution is need to find the pump laser fluence for this experiment. The fluence is calculated to be 120 µJ cm$^{-2}$ for the experimental pump pulses of .1 pJ. These numbers are similar to fluence seen in the literature for single particle [13-18] and ensemble measurements of II-VI semiconductor nanomaterials [11,67,68].
Figure 3.2: (a-c) Transient absorption traces from three different CdTe nanowires (dots) fitted to the a double exponential function (red line). The time constants of the fast decay from the fits are given in the figure. Each trace had a background signal similar in magnitude to the transient absorption signal subtracted out for the analysis.

Figure 3.2 displays three transient absorptions traces from different CdTe nanowires examined in the experiment. These traces demonstrate that the transient absorption signal can be easily detected with signals ($\Delta I/I$) on the order of $10^{-5}$ to $10^{-6}$, which mimic the signal levels of metal nanoparticles [49-51]. The signals we see in these experiments are linear with respect to the pump powers over the range of 0.02-0.3 pJ pulse$^{-1}$. This information proves that the optical transitions are not saturated in the
experiment. Caution is advised for higher power levels. The particles, or areas around them, have been observed to be damage after scans with pump pulses higher than 0.1 pJ. These damages manifested as a decrease in the transient absorption signal accompanied by a dimming or dulling of the scattered light images of the wires. It is possible that the damage is limited to the medium surrounding the wires. This possibility is supported by the observation that the wire is usually intact, instead of a complete break in the wire. The transient absorptions traces displayed in this work have had a background signal removed. This background signal is similar in magnitude to the transient absorption signal and is attributed to a photothermal lensing effect [69,71].

The background signal is the not the only oddity found in the traces. A few traces of CdTe nanowires yielded a few peculiar results, such as a bleach signal (positive $\Delta I/I$, see Figure 3.2 c, for example). The majority of transient absorption traces displayed an absorption signal (negative $\Delta I/I$). Another oddity seen is traces that started as absorption signals that deviate to a bleach signal (Figures 3.2 a and 3.2 b). These bleach signals are suspected to be caused by the filling of the electron states near the band edge the semiconductor material [72], and the absorption signals are thought to originate from the intraband (free carrier) transitions of excited charge carriers [12,14]. It has been proposed that the absorption signal could be caused by transitions of trapped charge carriers [73]. If this were the case, the traces would show a growth in the signal related to the trapping time. However, we do not see this, but rather a quick rise and decay, which is indicative of an absorption signal caused by the excitation and relaxation of free carriers.
The transient absorption spectra recorded in the ensemble experiments display bleach signals at the band edge and a weaker absorption at longer wavelengths [66]. This means that individual CdTe nanowires should show a bleach signal when the probe laser wavelength is at/near the band edge from that wire [66]. The fact that the sign of the signal change in this experiment means that different wires have different absorption onsets. Quantum confinement could be the cause of this shift in the band edge, but the wires in this study are too large for this effect. It might be possible that the CdTe nanowires producing a bleach signal are under the influence of an electric field causing the Stark effect. An electric field could be caused by trapped carriers at the nanowire surface, thus providing a shift in the absorption band [74]. This idea is not far fetched for CVD-grown wires, such as the ones in this study, because solution-grown nanowires have been shown to have long lived surface charges [75]. Since these trapped surface charges control the shifts in the spectra, then these spectral shifts are also dependent on the number and characteristics of the trapping states in that part of the wire probed. Therefore, the fact that different wires can exhibit a bleach signal or even changes in the signals from an absorption to a bleach should not come as a surprise.
Figure 3.3: (a) Transient absorption traces for the same point on a single nanowire taken at different pump laser powers. The fast decay time constant for the different traces is $\tau = 1.4 \pm 0.1$ ps. (b) The relative amplitude of the fast and slow components of the transient absorption signal for a different wire plotted as a function of pump power.

The traces in this experiment are fitted using a double exponential function utilizing an offset convoluted with the instrument response function. The fast time constants retrieved from the experiment are reported in the figures, and these time constants vary from wire to wire. As stated before, the transient absorption signal is
believed to arise from the excited charge carriers. However, there are many possible events among these charge carrier dynamics that lead to this decay in the transient signal seen in these nanowire traces. These events could be trapping at defects in the wire, Auger recombination, or electron-phonon coupling [11,12,76]. To determine which process gives rise to the signal in the CdTe nanowires, additional experimentation was performed. To test for any significant effect from Auger recombination, experiments where performed by varying the intensity of the pump beam on a given wire and comparing the results. Auger recombination has a few indicative signs, such as the intensity dependence of the time constant and the intensity dependence of the relative amplitude of the fast decay [11,12]. Figure 3.3 displays the experimental data that demonstrate that Auger recombination is not a major contributor to the transient signal. Figure 3.3 a shows three traces from the same spot on the same wire where the intensity was varied. There is no apparent dependency of the fast decay time constants on the power of the pump beam. This result demonstrates that, over the range of powers used in this experiment, Auger recombination does not appear to take place. Figure 3.3 b displays the relative amplitude (the amplitude of the fast decay divided by the amplitude of the longer time signal) versus the pump power for a different wire. This graph shows the relative amplitude is not affected by the pump power, which is inconsistent with Auger recombination [11]. These two pieces of information provide evidence that Auger recombination does not contribute to the transient signal.

If Auger recombination has been eliminated from the list of possible sources for the transient signal, then the remaining sources are charge carrier trapping or electron-phonon coupling [76]. Electron-phonon coupling can be eliminated from this list as well.
The CdTe nanowires in this experiment have widths greater than the Bohr radius of the exciton \[77\]. This implies that the electron-phonon coupling times should be similar to that of bulk CdTe \[76\], which is approximately 80 fs \[78\]. The electron phonon coupling time for the bulk material is much faster than the instrument response time of this experiment. In essence, the instrumental set up does not allow for the observation of the electron-phonon coupling. Any electron-phonon coupling event should be over by the time the first pump pulse has passed through the sample, and can hardly be expected to be the cause of a signal on the picosecond time scale. Thus, the fast time decay observed in the data presented is attributed to the process of charge carrier trapping at defects in the wire. Since the signal is the observation of charge trapping, the changes in the signals observed in Figure 3.2 can be further explained. If trapped charge carriers change the transient absorption spectrum, then it is reasonable that the transient absorption signal would change after trapping process.
Figure 3.4: (a) and (b) are transient absorption traces of CdSe nanowires under the same experimental conditions as the CdTe nanowires.

The literature commonly compares CdTe nanowires to CdSe nanowires, and this experiment intends to follow this trend. As previously stated, the CdTe nanowires were chosen for this experiment because their band gap energy is within the tuning range of the Ti:sapphire laser used in this experiment. The experimental system’s wavelength limitations hindered studies into CdSe nanowires. However, we were able to record a few traces with good signal to noise. Comparing the two different nanowires can potentially add insight into the behavior of either of these wires. The literature notes that the emission quantum yields [66] for CdSe nanowires are larger than the emission quantum yields for CdTe nanowires. This suggest that CdSe should not possess this fast charge carrier trapping that is observed in the CdTe nanowires. Data for CdSe nanowires...
is shown in Figure 3.4. The fast decay is clearly absent, implying that charge carrier trapping at the surface states does not occur. The signal of the CdSe nanowires is attributed to intraband absorption of excited charge carriers. The CdSe transient signals measured were all absorption signals, presumably because their band gap energy corresponds to a shorter wavelength than the probe wavelength used in this study [66,70]. Note that the signal from the CdSe nanowire has a magnitude similar to the magnitude of the CdTe nanowire signal. This is consistent with the ensemble transient absorption measurements of CdSe nanowire in the literature, which show that Auger recombination takes a significantly longer time (>100ps) than the time scale of our measurements [67].

Figure 3.5: Transient absorption traces recorded at different positions along the same single CdTe nanowire. The traces have been offset for ease of comparison of the signal form and time constants.
The data obtained from the CdTe nanowires shows that the time constants vary from wire to wire, ranging from the instrument response limit (less than .5 ps) to several picoseconds (as seen in Figure 3.2). These variations in the trapping time constants are hypothesized to be caused by variation in the surface chemistry of the nanowires (seen in Figure 3.1). Changes in the conditions of the surface composition through random variations in synthesis or oxidation could change the energies and density of surface tapping states, which ultimately would change the charge carrier trapping rate [79-82]. There is also heterogeneity in the ultrafast dynamics of a single wire, as shown in figure 3.5. Figure 3.5 shows transient absorption traces at different points along the same wire that are a few micrometers apart. The traces show that the general form and sign of the transient signal are the same, but the time constants can change from point to point in each wire. The similarity in form implies that the transient absorption spectra for the entire wire is similar, if not identical, but the change in time constant suggest that there is a change in the density of the trap states or a change in the energies of the trap states along the wire. This coincides with single wire emission studies that often show fluctuations in the emission quantum yield within a given wire [75]. This heterogeneity of trapping states has never been observed in ultrafast measurements previously.

3.2. Polarization Modulation Microscopy

3.2.1. Theoretical Model

To develop this polarization modulation microscopy (PMM) technique, we need to develop a theoretical model of the experiment. To begin with, an understanding of
how the probing beam and the sample (nanorod in this case) interact is needed. The probing beam is characterized as a Gaussian beam with an intensity distribution listed in Equation 1 [39].

\[ I(\rho, z) = \frac{2P}{\pi w(z)^2} e^{-2\rho^2/w} \]  

(1)

In this equation \( \rho \) is defined as \( \rho = \sqrt{x^2 + y^2} \), which is the radius of the beam from its center. The symbol \( z \) is defined as the distance from the focus and \( P \) is the power of the beam. The \( w(z) \) term is defined as the beam waist, which is characterized by

\[ w(z) = w_0 \left[ 1 + \left( \frac{z}{z_0} \right)^2 \right]^{1/2} \]

, in which \( z_0 \) is the Rayleigh range and \( w_0 \) is the beam waist at the focus. The intensity at the center of a focused beam (\( z = 0 \)) of this Gaussian description is \( I_0 = 2P/w_0^2 \). When a particle much smaller than the spot size of the beam and is in this middle of the focused Gaussian beam, the interaction that occurs with respect to the power of the beam can be characterized by \( P_t = P_i - \epsilon \) [29]. In this equation, \( P_i \) is the incident power, \( P_t \) is the transmitted power, and \( \epsilon \) is the extinction cross-section of the particle. Utilizing this relationship, the change in the detected signal is then

\[ \frac{\Delta P}{P} = -\epsilon \]  

(2)

In this equation, the \( \epsilon \) factor can be determined from the experimental images.
The technique is not limited to the cases where the sample material dimensions are much, much smaller than the spot size of the beam. To apply this technique to samples with a longer length dimensions that the spot size (but still retaining the thinness in the width, like a nanowire), the interaction of the extended cross-section needs to be accounted for across the intensity distribution of the beam in the direction of the nanowire. To do this, we integrate the cross-section multiplied by the intensity of the beam along the dimension of the length. Equation 3 is this principle applied to a wire with the length orientated along the $x$ axis passing through the center of a focused Gaussian beam.

\[
P_t = P_i - \frac{2P_i}{\pi w_0^2} \int_{-\infty}^{+\infty} \sigma_w e^{-\frac{x^2}{w^2}} \, dx
\]

In Equation 3, \( \sigma_w \) is the extinction cross-section of the wire. Assuming the extinction cross-section is constant across a wire, Equation 3 can be rewritten as

\[
\frac{\Delta P}{P} = -\sigma_w \left( \frac{2}{\pi} \right) x
\]

Equations 2 and 4 demonstrate that cross-sections for nanowires and nanoparticles are related to the change in power of the beam in different ways. Rearranging Equation 2 for the cross-section gives you Equation 5a for nanoparticles, and rearranging Equation 4 for the cross-section gives you Equation 5b for nanowires.

\[
\sigma_p = \frac{\pi w_0^2}{2} \left( \frac{2}{\pi} \right) x
\]
\[ \sigma_w = w_0 \sqrt{\frac{\pi}{2}} \times \]  

(5b)

Since the major component to this experimental technique is the modulation of the polarization, it is important that examine the effects of the PEM on the polarization of the probing laser beam. According to the results from ref. [83], a beam polarized at 45° with respect to the PEM axis entering into the PEM will produce a field characterized by Equation 6.

\[ \vec{E}_m = \frac{E_0}{\sqrt{2}} (i + e^{i\phi}) \]  

(6)

In equation 6, \( i \) and \( j \) are unit vectors parallel to the axes of the PEM and \( \phi(t) \) is the phase shift caused by the PEM. If an anisotropic sample were aligned parallel with the 45° polarized electric entering into the PEM, the unit vector description for this sample would be \( e_\parallel = (i + j) \) and \( e_\perp = (i - j) \). Describing the electric field after the PEM in terms of these vectors yields

\[ \vec{E}_m = \frac{E_0}{2} \left[ (1 + e^{i\phi(t)}) e_\parallel + (1 - e^{i\phi(t)}) e_\perp \right] \]  

(7)

This field is weakened due to the absorption of the particle. This allows us to express the intensity that will be detected as Equation 8.

\[ I_{\text{det}} = I_0 \left[ (1 + \cos \phi(t)) e^{-\sigma_\parallel} + (1 - \cos \phi(t)) e^{-\sigma_\perp} \right] \]  

(8)

In this equation, and are coefficients that describe how much the particle weakens the component of the beam that is polarized parallel or perpendicular to the
principle optical axis of the sample. In the limit of weak effect by the coefficients, Equation 8 can be expressed as

$$I_{\text{det}} = \frac{I_0}{2} \left[ 2 - (\alpha_{||} + \alpha_{\perp}) - (\alpha_{||} - \alpha_{\perp}) \cos \xi \right].$$

(9)

In Equation 9, $\phi(t)$ is the phase shift induced by the PEM. This phase shift is defined as $\phi(t) = \phi_0 \cos \omega t$, where $\phi_0$ is the PEM’s resonant frequency. According to Ref. [83], if the PEM is set to the $\lambda/2$ retardation setting, the cosine of the phase shift, $\cos \phi(t)$, should be expanded in a Fourier series. This expansion yields

$$\cos \phi(t) = J_0(\phi_0) - 2J_2(\phi_0) \cos 2\omega t.$$ Substituting the expanded term into Equation 8 yields

$$I_{\text{det}}(t) = I_0 J_2(\phi_0) \times (\alpha_{||} - \alpha_{\perp}) \times \cos 2\omega t$$

for the modulated signal. From this alternating signal, the lock-in amplifier records a signal at twice the resonant frequency of the PEM, is

$$V_{\text{sig}}(2\omega_m) = RI_0 J_2(\phi_0) \times (\alpha_{||} - \alpha_{\perp}).$$

(10)

The $RI_0 J_2$ term is an instrumental factor. To determine this factor, a polarizer is placed between the PEM and the detector in such a way as to extinguish the incoming beam with the PEM off. The $RI_0 J_2$ term can then be replaced with $V_{\text{ref}}(2\omega_m)$ (which is the lock-in signal under the conditions of determining the instrumental factor) which then yields

$$(\alpha_{||} - \alpha_{\perp}) = \frac{V_{\text{sig}}(2\omega_m)}{V_{\text{ref}}(2\omega_m)}.$$ .

In general, the sample forms a random angle $\beta$ with respect to the PEM axis due to the random orientation of the particles on the sample slide. The unit vectors for this situation are described as $e_{||} = \cos \beta i + s$ and $e_{\perp} = \sin \beta i - c$. The electric field
of the beam after it has been modulated by the PEM is described in terms of and is now

\[ E_m = \frac{E_0}{\sqrt{2}} \left[ \left( \cos \beta + e^{i\phi(t)} \sin \beta \right)e_\parallel + \left( \sin \beta - e^{i\phi(t)} \cos \beta \right)e_\perp \right]. \]  

(11)

With assumption that the changes in the probing beam are small, the signal to be detected by the lock-in is

\[ V_{sig}(2\omega_m;\beta) = R I_0 J_2(\phi_0) \times \left( \alpha_\parallel - \alpha_\perp \right) \times 2 \sin \beta \cos \phi. \]  

(12)

A $\lambda/2$ waveplate place between the PEM and sample is used to control the $\beta$ angle in the experiment. This control of the angle allows for the mathematical manipulation of Equation 12 and Equation 5(a or b depending on what is appropriate) to yield the extinction cross-section (specifically $\alpha_\parallel$ and $\alpha_\perp$) and the orientation of the nanostructure. The ability for determining orientation is only useful for particles smaller than the diffraction limited spot size of the probing laser, like the gold nanorods. This ability is not necessary for nanowires because you can observe the orientation of the wires by eye under the microscope. To accomplish the main aim of this experiment (which is determining anisotropic nanoparticle cross-sections), two images of the same particle, 45° degree of polarization apart, are taken. The cross-section can then be obtained by

\[ |\alpha_\parallel - \alpha_\perp| = \sqrt{\left( \frac{V_{sig}(2\omega_m;\beta)}{V_{ref}(2\omega_m)} \right)^2 + \left( \frac{V_{sig}(2\omega_m;\beta + 45^\circ)}{V_{ref}(2\omega_m)} \right)^2}. \]  

(13)

From Equation 13, the $\alpha$ values can be transformed into extinction cross-sections by the appropriate Equation 5. The following section will provide experimental data
from a gold nanorod sample to demonstrate the validity of this PMM technique for determining the extinction cross-sections of anisotropic nanostructures.

3.2.2. Experimental Development

Gold nanorods provided an ideal system to demonstrate the PMM technique. These particles have a strong longitudinal plasmon resonance in the near infrared (IR), which acts like a perfect dipole; meaning \( \alpha_\perp \) can be assumed [33]. The images in Figure 3.6 a and b were taken of the same gold nanorod, but Figure 3.6 b was probed by a beam that had an additional polarization rotation of 90°. These two pictures demonstrate the change in sign that occurs when the longitudinal plasmon resonance shifts from being parallel to the PEM axis (positive in this experiment) to perpendicular to the PEM axis (negative in this experiment). This sign change fits well with the expectation given by Equation 12. A second, unintentionally scanned nanorod in the upper part of the image shows the same trend, just in the opposite order. Utilizing the ability to rotate the PEM axis any amount due to the \( \lambda/2 \) waveplate, Figure 3.6 c was obtained and demonstrates that the intensity behaves as expected. Figure 3.6 c plots the normalized signal detected \( \frac{V_{\text{sig}}(2\omega_m)}{V_{\text{ref}}(2\omega_m)} \) against the rotated degree of the PEM axis for another gold nanorod at 760 nm. The points in the figure are fitted using a \( \cos(\alpha - \alpha_0) \times \sin(\alpha - \alpha_0) \) function, as to fit the theory from Equation 12. From this chart, the orientation of the rod in can be determined. The maximum occurs when the PEM axis has been rotated approximately 63° by the \( \lambda/2 \) waveplate, which is the equal to the orientation of the nanorod in the sample frame. As further demonstration, rotating the polarization an
additional 90° gives a minimum of approximately the same intensity, denoting the change of the detected signal from $\alpha_\parallel$ to $\alpha_\perp$.

Figure 3.6: (a) and (b) 0.4x0.4 µm images of the sign change experience by a single gold nanorod at two different polarizer angles (wavelength = 800 nm). (c) Normalized signal versus angle for a different Au nanorod at 760 nm. The line is a fit using Equation 11. (d) Z-scan traces at different laser polarizations for the nanorod in (c).

Figure 3.6 d displays the normalized signal versus the Z-position (z=0 is the focus at the sample) while taking into account the polarization angle (using the same particle as in figure 3.6 c). This Z-scan shows the expected single maximum at the focus, which is characteristic for signals arising from extinction of the beam [37]. The Z-scan profile stands in direct contrast to the z-scan profiles of PHI for gold nanoparticles [35]. The
beam waist, $w_0$, can be extracted from Figures 3.6 a, 3.6 b, and 3.7 d, which is required to determining the extinction cross-section. Using Equation 1, an analysis of contour plot data reveals the beam waist, $w_0$, to be $0.38 \pm 0.01 \, \mu m$. The $Z$-scan data is fitted to

$$\frac{1}{1 + \left(\frac{z}{z_0}\right)^2}$$

producing $z_0 = 0.45 \pm 0.02 \, \mu m$ for the Rayleigh range of the probe beam. The Rayleigh range then yields the beam waist value through its $z_0 = \frac{\pi w_0^2}{\lambda}$ relationship. Given the Rayleigh range, the beam waist value works out to be $0.33 \pm 0.01 \, \mu m$. These two calculated beam waist values are in decent agreement. The cross-section calculations commonly utilize the beam waist derived from the contour plot [29], and this practice was continued in calculating the cross-section in this experiment.

To calculate a meaningful extinction cross-section, it is important that the measurements listed above take place at the maximum absorbing wavelength. The limited tune ability of the laser used in the measurements provided a difficult challenge in locating the maximum absorption (i.e. longitudinal plasmon resonance) for every given particle. In one case where the aforementioned measurements were observed at the approximate absorption maximum (780 nm), $\frac{V_{sig}}{V_{ref}} = 0.052 \pm 0.001$. Utilizing the relationship $\sigma_{\parallel} = \frac{(\pi w_0^2)}{2} \times \left(\frac{V_{sig}}{V_{ref}}\right)$, the extinction cross-section was found to be $0.0118 \pm 0.0006 \, \mu m^2$. The absorption cross-section was estimated to be $5.4 \times 10^{-3} \, \mu m^2$ using Gans theory and the average dimensions of the rods in the sample [84]. The variation in the dimensions of the nanoparticles of the sample is assumed to the cause of the deviation between the experimental and calculated cross-sections. A histogram of the measured cross-sections presented in Figure 3.7 shows a wide distribution, in particular at low values of the cross-section. The wide distribution is attributed to the fixed
wavelength at which the histogram values were taken, which means many of the nanorods were not at the absorption maximum.

Figure 3.7: Histogram of the cross-sections of the gold nanorods measured. The distribution of the cross-sections seems centered around $\sim 5 \times 10^{-3} \mu m^2$. 
4.1. Transient Absorption

Single particle transient absorption measurements have been performed for II-VI semiconductor nanowires. The transient absorption signal in this experiment shows a fast decay for the CdTe nanowires. This fast decay is attributed to charge trapping at surface states. The times constants have been shown to vary between wires, and they even vary among the different parts on the same wire. This decay inconsistency is attributed to variability in the energy or density of the trap states (probably both), and it is thought to arise from differences in the surface chemistry of each wire. The fast charge trapping that appears in the CdTe nanowires is absent in the CdSe nanowires. This proves to be logically consistent with the literature information about CdTe nanowires having a much smaller emission quantum yields than CdSe nanowires [66]. Finally, the observance of the variation of the forms of the transient absorption traces and time constants from wire to wire demonstrates the unique information that can only be obtained from single particle measurements on these systems. Thus, single particle spectroscopy is necessary for a more complete understanding of these types of systems.
4.2. Polarization Modulation Microscopy

The polarization modulation microscopy (PMM) technique utilizes a PEM to rapidly rotate the polarization of a laser beam (100 kHz). Coupled with a microscope and a high numerical aperture objective this polarization rotation is brought to a diffraction-limited focus onto a sample. The collected signal is detected at twice the resonant frequency of the PEM using a lock-in amplifier. This measures the $\cos \phi$ for the nanoparticle. This technique has produced high signal-to-noise images from single gold nanorods averaging 51 ± 10 nm in length and diameter of 13 ± 2 nm. These accomplishments indicate that PMM is a sensitive technique for nanomaterial investigation.

The PMM technique has demonstrated its ability to study single anisotropic nanoparticles through absorption. In the literature, the most common ways to do single particle absorption measurements are photothermal heterodyne imaging [28] and spatial modulation spectroscopy [29]. Compared to PMI, PMM is not as sensitive. However, only low pump fluences are needed for PMM. The low fluence aspect gives the PMM technique the advantage when power sensitive materials or processes, like Auger recombination, are a factor. When the PMM technique is compared to spatial modulation spectroscopy, the PMM demonstrates the same ability to measure the cross-section data directly and shows an improvement in 1/f noise due to the high frequency (100 kHz) polarization modulation of the PEM. However, despite the positive aspects of the PMM technique (accurate images of the extinction cross-section, low pump fluence, high frequencies, etc.), this technique is limited to investigations of anisotropic nanostructures, like rods and wires. This limitation should not render this technique useless due to the
activity of research with various types of anisotropic materials. Given all of the benefits, polarization modulation microscopy should be a useful single particle absorption technique for investigating the properties of anisotropic nanomaterials.
BIBLIOGRAPHY


