### Spectroscopic Studies of Hole Transfer to and Diffusion Along Semiconductor Surfaces for Water Oxidation

by

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#### Abstract

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Artificial photosynthesis holds promise as a solution to the intermittency problem of solar photovoltaics. By storing the energy of sunlight in the chemical bonds of hydrogen, solar power can be generated around-the-clock and carbon-free. Current state-of-the-art devices for artificial photosynthesis, however, are not efficient, stable, and inexpensive enough to allow mainstream adoption of the technology. The efficiency problem stems from the ratelimiting water oxidation reaction at the anode of the device. While some of the molecular intermediates of the water oxidation reaction on the surface of the anode are known, a complete picture of the reaction requires knowledge of the behavior of the charge carriers from generation in the bulk of the device to reaction at the anode/electrolyte interface. In this thesis, two principal experiments are described. The first details a novel spectroscopic method to detect charge carrier motion within a model device as well as charge carrier arrival at a catalytic surface layer. The second experiment describes new applications of transient grating spectroscopy to track important changes in the *in situ* behavior of surface charge carriers at a catalyst surface.

A common photoanode geometry incorporates a catalytic overlayer with a light-absorbing substrate, connected by a buried junction. The magnitude and band bending of the electric field at the buried interface is crucial for device quantum efficiency, but no reliable metric exists to measure either quantity in real devices. Chapter 3 describes initial transient absorption spectroscopy (TAS) experiments designed to probe charge injection and electric field magnitude at a buried junction. A model photoanode device consisting of a np-GaAs junction and transition metal oxide (TMO) overlayer was designed to allow TAS with photoexcitation from either side of the device. Large coherent acoustic oscillations are observed only when the TMO overlayer is present and when probing with a laser wavelength that has a penetration depth on the order of the TMO film thickness. The oscillations are shown to possess two distinct frequencies that vary with probe wavelength and correspond to coherent longitudinal acoustic phonons (CLAPs) in the GaAs light absorber and TMO film, respectively. Additionally, large acoustic echoes are shown to originate from both the np-GaAs junction electric field and the p-GaAs/TMO interfacial electric field. The echoes traverse the length of the photoanode device with an amplitude that is proportional to the electric field strength at the location of the echo origin. The generation of the CLAP oscillations is attributed to charge carrier injection at the np-GaAs interface and the p-GaAs/TMO interface; the charge carriers screen the electric field at those locations, causing phonon emission via the inverse piezoelectric effect (IPE). The varied echo magnitude, experiments with varied pump fluence, and initial experiments in electrolyte environment strongly support the assignment of phonon generation to the IPE. With further development, the technique shows promise as a quantitative measure of charge carrier injection and electric field strength at buried interfaces in artificial photosynthesis devices.

Chapter 4 describes the development of a novel application of transient grating spectroscopy (TGS) to connect the diffusivity of charge carriers at an n-GaN surface to the reactivity of that surface. GaN is widely studied both experimentally and theoretically as a model for applications in catalysis because of its interesting surface chemistry. TGS was used to measure the diffusivity of surface holes in the presence and absence of water oxidation intermediates on the surface. Results show that the lateral, interfacial hole diffusivity increases by a factor > 2 from air at the n-GaN/aqueous electrolyte interface for both pH = 1.4 (0.1 M HBr) and  $pH = 7 (0.1 \text{ M Na}_2 \text{SO}_4)$ . The increase in diffusivity is not reproduced on undoped GaN, where there is not a large density of surface intermediates, and is not sensitive to defect centers, since the surface recombination velocity, also obtained from the TGS kinetics, differs by almost an order of magnitude between the two electrolytes. The origin of this increase in diffusivity in n-GaN is attributed to a new current pathway for surface holes due to the presence of mobile intermediates of the water oxidation reaction on the surface of the n-GaN. In essence, surface holes move faster when they encounter a surface adsorbed with reaction intermediates. The result shows for the first time a connection between surface charge diffusivity and surface reactivity.

To my parents

# Contents

Contents				
List of Figures iv				
Li	st of	Tables	viii	
Li	st of	Abbreviations and Symbols	ix	
1	Intr	roduction	1	
	1.1	Photoelectrochemical water splitting	2	
	1.2	Overview	4	
<b>2</b>	Exp	perimental	6	
	2.1	Transient absorption spectroscopy	6	
		2.1.1 Laser spectroscopic setup	7	
	2.2	Reactive Sputtering	9	
	2.3	Solid-state semiconductors	11	
		2.3.1 Semiconductor junctions	13	
	2.4	Semiconductor-electrolyte interface	16	
		2.4.1 Electrochemical techniques	18	
3	Spe	ctroscopic Probe of Coherent Acoustic Oscillations Originating from		
	Bur	ied Interfaces	20	
	3.1	Introduction	20	
	3.2	GaAs device structure	21	
		3.2.1 GaAs device calculations	22	
		3.2.2 Methods	24	
		3.2.3 Device current properties	26	
		3.2.4 Device Quantum Efficiency	34	
		3.2.5 Fitting and FFT adjustment procedure	36	
	3.3	Spectroscopic Results	38	
		3.3.1 800 nm probe	39	
		3.3.2 400 nm probe	41	

	3.4 3.5	Mechanism       5         Conclusion       5         3.5.1       Proposed Future Experiments		
	3.0	Conclusion		
4	Tra	Transient Grating Spectroscopy as a Probe of Surface Hole Diffusivity		
	4.1	Introduction	59	
	4.2	Transient Grating Spectroscopy	61	
		4.2.1 Formation of the transient grating	61	
		4.2.2 Probing the transient grating	63	
		4.2.3 Decay of the transient grating	65	
		4.2.4 Angle change in electrolyte	68	
		4.2.5 Heterodyne detection	69	
		4.2.6 Extraction of TG signal	73	
	4.3	Experimental Setup	73	
	4.4	Properties of gallium nitride	77	
		4.4.1 Electrochemical measurements	79	
	4.5	Results	84	
		4.5.1 Surface diffusivity of holes in GaN	84	
		4.5.2 Kinetic Voltage Dependence	89	
	4.6	Next Steps	91	
		4.6.1 TGS on n-GaN with cocatalysts	93	
		4.6.2 TGS on other catalyst and electrode materials	94	
		4.6.3 Heterodyne-dependent experiments	94	
		4.6.4 TGS in full 3-electrode setup	95	
	4.7	Conclusion	96	
$\mathbf{A}$	TG	S processing code and Labview programs	97	
	A.1	Main TGS data collection Labview program	97	
	A.2	Other useful Labview VIs	98	
		A.2.1 Signal oscillation at fixed time delay	98	
		A.2.2 Kinetic decays at fixed coverslip angle	98	
		A.2.3 Signal over absolute time at fixed coverslip angle and time delay position	n 99	
		A.2.4 Signal versus sample z-axis position at fixed coverslip angle and time		
		delay position	99	
	A.3	Igor scripts for TGS processing	99	
Bibliography 113				

# List of Figures

1.1	An example photovoltaic design and an example PEC cell	2
2.1	Schematic diagram of the laser setup from generation to sample.	8
2.2	Scale model of the laser table setup near the sample.	10
2.3	Schematic of the process of reactive sputtering.	11
2.4	Diagram of a semiconductor lattice with and without n- and p-dopants	12
$2.5 \\ 2.6$	Diagram of equilibration of Fermi levels and formation of an n-p junction Example IV curve of a p-n junction. Representative band diagrams and spatial	14
2.0	pictures including potential barrier qV, depletion width W, and junction electric	15
2.7	Equivalent circuits for semiconductor/electrolyte interface with and without sur-	19
	face states.	18
3.1	Diagram of the two GaAs layered samples used in this study	22
3.2	Distribution of electric field within the GaAs np junction.	23
3.3	Schematic of etching procedure used to prepare samples for spectroscopy	26
$3.4 \\ 3.5$	Prototype design of a Teflon cell for etching the GaAs samples	27
	photocurrent plots.	27
3.6	Current-voltage curves for np-GaAs and npp <sup>+</sup> GaAs samples in the pump front and pump back geometries, illuminated with 800 nm fs laser (top graphs) or 808	
	nm CW laser illumination (bottom graphs).	29
3.7	Open-circuit photocurrent versus excitation wavelength for np-GaAs samples with no Co $\Omega$ and 20 nm Co $\Omega$ overlayer and npp <sup>+</sup> Co $\Lambda$ s with 80 nm Co $\Omega$	
	overlayer. $\ldots$	31
3.8	Photocurrent versus excitation wavelength for $npp^+$ GaAs samples with no $Co_3O_4$	
	and 20 nm $Co_3O_4$ overlayer, obtained with 150 fs pulsed OP output.	32
3.9	Photocurrent density of np-GaAs with 80 nm $Co_3O_4$ overlayer and npp <sup>+</sup> GaAs	
	with 80 nm $Co_3O_4$ overlayer, illuminated at 0.4 mJ cm <sup>-2</sup> with 800 nm 150 fs	
	pulsed laser illumination from the back, front, or both front and back	33
3.10	Photocurrent density of np-GaAs samples with varying thicknesses of $Co_3O_4$ over-	
	layer for low and high power and front and back illumination with a 150 fs laser.	34

3.11	Calculated absorbed photon density per pulse $(cm^{-3})$ versus incident laser fluence $(mJ cm^{-2})$ for pump front and pump back geometries for all TMO types used in	
	this study.	35
3.12	An explanation of the procedure used to generate FFT spectra	37
3.13	Pump-probe reflectivity spectra of np-GaAs (pumped from the back and probed	
	from the front with $\lambda_{pump} = \lambda_{probe} = 800$ nm) with no TMO, 4 nm Ir + 15 nm	
	$IrO_2$ , 10 nm sputtered $Co_3O_4$ , and 25 nm 300° C ALD $Co_3O_4$ overlayers, displayed	
	with unnormalized data (left column) and normalized data (right column)	40
3.14	Pump-probe reflectivity spectra of np-GaAs (pumped from the back and probed	
	from the front with $\lambda_{pump} = \lambda_{probe} = 800 \text{ nm}$ ) for two sets of purportedly identical	
	samples with 10 nm sputtered $Co_3O_4$ and $300^\circ$ C ALD $Co_3O_4$ overlayer	41
3.15	Transient reflectivity for np-GaAs device pumped in the back at 800 nm with	
	a fluence of 3.6 mJ $\mathrm{cm}^{-2}$ without TMO overlayer probed at 800 nm, without	
	TMO overlayer probed at 400 nm, with 15 nm $IrO_2$ overlayer probed at 800 nm,	
	and with 15 nm $IrO_2$ overlayer probed at 400 nm	42
3.16	Pump-probe reflectivity spectra of np-GaAs (pumped from the back and probed	
	from the front with $\lambda_{pump} = 800$ nm and $\lambda_{probe} = 400$ nm) with no TMO, 4	
	nm Ir + 15 nm IrO <sub>2</sub> , 10 nm sputtered Co <sub>3</sub> O <sub>4</sub> , and 25 nm 300° C ALD Co <sub>3</sub> O <sub>4</sub>	
	overlayers, displayed with unnormalized data (left column) and normalized data	4.4
2 17	(right column)	44
0.17	pump back (black) and pump front (rod) geometries with $\lambda = -800$ pm at 3.6	
	pump back (black) and pump none (red) geometries, with $\lambda_{pump} = 600$ mm at 5.0 mJ cm <sup>-2</sup> and $\lambda_{max} = 400$ nm	45
3.18	Zoom on echoes in transient reflectivity for np-GaAs with 100° C ALD overlayer	10
0.10	for pump back (black) and pump front (red) geometries.	46
3.19	Transient reflectivity for np-GaAs with TMO overlayers as noted in the legend,	
	using the pump back geometry with $\lambda_{pump} = 800 \text{ nm at } 3.6 \text{ mJ cm}^{-2} \text{ and } \lambda_{probe} =$	
	400 nm. Major echoes appear even in samples with course time steps and recur	
	in 415 ps intervals. $\ldots$	46
3.20	Transient reflectivity spectra with $\lambda_{pump} = 800$ nm and $\lambda_{probe} = 400$ nm for	
	np-GaAs with all overlayers considered in this study, with corresponding fluence-	
	adjusted FFT spectra.	48
3.21	Normalized transient reflectivity for np-GaAs with $4 \text{nm} \text{ Ir} + 15 \text{ nm} \text{ IrO2}$ overlayer	10
9 99	under different pump fluence intensity.	49
3.22	Variation of observed oscillation period with probe wavelength for $IrO_2$ and $100^{\circ}$ C ALD Co overlawore pumping the front side of the device with pro-	
	$100$ C ALD $Co_3O_4$ overlayers, pullipling the front side of the device, with pre-	
	with $100^{\circ}$ C Co <sub>2</sub> O. ALD overlayer and IrO <sub>2</sub> overlayer, pumping the front side of	
	the device and probing with wavelength noted in the figure $\frac{1}{2}$	51
3.23	(a) Transient reflectivity for n-p GaAs with 4 nm Ir $+$ 15 nm IrO <sub>2</sub> overlaver in the	σı
0.20	pump front geometry under pump fluence intensity ranging from $0.37-20 \text{ mJ cm}^{-2}$ .	
	(b) Extracted FFT amplitude from data in (a).	54

v

3.24	Pump-back transient reflectivity of np-GaAs with 300° C ALD $Co_3O_4$ overlayer in air and 0.1 M NaOH and IrO <sub>2</sub> overlayer in air, DI water, and 0.1 M H <sub>2</sub> SO <sub>4</sub> .	55
4.1	Graphic description of laser pulse interference for two Gaussian beams at small and large angles.	62
4.2	Wavevector description of the interference of two Gaussian pulses with wavevec-	-02
4.3	tors $k_1$ and $k_2$ resulting in grating wavevector $q = \pm (k_1 - k_2)$ Left: calculation of the number of photoexcited charge carriers 25 nm into an n-GaN surface and 10 ps after pump excitation. Carrier density is modulated along the surface due to the interference of the pump beams. Bight: The resultant	62
	change in refractive index as calculated using equation 4.3	63
4.4	Diagram of grating formation by overlapped pump beams and grating probing	00
	with time-delayed probe	64
$4.5 \\ 4.6$	Mechanisms of grating decay and example transient decay curves for varied $\Lambda$ . Angle change of pump beams due to differing refractive indices of air and water	67
	phases.	68
4.7	Example oscillatory detector signal and example TG and PP decay curves	71
4.8	Example plot of $\tau_q^{-1}$ vs. $q^2$ for extraction of diffusion constant D	73
4.9	Diagram of transient grating setup	74
4.10	Cross-sectional view of pump and probe beams in boxcar geometry	75
4.11	(0001)-GaN unit cell displaying Wurtzite structure with Ga-polarity at the c-	
	plane surface.	77
4.12	Diagram of n-GaN/electrolyte interface with energetic position of redox couples.	78
4.13	Dependence of APCE of n-GaN on wavelength of excitation and fluence value.	79
4.14	Mott-Schottky plots for n-GaN in all electrolytes in dark and illuminated conditions.	81
4.15	A.C. voltammetry and Mott-Schottky plots in dark and under 266 nm pulsed	~~~
1 1 0	laser illumination for n-GaN in all electrolytes.	82
4.10	OCP values versus time, redox potential position, and fluence for n-GaN in all	0.9
1 17	electrolytes illuminated with pulsed 267 nm light	83
4.17	1GS spectrum decays ( $\gamma_g$ vs. $q$ ) for undoped GaN and n-GaN in air and electrolyte. Modeling fits of $\tau$ decay for undoped CaN and n CaN in air and	
	electrolyte. Modeling its of $\gamma_g$ decay for undoped Gain and it-Gain in air and electrolyte for all grating periods $\Lambda$	85
118	Inverse kinetic decay $\sigma^{-1}$ versus $\sigma^2$ for n CaN in air at varied pump fluence levels	00 86
4.10	Schematic of $G_{2N}(0001)$ surface with $G_{2N}$ sites terminated by $H_{2O}$ OH and O*	80
4.15	after equilibration with an aqueous 0.1 M HBr electrolyte	88
4 20	TGS kinetic traces of n-GaN with $\Lambda = 5.6 \ \mu m$ and pump-probe kinetic traces of	00
1.20	n-GaN with applied voltages	89
4.21	Comparison of single exponential, double exponential, and stretched exponential	00
*	fitting procedures on TGS kinetic data with $\Lambda = 5.6 \ \mu m$ at -0.3 V applied bias	
	and $+1.2$ V applied bias.	91
4.22	A summary of the most important parameters of the fits to the data summarized	
	in Figure 4.21	92

4.23	SEM images of n-GaN with (a) no overlayer deposited, (b) 5 nm of $Co_3O_4$ de-	
	posited via sputtering, and (c) the same film as (b) after approximately 1 hour	
	exposure to to 0.1 M HBr electrolyte	94

# List of Tables

3.1	Quantum efficiencies for 20 nm $Co_3O_4$ overlayer (from Figure 3.6b)	36
3.2	Light Transmitted to GaAs junction. [74–77]	38
3.3	Prominent frequencies displayed in Figure 3.20	47
4.1	Surface charge and potential distribution	84
4.2	Variables obtained from fits using diffraction efficiency model	86
A.1	TGS Labview program data for 2 detectors and $n$ coverslip angle points	100

# List of Abbreviations and Symbols

C	capacitance
C	capacitance of Helmholtz lavor
$C_H$	capacitance of the space charge region
$C_{SC}$	capacitance of the space charge region
D	diffusion constant
$D_h$	hole diffusion constant
$E_{bi}$	built-in voltage
$E_f$	Fermi level
$L_p$	hole diffusion length
N(x, z, t)	carrier density
$N_d$	dopant density
P	polarizability
S	surface recombination velocity
$V_H$	potential drop in the Helmholtz layer
$V_{fb}$	flatband potential
$\dot{V_{ph}}$	open-circuit photovoltage
$V_{redox}$	redox potential
$V_{sc}$	band bending potential
W	depletion width
$\Delta N_e$	injected electron concentration
$\Delta N_h$	injected hole concentration
$\beta$	absorbed power
$\chi$	electric susceptibility
$\epsilon$	dielectric constant
$\eta$	diffraction efficiency
$\gamma$	quantum efficiency
$\kappa$	imaginary part of refractive index
$\mu_h$	hole mobility
$\phi$	beam angle relative to normal
$\psi$	addition of phases of all beams
/	1

$ au_d$	diffusion time constant
$ au_g$	total grating decay time constant
$ au_r$	recombination time constant
$\theta$	angle between TGS pump beams
$\tilde{n}$	complex refractive index
$\varphi_s$	phase shift due to diffraction
ξ	phase
d	DO grating fringe spacing
j	current
k	wavevector
$k_B$	Boltzmann constant
$m_{eh}$	$m_{eh} = (1/m_e + 1/m_h)^{-1}$
$m_e$	effective mass of an electron
$m_h$	effective mass of a hole
n	real part of refractive index
$n_0$	instrinsic doping concentration of sample
q	grating wavevector
$q_H$	Helmholtz layer charge
$q_{sc}$	depletion layer charge
$q_{ss}$	surface state charge
ALD	atomic layer deposition
CB	conduction band
CCD	charge-coupled device
CL	collimating lens
CLAP	coherent longitudinal acoustic phonon
CV	cyclic voltammetry
CW	continuous wave
$\mathrm{DFT}$	density functional theory
DO	diffractive optic
DP	deformation potential
EIS	electrochemical impedance spectroscopy
FFT	fast Fourier transform
$\mathrm{FL}$	focusing lens
FLP	Fermi level pinning
IPE	inverse piezoelectric effect
IV	current-voltage
LO	longitudinal optical

- LOPC longitudinal optical phonon-plasmon coupling
- NHE normal hydrogen electrode
- OCP open circuit potential
- OER oxygen evolution reaction
- OPA optical parametric amplifier
- PEC photoelectrochemical
- PVD physical vapor deposition
- PZC point of zero charge
- RF radio frequency
- SI semi-insulating
- STH solar-to-hydrogen
- TAS transient absorption spectroscopy
- TE thermoelastic
- TGS transient grating spectroscopy
- TMO transition metal oxide
- VB valence band
- WOC water oxidation catalyst

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# Chapter 1 Introduction

He began then, bewilderingly, to talk about something called entropy.

The Crying of Lot 49 THOMAS PYNCHON

The world's dependence on fossil fuels for energy, combined with an increasing population that is expected to exceed 9 billion by the year 2050 [1], has caused atmospheric levels of carbon dioxide to exceed 400 ppm, a level that is of great concern. [2, 3] Rising temperatures promise to upend long-standing climate norms, change ecosystems and threaten both animal and human life. Global temperature rises of 2 degrees Celsius by the year 2100 are very likely and if emissions continue on the current trajectory, over 4 degrees warming is possible, as predicted by the Intergovernmental Panel on Climate Change. [4] While it is too late to eliminate any temperature rise, the rise may be contained if the usage of carbon-emitting fuel sources is quickly and steeply curtailed.

Energy sources that are plentiful, economical, and carbon-free are needed. Many renewable energy sources have been considered, including wind, [5, 6] biomass, [7–9] geothermal, [10] hydroelectric, and solar power. [11] Of these sources, solar has by far the greatest energy supply. The solar energy flux incident on the Earth in a single hour, if it were able to be stored, would be able to power all of humanity's energy needs for an entire year. [12] Solar energy, however, suffers from the fundamental problem of intermittency — no power can be generated during moments of overcast weather or at night. A medium for the storage of solar energy is thus badly needed. Storage in batteries is one option but scaling up to grid scale requires cost reductions that are not currently possible. [13] A promising alternative, called photoelectrochemical water splitting, involves storing the solar energy in the chemical bonds of hydrogen, a combustible, carbon-free fuel.

# 1.1 Photoelectrochemical water splitting

While solar photovoltaics use the energy from sunlight to create electricity, solar photoelectrochemical (PEC) cells store sunlight in chemical bonds for later use as fuel. The introductory processes for both methods are similar. A semiconductor (solid state or organic) absorbs an above-bandgap photon, creating an electron-hole pair. In the presence of a p-n junction, the electron and hole separate under the influence of the built-in electric field of the p-n junction. The two systems deviate at this point. In a photovoltaic system, the charges are driven through a resistive load to provide current (Figure 1.1a). Power is thus provided essentially at the same time as the arrival of the incident photon. A photoelectrochemical system, on the other hand, directs the photo-generated charges to complementary electrodes (holes to the anode and electrons to the cathode) immersed in a liquid electrolyte (Figure 1.1b). The charges undergo oxidation or reduction reactions with the electrolyte, chemically changing the electrolyte and storing the energy initially provided by the photon in the chemical bonds of the product molecule which, if chosen cleverly, can be subsequently used as a fuel to provide power.



Figure 1.1: (a) An example photovoltaic design. A p-n junction separates photo-excited charges towards electrodes, sending current through a circuit to power a load. (b) An example PEC cell. A p-n junction separates photo-excited charges towards electrodes (here, a water oxidation catalyst (WOC) as anode and platinum as cathode), which undergo reaction with water at the surface to produce hydrogen and oxygen as detailed in equations 1.1 and 1.2.

One of the most promising and sought-after applications of PEC cells is water splitting to create hydrogen gas. This process uses aqueous electrolyte to reduce protons at the cathode, creating hydrogen gas, and oxidize water at the anode, creating oxygen gas. The hydrogen can then be used as fuel in a hydrogen fuel cell to power an automobile or any number of things. [14, 15] The two half-reactions necessary for water splitting are:

$$2H^+ + 2e^- \rightarrow H_2 \quad E^0 = 0 \text{ V vs NHE}$$

$$(1.1)$$

$$2H_2O \rightarrow 4e^- + 4H^+ + 2O_2 \quad E^0 = 1.23 \text{ V vs NHE}$$
 (1.2)

where NHE is the normal hydrogen electrode. Early reports of photoelectrochemical water splitting with solar-to-hydrogen (STH) efficiency of under 1% came in the 1970s using TiO<sub>2</sub> electrodes. [16, 17] A system using an InP/Pt cathode and n-GaAs/Mn electrode exhibited 8% efficiency in 1987. [18] Work with many-layer multi-junction cells around the turn of the century used anodes consisting of GaInP, AlGaAs, and GaAs junctions to show STH efficiency levels between 12% and 18%. [19–21] More recently, attempts to create devices that utilize earth-abundant materials and eschew expensive materials such as platinum have shown efficiencies ranging between 2-5% without applied bias. [22, 23]

While the thermodynamic potential for water oxidation is 1.23 eV versus NHE, typically a larger bias (overpotential) must be applied to drive appreciable product formation. A common approach to lower overpotential and increase product formation is to use a water oxidation catalyst (WOC). One common sub-class of water oxidation catalysts, used for their resistance to chemical degradation and earth-abundant nature, are transition metal oxides (TMOs) such as  $IrO_2$ , NiO,  $RuO_2$  and  $Co_3O_4$ . [24] Water oxidation catalysts can be used as stand-alone electrodes [25, 26] or can be deposited as co-catalysts on a light-absorbing semiconductor material (*e.g.* GaAs, Si, GaN, or TiO<sub>2</sub>). [27–30]

The current understanding of how the water splitting reaction proceeds has identified the oxygen evolution reaction (OER) at the anode as the rate-limiting step. Water oxidation on the anode is expected to occur via intermediates that include hydroxyl, oxo, oxyl and oxygen radical species, but the exact mechanism by which the holes at the surface participate in these intermediate reactions is not well understood. [31–35] Overpotentials for water oxidation typically total 0.5-0.7 eV, whereas the equivalent value for proton reduction is 0.2-0.3 eV lower, bringing the total voltage required for the water oxidation up to approximately 1.8-2.0 V versus NHE. [36] The overpotential can be brought to as low as 0.3 eV by use of RuO<sub>2</sub>, IrO<sub>2</sub>, or Co<sub>3</sub>O<sub>4</sub>, making the use of a WOC essential for a scalable solar-to-fuels system.

In total, three main attributes are needed for a highly functional water splitting system: (1) efficiency, (2) chemical durability, and (3) scalability and low cost. In practice, finding a device system containing all three attributes has proven challenging. While relatively high efficiencies have been achieved using metal oxide WOCs consisting of primarily Ru or Ir, those metals are expensive and not earth-abundant enough to provide scalability. Alternative catalysts and electrodes that meet all three criteria have been sought using density functional theory and high throughput screening of ternary oxide mixes. [37–39] Even with efficient and earth-abundant device materials, most reported devices show a significant decrease in product formation over a period of tens of hours due primarily to corrosion by the electrolyte, well short of the thousands of hours necessary for a commercial application. [23]

One of the most promising device geometries for artificial photosynthesis involves decoupling the light-absorbing and catalytic duties of the device by depositing a catalytic WOC onto a light-absorbing semiconductor. This geometry relaxes the requirement of finding a WOC that is both a good light-absorber and a good catalyst, instead allowing the integration of multiple materials that are best at one of the two tasks. [27, 28] The device functions in three main steps:

- 1. Electron-hole pair creation in the light absorber
- 2. Transport of charge carriers to the catalytic interface
- 3. Charge transfer at the catalytic interface and reaction

In step one, incident light on the device creates electron-hole pairs in the light-absorbing component in a density dependent on the absorptivity of the light absorber and with an energy dependent on the bandgap energy of the absorptive semiconductor. In step two, charges are shuttled towards the catalytic layer(s) via the use of internal built-in fields at a surface or in a buried p-n junction. The photovoltage and photocurrent produced by the light-absorbing layer is passed onto the next layer, providing a boost in the total oxidizing or reducing power of holes or electrons, respectively. In the final step, the charge at the interface must navigate surface electric fields, traps, and recombination centers to find a suitable reaction partner on the electrolyte side of the interface.

### 1.2 Overview

This thesis will describe fundamental spectroscopic studies of holes in model photoanodes for the oxygen evolution reaction. The thesis is comprised of two main parts. In the first part (Chapter 3), transport of charge from the creation site to the reaction site on the catalytic overlayer is investigated by a novel spectroscopic method of probing buried electric fields in a multi-component device. Large coherent acoustic oscillations that report on the arrival of photo-generated holes at the anode surface are observed for a np-GaAs buried junction device with several different overlayer species. The oscillation frequency and magnitude display characteristics that change depending on the particular catalyst overlayer and the position at which the charges were created. The second part of the thesis (Chapter 4) describes the behavior of surface holes at a reactive surface of a GaN electrode. Transient grating spectroscopy is used to observe a 2.6x increase in the diffusivity of holes in conditions with a significant surface coverage of mobile water oxidation intermediates. This increase is attributed to hole hopping between the bulk GaN, surface GaN, and surface intermediates and represents the first observation of a dependence of surface charge diffusivity on the surface reactivity of an electrode. While Chapter 3 elucidates the variables necessary for successful charge transport towards a catalytic interface, Chapter 4 provides a new look at charge movement once the charge has reached its final reaction site.

# Chapter 2 Experimental

"In the name of the cathode, the anode, and the holy grid?" said Pökler.

"Yes, that's good," Mondaugen smiled.

Gravity's Rainbow THOMAS PYNCHON

# 2.1 Transient absorption spectroscopy

The expansion in the availability of Ti:Al<sub>2</sub>O<sub>3</sub> (Ti:Sapphire) laser setups with femtosecond resolution has made possible once unachievable experiments on the dynamics of charge behavior in condensed matter systems. Titanium: Sapphire lasers allow relatively facile production of femtosecond laser pulses, providing the time resolution needed to monitor charge carrier motion and relaxation in semiconductor systems, which typically occurs on a picosecond to femtosecond timescale. [40] Transient absorption spectroscopy (TAS) is a subset of a broader class of pump-probe techniques that has progressed from millisecond flash photolysis experiments in the 1940s to femtosecond transient absorption spectroscopy in the 1990s to the frontiers of attosecond transient absorption spectroscopy in current times. [41, 42] TAS is a method for monitoring chemical dynamics in which a strongly perturbing pump pulse resonantly excites the sample and is followed by a spatially coincident and weaker probe pulse that is delayed in time. Illuminating a semiconductor sample with a photon energy exceeding the bandgap energy of the system causes a change in the complex refractive index  $(\tilde{n})$  of the sample due to excitation of electron-hole pairs. The change in transmission of the probe pulse  $(\Delta T)$  with respect to time is then monitored to provide insight on the return of the system to equilibrium. This relaxation process is a finely tuned monitor of charge carrier recombination, scattering, and transfer of electrons and holes on a femtosecond to picosecond time scale. Comparing the kinetics of TAS experiments in varying conditions can give insight into the spatial and energetic positioning of key components of a chemical system. In heterogeneous catalysis, this leads to the ability to pinpoint the identity of reaction intermediates and provide timescales for essential motions of charge carriers and molecular species in a reaction pathway. [31, 32, 43–47]

In detail, transient absorption compares the percent reflectance (or equivalently, the percent transmittance) of the probe beam in conditions with the pump laser present (on) to the percent reflectance with the pump laser not present (off):

$$\frac{\Delta R}{R} = \frac{R_{on} - R_{off}}{R_{off}} \tag{2.1}$$

There are three general processes in a transient absorption experiment that affect the sign of equation 2.1. The pump will induce an excitation of a small fraction of the ground state charge carriers. This results in a decrease of the ground-state absorption of the probe and an increase in the reflected intensity  $(+\Delta R/R)$  onto the detector. An increase in the reflected intensity is also possible if the incident probe beam is resonant with a transition in the system and causes stimulated emission from the excited state. This causes relaxation to the ground state and emission of a photon at the same wavelength and in the same direction as the probe beam. In systems that possess a higher-lying state above the excited state that is resonant with the probe pulse, the probe photon can be absorbed in an excited state absorption, resulting in a decrease in the reflected intensity of light  $(-\Delta R/R)$  that reaches the detector. While the argument here has been presented in terms of reflectance, and transmission coefficients sum to equal 1, and the incident intensity  $I_0$  of a beam is partitioned between the processes as

$$I_0 = I_r + I_t + I_A \tag{2.2}$$

where  $I_r$ ,  $I_t$ , and  $I_A$  are the reflected, transmitted, and absorbed portions of the light, respectively.

#### 2.1.1 Laser spectroscopic setup

The pulsed laser output for all experiments in this thesis originates from a Legend Elite laser system (Coherent Inc., Santa Clara, CA). A schematic display of the full beam path is shown in Figure 2.1. Seed pulses are provided by a Coherent Vitesse Ti:Sapphire laser system with primary wavelength of 800 nm and a repetition rate of 80 MHz. These pulses enter the Legend Regenerative Amplifier along with frequency-doubled pump pulses provided by the Evolution Nd:YLF laser, which produces pulses with a wavelength of 527 nm and is Q-switched to maintain a repetition rate of 1000 Hz. The Evolution pulses selectively amplify a fraction of the seed pulses in the cavity Ti:Sapphire crystal. Output pulses pass



Figure 2.1: Schematic diagram of the laser setup from generation to sample.

through the Ti:Sapphire crystal  $\approx 15$  times before being outputted with a time duration of 150 fs, a repetition rate of 1000 Hz and a output power of 4 Watts. The beam is separated at a beamsplitter to generate pump and probe beams. The pump beam is directed towards the spectroscopic setup, traversing variable neutral density filters and telescoping and focusing optics. The probe beam is reflected from a retroreflector mounted on a computer-controlled optical delay stage (Model FMS300CC, Newport Inc., Santa Clara, CA) with a 300 mm ( $\approx 2$  ns) range and directed to the spectroscopic setup. The spectroscopic setup can be used for both heterodyne-detected transient grating spectroscopy (TGS) or transient absorption spectroscopy; the latter involves simply blocking half of the beams used in the former. A detailed description of the final lens setup directing the beams onto the sample, including practical tips on beam overlap and timing, can be found in Chapter 4 centered around Figure 4.9. Signal is detected with either one (for TAS) or two (for TGS) Si or GaP amplified photodiode detectors (DET\_A and DET\_K series, Thorlabs Inc.) which are connected to one (TAS) or two (TGS) lock-in amplifiers (SR810, Stanford Research Systems, Sunnyvale, CA). The pump laser on/off chopping rate is controlled by a single mechanical chopper

at 300 Hz, which is connected to both lock-in amplifiers. The data collection scheme is controlled by a Labview program, which coordinates the delay stage, TGS rotation stage (Chapter 4), and lock-in detection (see details in Appendix A).

A scale model of the laser table setup is displayed in Figure 2.2. Two identical TGS spectroscopy lens setups allow for back or front side pumping and probing of the sample. Starting at the top left of the diagram, the pump beam may optionally be transmitted through a series of BBO crystals to be converted from 800 nm to 266 nm (kit from EKSMA optics, Vilnius, Lithuania). The pump light is attenuated with a variable ND filter and can be directed with a flip mirror to either the front side or the back side lenses. Pump light is focused with a +1000 mm lens and transmitted through a diffractive optic (DO); the  $\pm 1$  orders of diffraction are kept. Engineering controls should be devised to block the other transmitted and reflected orders of diffraction for safety purposes. In the setup used here, this entailed installing wide beam blocks placed directly before and after the DO to allow only the input beam and the desired diffraction orders to transmit. Light is collimated by the first large achromatic doublet and focused onto the sample with the second.

The probe beam is reflected from the delay stage and enters a periscope to lower the height of the beam below that of the pump beam. After optional conversion to 400 nm with a BBO and spot size decrease with a telescope, the beam is reflected towards the lens setup, separating 800 nm light from 400 nm light with high reflector (HR) mirrors if necessary. The probe light is focused and enters the same diffraction grating as the pump beam (front side) or a diffraction grating with the same fringe spacing as the pump beam if pumping the sample from the back side. The probe light is collimated by the first large achromatic lens; probe beams propagate above the pump beams at this point. Between the two achromatic lenses, the probe beams pass through thin coverslips, one of which is mounted on a computer-controlled rotation stage (Newport CONEX-AGP-PR100P) for fine control of the relative phase of the probe beams. The probe beams are focused with the second large achromatic lens onto the sample. For a detailed accounting of sample alignment, phase control, and beam positioning, see Chapter 4 and Figure 4.9. Transmitted or reflected signal is picked off with a D-shaped mirror (Thorlabs PFD series of mirrors) and directed to the photodiode detectors after optionally passing through HR mirrors or polarizers for noise control.

# 2.2 Reactive Sputtering

Cobalt oxide and iridium oxide films were deposited by radio frequency (RF) magnetron reactive sputtering, a physical vapor deposition (PVD) process. RF sputtering involves ionizing a gas (generally argon at concentrations of approximately  $10^{-3}$  Torr) with a strong RF bias to create a plasma and accelerating the argon ions towards a target material (here, Co or Ir). The collision of the argon ions with the target material ejects target atoms and free electrons into the chamber. Collision of the free electrons with neutral argon atoms maintains the plasma. Some of the target atoms coat the sample substrate, mounted above the target materials and spinning to ensure an isotropic deposition. A schematic of the



Figure 2.2: Scale model of the laser table setup near the sample.

sputtering process is displayed in Figure 2.3. Magnetron sputtering incorporates magnets behind the target material to trap free electrons in the magnetic field around the target. This prevents sample damage caused by free electrons and increases the probability that a free electron will ionize an argon atom, increasing the rate and quality of deposition. Reactive sputtering involves incorporating a reactive gas (here, oxygen) into the chamber. Ejected target materials react with the oxygen to create an oxide of the target material. The stoichiometry of the oxide film depends on substrate temperature and the partial pressures of argon and oxygen in the chamber. The sputtering system used (AJA International, Scituate, MA) was provided graciously by the Joint Center for Artificial Photosynthesis in Berkeley, CA.



Figure 2.3: Schematic of the process of reactive sputtering.

## 2.3 Solid-state semiconductors

Semiconductors are crystals with a periodic array of atoms, either elemental (e.g. Si, Ge) or compound (e.g. GaAs, InAs, GaInP, etc.). Unlike molecules, which contain discrete energy states, periodic solids possess energy bands. These bands can be thought of as the bonding and antibonding orbitals of a molecular orbital diagram in the limit of Avogadro's number of atomic orbital inputs – as more and more discrete energy states are packed into the same area, the states become continuous. [48]

The overlap of the orbitals in the solid will form the continuous bands at different absolute energy positions depending on the specific atomic orbitals that are overlapping, leaving gaps between the various bands. The gap between the highest occupied band (valence band, VB) and the lowest unoccupied band (conduction band, CB) defines the bandgap, the size of which determines whether a solid is considered an insulator, semiconductor, or metal. While insulator bandgaps are very large (several eV), semiconductor bandgaps are smaller (zero to a few eV), and metals possess no band gap (the conduction band is filled at equilibrium). The degree of electron filling is given by the Fermi level  $(E_f)$  of the material, which defines the energetic position at which there is a 50% probability of electron occupation at equilibrium. For intrinsic semiconductors (no dopants), this value lies in the middle of the band gap. The absolute energetic position of the conduction band edge is measured by the electron affinity, defined as the energy required to remove an electron from the conduction band to the vacuum level. Another useful quantity is the work function, defined as the energy required to remove an electron from the conduction band edge, required to remove an electron from the conduction band edge, the position of the conduction band edge, valence band edge, and Fermi level can be compared across many semiconductors relative to the vacuum level or another known reference such as the normal hydrogen electrode (NHE), useful for electrochemical experiments. [24, 49, 50]



Figure 2.4: (a) an intrinsic lattice of Si atoms has a Fermi level in the middle of the bandgap. (b) Replacing silicon atoms with boron adds a free hole, decreasing the Fermi level. (c) Replacing silicon atoms with phosphorus adds a free electron, increasing the Fermi level.

The Fermi level can be adjusted by introducing elements into the lattice from elemental groups containing one less valence electron (p-doping) or one more valence electron (n-doping). Figure 2.4 displays intrinsic silicon, silicon doped with boron, and silicon doped with phosphorus along with schematic band diagrams for illustrative purposes. Doping with n-dopants or p-dopants introduces dopant levels that sit within the bandgap very near (less than  $k_BT$  at room temperature) to the conduction or valence band edges, respectively. These dopant levels inject their electrons (holes) into the conduction (valence) bands, raising (lowering) the Fermi level and leaving behind an uncompensated positively charged donor atom or uncompensated negatively charged acceptor atom. The deviation of the Fermi levels from the intrinsic Fermi level for n- and p-doping can be determined as:

$$E_{f,n} - E_{f,i} = k_B T \ln(\frac{N_d}{n_i}) \qquad \qquad E_{f,p} - E_{f,i} = k_B T \ln(\frac{N_a}{n_i}) \tag{2.3}$$

where  $E_{f,n}$  and  $E_{f,p}$  are the Fermi levels after doping with n- and p-dopants, respectively,  $E_{f,i}$  is the intrinsic doping level,  $k_BT$  is the Boltzmann constant times temperature, and  $N_d$ ,  $N_a$ , and  $n_i$  are the n-dopant density, p-dopant density, and intrinsic doping density, respectively. [51]

#### 2.3.1 Semiconductor junctions

Bringing together a n- and p-doped semiconductor of the same composition results in a semiconductor homojunction (This is not how junctions are made in practice, but works for instructive purposes here). Prior to contact, electrons in the n-doped semiconductor contain higher chemical potential than their counterparts in the p-doped semiconductor, as noted by the higher Fermi level (Figure 2.5a). Once contacted, electrons will diffuse from the n-doped semiconductor into the p-doped semiconductor, leaving behind positively charged donor ions on the n-side and negatively charged acceptor ions on the p-side (Figure 2.5b). An electric field that opposes the charge carrier diffusion builds up in the region of left-behind donors and acceptors (called the space-charge or depletion region), eventually halting the diffusion process to produce a depletion region that possesses a width W dependent on the density of donor and acceptor atoms on each side of the material:

$$W = \left(\frac{2\epsilon\epsilon_0 k_B T}{q^2} * \ln\left(\frac{N_a N_d}{n_i^2}\right) * \left(\frac{1}{N_a} + \frac{1}{N_d}\right)\right)^{1/2}$$
(2.4)

As will be detailed in Chapter 3, a highly-doped junction will possess a small depletion width and a lightly-doped junction will have a large depletion width. In a junction with one highly-doped side and one lightly-doped side, the lightly-doped side will have a long depletion width, in contrast to the highly-doped side.

Junctions can also be formed by bringing together two materials of different composition. This results in a semiconductor heterojunction. Whereas homojunction formation depends only on the relative Fermi levels of the two materials, heterojunction formation depends on both the relative Fermi levels as well as the energetic difference between the valence bands and conduction bands of the two materials. Depending on the lineup of these band edges, heterojunctions can create devices that possess differently sized barriers for electrons and holes, in contrast to homojunctions. Quantum wells are one well-known application of semiconductor heterojunctions [52]. A full review of heterojunctions is outside the scope of this thesis and the reader is directed to the references for more information. [51, 53–55]



Figure 2.5: (a) p- and n-doped semiconductors of the same composition before equilibration. (b) A p-n homojunction. Electron diffusion from the n- to the p-side and hole diffusion from the p- to the n-side creates an electric field E which opposes the diffusion, forming a charged depletion region.

#### 2.3.1.1 Current-voltage properties of p-n junctions

A bias applied across a p-n junction will affect the size of the depletion region and the amount of current flowing through the junction. The left side of Figure 2.6 shows a typical p-n junction diode current-voltage (IV) plot, defined with positive voltages representing the p-doped side biased positively relative to the n-doped side (forward bias), and negative voltages representing the p-doped side biased negatively relative to the n-doped side (reverse bias). The right side of Figure 2.6 displays the effect of forward and reverse bias on the energy bands and the depletion region of the semiconductor. As greater reverse bias is applied, the band bending and depletion region width in the junction grow larger. Greater forward bias causes the opposite effect, with smaller band bending and a smaller depletion region width. The current shown in Figure 2.6 stems from two processes:

- 1. Diffusion current
- 2. Drift (or generation) current

Diffusion current occurs when majority carriers (electrons on the n-side, holes on the pside) are able to cross the depletion region against the energy barrier. At open circuit and under reverse bias, this current is small, as the probability that a carrier crosses the barrier is its equilibrium (open circuit) probability multiplied by  $\exp(qV_{app}/k_BT)$ , where  $V_{app}$  is the applied bias on the sample. This probability is small at open circuit and is reduced exponentially with voltage under reverse bias conditions. The diffusion current is, however, also exponentially increased with forward bias – this results in the exponential growth in current seen in Figure 2.6 in the positive voltage regime.



Figure 2.6: Left: Current-voltage (IV) curve of a p-n junction diode with positive voltage corresponding to positive bias on the p-side of the junction relative to the n-side. Regions 1, 2, and 3 correspond to reverse bias, open circuit, and forward bias, respectively. Right: Band diagrams defining the potential barrier qV and spatial pictures corresponding to each region shown in the IV curve at left, with magnitude of the depletion width W and junction electric field E noted.

Drift current occurs when minority carriers (holes on the p-side, electrons on the n-side) drift across the depletion region under the impulse of the junction electric field. This effect is relatively insensitive to the height of the potential barrier in the depletion region, since the important metric is not how fast carriers drift across the depletion region, but rather how often they cross. Since there are few minority carriers on each side of the junction, any carrier that is within a diffusion length of the depletion region will drift across it regardless of how large the band bending is. Drift current is thus independent of applied voltage in an ideal diode. This can be seen in the reverse bias region of Figure 2.6. As higher negative voltages are applied, the potential barrier between n and p-regions of the device grows. Current, however, maintains a low, constant value. The small level of current at reverse bias is called "generation current", since it stems from minority carriers created when electron-hole pairs are generated within a diffusion length of the depletion region.

At open circuit, diffusion and drift currents cancel. Current in an ideal diode is thus zero at zero voltage. The full current I in a p-n junction diode can be calculated by the diode equation:

$$I = qA\left(\frac{D_p}{L_p}p_n + \frac{D_n}{L_n}n_p\right)\left(e^{qV_{app}/k_BT} - 1\right)$$
(2.5)

where q is the elementary charge, A is the cross-sectional area of the junction,  $D_p$ ,  $D_n$ ,  $L_p$ , and  $L_n$  are the diffusion constant (D) and diffusion length (L) for holes (p) and electrons (n),  $p_n$  is the concentration of holes on the n-side of the junction,  $n_p$  is the concentration of electrons on the p-side of the junction, and  $V_{app}$  is the applied voltage. This equation describes the combined effect of drift and diffusion current at forward or reverse biases. [51]

Illuminating the junction with above-bandgap light increases the number of electron-hole pairs generated within one diffusion length of the depletion region. This increases both the generation current and the diffusion current. With a generation rate of g, the total increase in the number of electron-hole pairs created in the depletion region or within one diffusion length of the depletion region will be  $Ag(L_p + L_n + W)$ . This will change equation 2.5 into:

$$I = qA\left(\frac{D_p}{L_p}p_n + \frac{D_n}{L_n}n_p\right)\left(e^{qV_{app}/k_BT} - 1\right) - qAg(L_p + L_n + W)$$
(2.6)

This results in the entire IV-curve decreasing in a negative direction. This can be seen by considering equation 2.6 at  $V_{app} = 0$ . The first term becomes zero, leaving the current due to illumination, which is insensitive to applied voltage. The effect of illumination on current properties will be further considered in Chapter 3.

## 2.4 Semiconductor-electrolyte interface

Redox species in electrolyte solutions possess defined energy levels. A semiconductor that comes into contact with an electrolyte solution must equilibrate its Fermi level with the redox level of the solution. The equilibration process (equations 2.7 and 2.8) involves the transfer of electrons from the conduction band into the oxidized form of the redox couple (Ox) to form the reduced form of the redox couple (Red) or the transfer of holes from the valence band to initiate the opposite process. [56]

$$Ox + e_{(CB)} \rightarrow Red$$
 (2.7)

$$\operatorname{Red} + h^+_{(VB)} \to \operatorname{Ox} \tag{2.8}$$

The process that occurs depends on the relative positioning of the potential of the redox couple and the Fermi level in the semiconductor. A semiconductor with a Fermi level that lies higher than the redox potential will equilibrate by transferring electrons, resulting in the formation of a positive space charge region at the interface and upward band bending. A semiconductor with a Fermi level that lies lower than the redox potential, on the other hand, will equilibrate by transferring holes, resulting in the formation of a negative space charge region at the interface and downward band bending. The width of the space charge region is determined by the band bending  $V_{sc}$  and the dopant density N:

$$W = \sqrt{\frac{2\epsilon_r \epsilon_0 V_{sc}}{eN}} \tag{2.9}$$

where e is the elementary charge. [57] On the electrolyte side of the interface, ions in the electrolyte will gather to counteract the charge formed in the semiconductor space charge region. This region is called the Helmholtz layer. The effect of the two opposing layers of charge is to form a parallel-plate capacitor with a capacitance C of

$$C = \frac{\epsilon_0 \epsilon_r}{4\pi d} \tag{2.10}$$

where d is the distance between the layers of charge. This can be further broken down into an equivalent circuit incorporating two capacitors in series (Figure 2.7a), one for the semiconductor space charge region with a capacitance  $C_{SC}$  and one for the Helmholtz layer  $(C_H)$ :

$$\frac{1}{C_{eq}} = \frac{1}{C_{SC}} + \frac{1}{C_H}$$
(2.11)

The voltage across the semiconductor and Helmholtz layer region drops in a linear fashion. The charge density of a 0.1 M solution is typically on the order of  $10^{20}$  cm<sup>-3</sup>, whereas a typical dopant density in a semiconductor can range from  $10^{15}$ - $10^{19}$  cm<sup>-3</sup>. Since the absolute value of the total charge on each side of the interface is equal  $(q_{sc} = -q_H)$  and C = q/V, most of the voltage drops over the semiconductor in the space charge region. [57] Typically  $C_H$  ranges from 10-100  $\mu \text{F}$  cm<sup>-2</sup> and is much larger than  $C_{SC}$ . [58, 59] When this is the case, the band edges of the semiconductor are pinned and the Fermi level shifts with redox potential. This, however, breaks down with the introduction of surface states on the sample. Surface states originate from a number of sources, such as unterminated surface bonds or intermediate adsorbed species, and have their own discrete energy levels within the semiconductor bandgap. At densities above  $10^{13}$  cm<sup>-2</sup>, these surface states can form surface bands that mediate charge transfer during the equilibration process between the semiconductor and the electrolyte. Once the quantity of surface charge rises above 1% of the quantity of charge in the semiconductor space charge region, it can no longer be assumed that most of the voltage drops across the semiconductor space charge region. The adjusted equivalent circuit diagram is that shown in Figure 2.7b, with the parallel capacitances of



Figure 2.7: (a) equivalent circuit for a semiconductor/electrolyte interface with negligible surface state density. (b) equivalent circuit for a semiconductor/electrolyte interface with large surface state density.

the surface states and the space charge region in series with the Helmholtz capacitance. In this case, a phenomenon called Fermi level pinning (FLP) occurs, in which the Fermi level is fixed and the band edges move with the redox potential. [60] Complete Fermi level pinning or complete band edge pinning are extreme limits and intermediate cases are possible; as the density of surface states grows, the Fermi level becomes more pinned. The degree to which a surface exhibits Fermi level pinning can be determined by plotting the measured photovoltage of the sample versus the redox potential of the electrolyte. For a completely unpinned surface, the Fermi level will move with the redox potential and the slope will be unity. Fermi level pinning will result in a slope below one (see Figure 4.16 and surrounding text). [61]

#### 2.4.1 Electrochemical techniques

Electrochemical experiments were carried out in a custom Teflon three-electrode cell. A three-electrode cell consists of a working, counter, and reference electrode. The working electrode is the sample being measured. In the experiments in this thesis, all three-electrode measurements use the working electrode as an anode. The counter electrode completes the circuit and is free to handle the duties of the cathode. The counter electrode is chosen such that the reduction half-reaction is not rate-limiting and does not impede processes measured on the working electrode. All experiments described in this thesis use a platinum wire as counter electrode. The potential of the working electrode is maintained by measuring against the reference electrode. A reference electrode needs to be maximally non-polarizable, *i.e.* its voltage must remain fixed over a wide range of current values. Scanning the voltage on the working electrode will thus not change the voltage on the reference electrode, providing an absolute reference. [56] The reference electrode used in all experiments in this thesis

is a Ag/AgCl (in saturated NaCl) electrode (MF-2021, BASi, West Lafayette, IN). The standard redox potential for Ag/AgCl is 0.206 V versus the normal hydrogen electrode (NHE). Measurements were performed using a CHI1140B or CHI700E potentiostat from CH Instruments (Austin, TX).

Two principal electrochemical techniques are used to monitor the properties of the materials in this thesis. Current is monitored by scanning the voltage sequentially in the positive and negative directions with cyclic voltammetry (CV) scans. CV scans produce current spectra with characteristic shape, allowing for fast determination of the state of the sample surface. Comparing different CV spectra before and after spectroscopic scans allows identification of possible sample damage that warrants further investigation. For anodes doing the water oxidation reaction, a large increase in anodic current indicates the onset of  $O_2$ evolution. The shift of current onset potential in the CV due to illumination can be used as a tool to determine the flat band potential. The capacitance of the space charge region  $(C_{SC})$  can be determined using electrochemical impedance spectroscopy (EIS). EIS applies an alternating current at a defined and alterable frequency.  $C_{SC}$  can be determined by using a Mott-Schottky plot as

$$\frac{1}{C_{SC}^2} = \frac{2}{eA^2\epsilon_r\epsilon_0 N} \left( |V - V_{fb}| - \frac{k_B T}{e} \right)$$
(2.12)

where A is the area of the electrode, N is the dopant density, V is the applied potential, and  $V_{fb}$  is the flat band potential. The dopant density and the flat band potential can be found from the slope and the intercept of the plot, respectively. The usage of equation 2.12, however, requires a few assumptions. It is assumed that surface state density is low, *i.e.*  $C_H \gg C_{SC}$ . In addition, interfacial layers, such as an oxide between the material under study and the electrolyte, must be absent. [59, 62] The energetic positioning and kinetic role of surface states can still be probed with clever variance of input frequency, making EIS a useful tool for the electrochemical characterization of surface fields. [63, 64]

# Chapter 3

# Spectroscopic Probe of Coherent Acoustic Oscillations Originating from Buried Interfaces

Mondaugen set out for his turret and oscillograph, and the comforts of Science, which are glacial and few.

V.Thomas Pynchon

## **3.1** Introduction

Modern buried junction photoanodes contain not only the p-n junction electric field in the light absorber, but also interfacial electric fields at the interface between the light absorber and the catalytic surface layer. The materials used for water splitting predominantly involve thin-film transition metal oxides (TMO) for the catalytic overlayer with III/V or Si semiconductors for the underlying light absorber [29, 30, 65, 66]; an appropriately chosen transition metal oxide can simultaneously perform duties of  $O_2$  evolution, protection of the semiconductor light absorber from degradation in aqueous solution, and reduction of surface recombination by passivation of surface defects.

Efficient device function requires that a charge carrier created in the light absorbing layer of the device be able to seamlessly transfer from the light absorber to the catalytic component of the device. This requires an Ohmic junction between the two components; other electric field structures, such as Schottky barriers, can detrimentally impede the current flow into the catalytic overlayer. Knowledge of the nature of the electric field at the interface between light absorber and catalytic layer is thus essential to the functioning of the overall device. However, typical photoelectrical measures of device function, such as photocurrent and photovoltage measurements, report on the functioning of the entire device and are
unable to isolate the performance of a single interface. In this chapter, an all-optical way of detecting the charge separated carriers that cross the semiconductor/TMO interface within a GaAs/TMO buried junction model photoanode is described. Coherent longitudinal acoustic phonon (CLAP) waves resulting from the inverse piezoelectric effect, in which drifting charge carriers screen interfacial electric fields, cause large signal oscillations in transient reflectivity data. These oscillations have characteristic magnitude and frequency depending on whether they originate in the GaAs or TMO. The results open the door for better interface-specific quantification of electric field strength, both by theoretical modeling and further experiments.

The chapter is organized as follows. Section 3.2 describes the model photoanode devices, including junction electric field magnitudes, processing techniques, and current-voltage properties. Section 3.3 describes the main spectroscopic results. Initial studies using probe illumination at 800 nm and 400 nm are described, followed by investigation and identification of CLAP waves induced by arrival of charge carriers. Section 3.4 discusses the origin of the phonons. Finally, section 3.5 discusses how this technique sets the groundwork for quantitative all-optical characterization of interfacial electric fields and proposes further experiments.

#### 3.2 GaAs device structure

Two model buried junction photoanodes were designed to test the transport of charge through the device and purchased from Intelligent Epitaxy Technology, Inc. (Richardson, TX 75081). The first device, called "np-GaAs" in this thesis, consists of a thick semiinsulating (SI) GaAs (100) substrate with epitaxial layers of, in order, 100 nm In<sub>0.485</sub>Ga<sub>0.515</sub>P doped with silicon at a density of  $2.0 \times 10^{19}$  cm<sup>-3</sup>, 50 nm n-GaAs doped with silicon at a density of  $2.0 \times 10^{19}$  cm<sup>-3</sup>, and 860 nm p-GaAs doped with beryllium at a density of  $3.0 \times 10^{15}$  cm<sup>-3</sup>. The second device, called "npp<sup>+</sup> GaAs" in this thesis, is deposited on a n-doped GaAs substrate and contains InGaP and GaAs layers with thicknesses and dopant densities identical to the first but includes a 70 nm thick capping layer of  $p^+$  GaAs doped at  $2.0 \times 10^{19}$  cm<sup>-3</sup>. Both devices are depicted in Figure 3.1 with a schematic band bending to depict the direction of charge carrier drift. Throughout this thesis, the left side of the device (InGaP and n-GaAs side) in Figure 3.1 will be referred to as the "back side" of the device, and the right side of the device (p-GaAs and TMO side) will be referred to as the "front side". The thick substrate layer provides mechanical support for the epitaxial layers, the InGaP layer serves as an etch stop (etching procedure described in section 3.2.2), and the np-GaAs junction provides an upward bending electric field to shuttle holes to the front end of the device. Samples of about one square centimeter were scored and removed from the 4" diameter master sample.

TMO layers are notated as follows. Samples with a 4 nm Ir adhesion layer topped by 15 nm sputtered IrO<sub>2</sub> are labeled "4 nm Ir + 15 nm IrO<sub>2</sub>", "15 nm IrO<sub>2</sub>", or simply "IrO<sub>2</sub>". All refer to the same deposition recipe of 4 nm Ir plus 15 nm IrO<sub>2</sub>. Samples with PVD (sputtered)  $Co_3O_4$  are labeled "PVD  $Co_3O_4$ " or "sputtered  $Co_3O_4$ " for both 10 and 80 nm depositions. Samples deposited with  $Co_3O_4$  by atomic layer deposition (ALD) at 300° C

or 100 °C are notated "300° C ALD Co<sub>3</sub>O<sub>4</sub>", "300° C ALD", or the analogs for 100 °C as appropriate.



Figure 3.1: Diagram of the two GaAs layered samples used in this study, denoted as (a) np-GaAs and (b) npp<sup>+</sup> GaAs.

#### 3.2.1 GaAs device calculations

As most experiments in this thesis used the np-GaAs sample rather than the npp<sup>+</sup> GaAs sample, and the devices differ only in the substrate and capping layer, calculations will be given for the former and not the latter unless noted.

#### 3.2.1.1 Device junction details

The depletion width W of the np-GaAs junction can be found by [51]

$$W = \left(\frac{2\epsilon\epsilon_0 k_B T}{q^2} * \ln\left(\frac{N_a N_d}{n_i^2}\right) * \left(\frac{1}{N_a} + \frac{1}{N_d}\right)\right)^{1/2}$$
(3.1)

where  $\epsilon \epsilon_0$ , k, T, q,  $N_a$ ,  $N_d$ , and  $n_i$  are the relative permittivity of GaAs, the permittivity of vacuum, the Boltzmann constant, temperature, elementary charge, doping density for p- and n-GaAs, and intrinsic doping of GaAs, respectively. Applying Eq. 3.1 yields a junction width of 770 nm. The width on each side of the junction is calculated with

$$W_n = \frac{W}{1 + N_d/N_a} \qquad \qquad W_p = \frac{W}{1 + N_a/N_d} \tag{3.2}$$

on the n- and p-sides, respectively. Eq. 3.2 yields a junction that is nearly entirely on the p-side, with  $W_n = 1$  nm; the approximation  $W_p = W$  is used here. The electric field is a maximum at the center of the junction and can be calculated via

$$E_{x=0} = -\frac{qN_aW_p}{\epsilon\epsilon_0} = -\frac{qN_dW_n}{\epsilon\epsilon_0}$$
(3.3)

Applying Eq. 3.3 gives an electric field of 32 kV/cm at the center of the junction. Under the depletion approximation, this electric field decreases to zero at the edges of the depletion region, represented graphically in Figure 3.2.



Figure 3.2: Distribution of electric field within the GaAs np junction. Center of the junction is represented as x = 0.

The built-in voltage of the GaAs junction can be found by calculating the deviation of the Fermi levels from the intrinsic Fermi level on the n- and p-sides of the junction:

$$E_{f,n} - E_{f,i} = k_B T \ln(\frac{N_d}{n_i}) \qquad \qquad E_{f,p} - E_{f,i} = k_B T \ln(\frac{N_a}{n_i}) \tag{3.4}$$

where  $E_{f,n}$ ,  $E_{f,p}$ ,  $E_{f,i}$  are the Fermi levels on the n- and p-sides of the junction and the intrinsic Fermi level, respectively. Applying Eq. 3.4 gives a shift of 0.68 eV on the n-side and a shift of 0.55 eV on the p-side, giving a total built-in voltage of 1.23 eV.

The velocity of holes as they move under the impulse of the built-in field is estimated by multiplying the hole mobility ( $\mu_h = 400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) and the built-in field magnitude ( $\text{E}_{bi}$ = 32 kV/cm). This estimates the velocity of holes  $v_h$  to be ~ 10<sup>7</sup> cm/s, in agreement with measured results. [67–69] The time required for a hole originating at the junction center to travel across the GaAs device can be calculated as  $W/v_h$ . This produces an estimated hole transit time of 7 ps through the junction.

#### 3.2.1.2 Photo-induced temperature rise

The temperature increase of the GaAs sample due to pump laser illumination can be estimated as

$$\Delta T = \frac{I_{abs}m}{\rho C_p} * \frac{E_{photon} - E_g}{E_g}$$
(3.5)

where  $I_{abs}$  is the absorbed pump fluence (J cm<sup>-3</sup>) per pulse within the excitation volume, m is the molar mass of GaAs (g mol<sup>-1</sup>),  $\rho$  is the mass density of GaAs (g cm<sup>-3</sup>),  $C_p$  is the heat capacity of GaAs (J mol<sup>-1</sup> K<sup>-1</sup>),  $E_g$  is the bandgap energy, and  $E_{photon}$  is the pump photon energy. This equation assumes that only the portion of the pump photon energy that exceeds the bandgap energy will be converted to heat as photo-excited carriers thermalize to the band edge. For an absorbed pump fluence of 0.001 J cm<sup>-3</sup> at  $E_{photon} = 1.55$  eV, and given GaAs values of m = 144.5 g mol<sup>-1</sup>,  $\rho = 5.32$  g cm<sup>-3</sup>, and  $C_p = 47.0$  J mol<sup>-1</sup> K<sup>-1</sup>, the temperature increase is estimated to be 0.9 K. [70, 71]

#### 3.2.2 Methods

Transient reflectivity measurements were performed with a pump-probe geometry using ~150 fs laser pulses from a Ti:sapphire laser with a fundamental wavelength of 800 nm. 400 nm probe light was generated by reflecting a portion of the fundamental with a beam splitter and directing the beam onto a beta barium borate (BBO) crystal. Probe wavelengths between 475-700 nm were generated by focusing the fundamental beam through a sapphire plate. Probe wavelengths between 400-475 nm and below 400 nm were generated with an OPerA Solo optical parametric amplifier (OPA) from Coherent Inc. (Santa Clara, CA). The 800 nm pump beam was focused on the sample from either the back (n-p junction) side or the front (TMO) side, depending on the particular experiment, while the probe beam was focused on the sample from the front, as shown in Fig. 3.1. The reflected 400 nm probe beam was collected on a Si photodiode and recorded with a lock-in amplifier. Probe wavelengths between 400-475 nm and below 400 nm were collected with a charge-coupled device (CCD) from Ultrafast Systems (Sarasota, FL). Changes in reflectivity ( $\Delta R/R$ ) were monitored by

delaying the probe pulse in time with respect to the pump pulse using an optical delay stage. The pump beam was mechanically chopped at 300 Hz when using lock-in detection.

10-80 nm  $\text{Co}_3\text{O}_4$  and 15 nm  $\text{IrO}_2$  were grown on top of the np-GaAs device by either physical vapor deposition (PVD) or atomic layer deposition (ALD).  $\text{Co}_3\text{O}_4$  and  $\text{IrO}_2$  were deposited by RF reactive sputtering using a 3 inch Co and Ir target, respectively.  $\text{Co}_3\text{O}_4$ deposition used a power of 200 W, a 9:1 ratio of  $\text{Ar:O}_2$  at a total pressure of 5 mTorr, and a substrate temperature of 500 °C.  $\text{IrO}_2$  deposition used a power of 75 W, a 3:2 ratio of  $\text{Ar:O}_2$  at a total working pressure of 5 mTorr, and a substrate temperature of 300° C. ALD-deposited  $\text{Co}_3\text{O}_4$  was deposited in an Oxford FLexAl system at either 300° C or 100 °C from a  $\text{CoCp}_2$ precursor with oxygen plasma as the oxidant. PVD samples were sonicated in acetone and isopropanol prior to deposition, and ALD samples were subject to a 2-minute buffered HF etch prior to deposition to remove the native oxide of the material. ALD deposition was conducted by Dr. Jinhui Yang of the Joint Center for Artificial Photosynthesis.

The etching procedure used to prepare samples for spectroscopy is depicted in Figure 3.3. Kapton (polyimide) tape is used to cover the back side and about 80% of the front side of the sample for front side etching to the InGaP layer. The sample is immersed in a "Piranha" solution consisting of a volumetric ratio of 5:1:1 of  $H_2SO_4:H_2O_2:H_2O$ . Preparation of the Piranha solution releases large amounts of heat and requires protective gloves, a chemical apron, and a face shield. The solution must be disposed of properly and carefully after etching. Upon removal from the etch solution, the samples are rinsed and the tape is removed to reveal a shelf on the sample that reaches to the InGaP layer. Contact profilometry measurements confirm that distance from the top of the sample to the InGaP level is  $\approx 900$  nm. With the shelf present, thin film deposition, if necessary, may occur as described in the last paragraph. In order to expose the np-GaAs junction from the back side, the semi-insulating GaAs substrate is selectively removed down to the InGaP layer by wet etching with a 4.2 M solution of citric acid mixed with 30% hydrogen peroxide in a 5:1 volume ratio. The n-p junction is protected from the etch solution by adhering a silicon wafer with Crystalbond 509 adhesive, and an etch mask is formed with Kapton tape around all but the area to be etched. The etch proceeds at a rate of  $\sim 10$  microns per hour at room temperature. This etch, while slower than the Piranha etch, requires far fewer safety precautions and the Kapton mask can protect the sample from the solution much more effectively. After removing the sample from the etching solution and rinsing with water, the Kapton tape is removed. The protectant silicon wafer is removed by heating the sample on a hot plate to  $\approx 110^{\circ}$  C to melt the Crystalbond 509, then carefully sliding the sample off of the silicon. The remaining adhesive is dissolved by immersing the sample in acetone for a few minutes. Nitrogen is used to dry the sample. Each of the steps after the citric acid etch must be done gently, as the InGaP/n/p-GaAs window is only about one micron thick. Touching the window with tweezers, dropping the sample, or even blowing on the sample too hard with the nitrogen source can cause the sample window to break. A successful etch can be verified by holding the sample up to a light source. The etched window depth of about one micron represents approximately one penetration depth of light in GaAs, so the light will be visible but attenuated through the window, while no light will transmit through the unetched area around

the window.



Figure 3.3: Schematic of etching procedure used to prepare samples for spectroscopy. Beginning with an np-GaAs sample, (a) Kapton tape is used to mask the back side and  $\approx 80\%$ of the front side of the sample. (b) A  $\approx 60$  second dip in Piranha solution (described in text) removes the n- and p-GaAs layers, leaving the InGaP exposed from the front for contacting. (c) Thin film deposition occurs if necessary. (d) The topside of the sample is protected with a silicon wafer, and the whole assembly is masked with Kapton tape, leaving a small area to be etched on the back side. (e) Etching in citric acid solution (described in text), removal of the tape and silicon, and washing in acetone produces the final sample.

A suggestion for future researchers would be to consider eliminating the Piranha etching step entirely, instead etching both the front and back side with the citric acid etch. While this etch will proceed more slowly, it should still finish within 6 minutes given an etch rate of about 10 microns per hour, without the protective measures and caustic chemicals needed for the Piranha etch. A good resource for GaAs etching techniques is Ralph Williams' *Modern GaAs Processing Methods*, cited here. [72] A further suggestion would be to eliminate Kapton tape as the masking medium for the citric acid etch. While functional, the Kapton tape application is time-intensive and occasionally ineffective, as etching solution leaks under the Kapton tape and partially dissolves the GaAs or overlayer film. This could be avoided by designing a reusable etching cell made of Teflon that uses chemically resistant O-rings to restrict the etchant to just the desired areas of the sample. A prototype design for a Teflon cell designed to etch a single sample is depicted in Figure 3.4. The design could easily be scaled up to allow for the etching of many samples at one time.

#### **3.2.3** Device current properties

Current-voltage (IV) measurements were used to quantify the amount of charge reaching each end of the GaAs device and verify that holes are being driven towards the p-GaAs/air



Figure 3.4: Prototype design of a Teflon cell for etching the GaAs samples. Two Teflon slabs of 5 mm thickness are used to sandwich an O-ring to isolate the sample chamber from the etchant. A second set of O-rings is used to isolate just the portion of the sample that requires etching. Screws at the corners clamp the large O-ring, and a drilled hole in the center of the top Teflon slab allows etchant access to the sample.



Figure 3.5: (a) Current-voltage curves are measured with a Keithley 2400 SourceMeter connected to the sample with a Ga-In eutectic contact on InGaP and a silver paste contact on TMO overlayer (b) illuminated data shows increase in current in reverse bias region (negative voltages). (c) photocurrent is calculated by subtracting dark current from illuminated current. Photocurrent density is calculated by dividing photocurrent by the area of the illuminated spot.

interface. Figure 3.5a shows a schematic of the IV testing setup. A voltage was applied with a Keithley 2400 SourceMeter and current was measured by connecting leads to the exposed InGaP layer with Ga-In eutectic and to the TMO layer with silver paste, or to p-GaAs with a sputtered gold film in samples with no TMO layer. These contacts were selected due to their ohmic current properties. The InGaP layer was dipped in 20% ammonium hydroxide prior to contact application to remove the native oxide layer of the InGaP. Illumination during measurements was applied from the front or the back of the device as defined in Figure 3.5a. Figure 3.5b displays example IV curves in the dark (blue) and under 5.4 mJ cm<sup>-2</sup> fs laser illumination. Current follows a diode-like shape, deviating at larger negative voltages due to bulk-defect-state-mediated charger carrier creation that grows larger with increasing reverse bias. [51] Photocurrent (Figure 3.5c) is calculated by subtracting current in the dark from current under illumination. Typical photocurrent levels for the np-GaAs junctions are in the single  $\mu A$ . Photocurrent density is calculated by dividing the photocurrent by the area of the illuminated spot, giving values of a few mA  $\rm cm^{-2}$ . Samples were found to be more sensitive to illumination power rather than illumination power density, making comparison of photocurrent density values only possible if similar illumination spot sizes were used. In this thesis, femtosecond laser results used similar spot sizes and are reported as photocurrent density. Diode laser results, however, sometimes used different illumination spot sizes. In the cases where different illumination spot sizes were used, photocurrent is reported rather than photocurrent density.

Figure 3.6 displays IV curves for np-GaAs and npp<sup>+</sup> GaAs samples. Each lettered graph denotes a different sample with (a) np-GaAs with no TMO overlayer, (b) np-GaAs with 20 nm  $Co_3O_4$  overlayer, (c) and (d) np-GaAs with 80 nm  $Co_3O_4$ , and (e) npp<sup>+</sup> GaAs with 80 nm  $Co_3O_4$  overlayer, with IV data from illumination with 120 fs 800 nm laser illumination (top plot) and continuous wave (CW) diode illumination at 808 nm (bottom plot). Data is presented for back side (black) and front side (red) illumination at low (dotted) and high (solid) power or fluence levels. A number of trends can be seen in the data:

- 1. Each sample displays a diode-like turn-on at a voltage of 0.5 V.
- 2. CW diode illumination produces smooth I-V curves in all cases. The fs pulsed illumination shows greater noise in all cases, despite using the same contacts on the same sample. A magnifier for this noise is the absence of a TMO overlayer.
- 3. The pulsed femtosecond illumination shows higher current density when using front illumination rather than back illumination in all cases. The current levels in the CW diode illumination does not have a definitive geometry preference.
- 4. The npp<sup>+</sup> GaAs sample yields greater current levels than the np-GaAs samples under femtosecond illumination.

Item 1 above stems from using the same master sample of high-quality epitaxial junctions for all devices tested. The uniformity of the GaAs junction regardless of type of TMO



Figure 3.6: Current-voltage curves for np-GaAs and npp<sup>+</sup> GaAs samples in the pump front (red) and pump back (black) geometries. The top graph in each pair shows 800 nm fs laser photocurrent density at 0.4 mJ cm<sup>-2</sup> (dotted) and 5.4 mJ cm<sup>-2</sup> (solid), and the bottom graph in each pair shows 808 nm continuous wave diode laser illumination photocurrent at 20 mW cm<sup>-2</sup> (dotted) and 200 mW cm<sup>-2</sup> (solid). (a) np-GaAs without TMO overlayer, (b) np-GaAs with 20 nm sputtered Co<sub>3</sub>O<sub>4</sub> overlayer, (c) and (d) np-GaAs with 80 nm sputtered Co<sub>3</sub>O<sub>4</sub> overlayer.

layer assures that current-voltage data will be comparable across multiple samples, since the photocurrent originates in the GaAs junction. Small changes between similar samples, such as the slightly different current levels observed between samples with 80 nm PVD  $Co_3O_4$  (Figure 3.6c and d), are thus not due to differences in the GaAs junction, but rather due to contact issues or slight differences in the interface between GaAs and TMO, which can impede current flow.

Item 2 is postulated to be a product of the pulsed nature of the femtosecond illumination. Integrated over a full second, the pulsed femtosecond illumination deposits  $5.4 \text{ W cm}^{-2}$  onto the sample, far higher than the  $0.2 \text{ W cm}^{-2}$  highest level for the diode illumination. This level of illumination delivered in short bursts jolts the system out of equilibrium every time a pulse is delivered and can negatively affect the rectification of current both from the GaAs to the contacts and from the contacts into the leads of the measurement device. This line of reasoning is supported by noting that the greatest noise occurs for femtosecond illumination of the sample with no TMO layer deposited (Figure 3.6a). This sample used a  $\approx 100$  nm sputtered gold contact on the p-GaAs, making contact with the measurement device only at the needle tip. In contrast, other samples used silver paste as a contact, which is amorphous, has a thickness on the order of microns, and can better envelop the measurement probe. Any lattice perturbation or electric field changes due to charge carrier influx at the GaAs/Au or Au/probe interfaces could result in momentary disturbances to charge flow. Note that the noise of large magnitude seen in Figure 3.6a is only present at the highest power levels and with femtosecond illumination and is not present in other samples at the highest power levels, proving the issue to be with the combination of gold contacts, high power, and pulsed illumination. Other samples also experience noise of a smaller magnitude with femtosecond illumination and high power (notably Figure 3.6e), but the magnitude is significantly lower due to the use of silver paste as a contact to the TMO.

Item 3 suggests that illumination in closest proximity to the p-GaAs (front side) contact results in higher photocurrent. Upon illumination, charge carriers must make their way to the contact to be measured. Due to the band bending in the device (Figures 3.1 and 3.2), holes are driven to the p-GaAs or TMO contact and electrons to the Ga-In contact on the InGaP. Illumination in the back creates most charge carriers far from the p-GaAs contact, forcing photoelectrons to move a short distance to be collected and photoholes to move a long distance to be collected. Illumination in the front yields the opposite situation, with photoholes needing to move a shorter distance than photoelectrons. The lower photocurrent in back illumination may reveal that photohole transport and collection at the contact is the limiting process in the device. Holes in GaAs have a mobility and diffusion constant over 20 times smaller than electrons, and photoholes deposited primarily near the back side of the device would need to traverse the length of the device before collection, a process calculated to take about 10 ps (section 3.2.1). [51] Transient absorption measurements using back side illumination (detailed below in figure 3.13) note approximately a 50% decrease in signal 10 ps after photoexcitation, suggesting that recombination of photoholes could significantly decrease photocurrent by the time the holes arrive at the contact. A definitive conclusion is not provable without a systematic study of the photocurrent in devices with variable junction

length and variable doping.

Lastly, item 4 is a result of the altered band bending at the front end of the device. With a strongly doped p-GaAs capping layer, the bands of the device will bend sharply upwards, driving holes to the collection point. The  $p^+$  GaAs is not thin enough to serve effectively as a tunnel junction, suggesting that the increased current stems directly from the larger band bending (and consequent increased electric field). This serves as further evidence that photoholes, rather than photoelectrons, determine the current properties of the junction, since the increase in upward band-bending at the interface will affect hole transport and impede electron transport to the silver paste contact. A systematic study involving GaAs capping layers of variable thickness and variable doping level would be needed to definitively prove the mechanism of the higher current in the npp<sup>+</sup> devices.



Figure 3.7: (left-axis) Open-circuit photocurrent versus excitation wavelength for np-GaAs samples with no  $\text{Co}_3\text{O}_4$  (red squares) and 20 nm  $\text{Co}_3\text{O}_4$  (red triangles) overlayer, and npp<sup>+</sup> GaAs with 80 nm  $\text{Co}_3\text{O}_4$  (red circles) overlayer, obtained with monochromated Xe lamp excitation. (right-axis) Penetration depth of light through GaAs and  $\text{Co}_3\text{O}_4$ .

The photocurrent properties were further tested at a power of 20  $\mu$ W by varying the wavelength of excitation with an incoherent broadband xenon lamp and monochromator. Figure 3.7 displays front illumination photocurrent (red traces, left axis) for np-GaAs samples with 80 nm Co<sub>3</sub>O<sub>4</sub> (circles) and 20 nm Co<sub>3</sub>O<sub>4</sub> (triangles) and npp<sup>+</sup> GaAs with no TMO overlayer (squares). Also shown (blue traces, right axis) are the penetration depth of light in GaAs (solid) and Co<sub>3</sub>O<sub>4</sub> (dotted). Beginning with longer wavelengths, a steep drop-off in photocurrent is noted at the bandgap of GaAs (885 nm), reflecting the origin of the photocurrent in the np-GaAs diode. The sample with no TMO overlayer has a decrease in photocurrent that closely follows the decrease in the penetration depth of the light. The

other two samples with TMO overlayers see similar decreases in the photocurrent of light as wavelength decreases, but with an added depression due to the TMO overlayer blocking a certain portion of light from reaching the GaAs junction. The influence of the TMO overlayer becomes progressively greater with larger thickness. This can be seen by comparing the penetration depth of light in the  $Co_3O_4$  with the photocurrent data for the 80 nm  $Co_3O_4$  sample. Both the photocurrent and the penetration depth plateau in the 600-800 nm region. The TMO overlayer is thus blocking light from reaching GaAs region in which the photocurrent is produced. As the  $Co_3O_4$  becomes more transmissive in higher wavelength regions, more light reaches the GaAs, producing more photocurrent.

The photocurrent response at longer wavelengths was tested by illuminating the sample from the front with 150 fs pulsed output from an OPA. Figure 3.8 displays photocurrent measured on the same sample of npp<sup>+</sup> GaAs with 80 nm Co<sub>3</sub>O<sub>4</sub> used in Figure 3.7 (red) as well as a sample of npp<sup>+</sup> GaAs with no TMO overlayer (blue). Although the photocurrent does drop off at a wavelength value corresponding to the bandgap, there is still appreciable photocurrent at infrared wavelengths. This photocurrent persists until 1800 nm, where it decreases to near zero for the sample with no TMO overlayer and 0.2  $\mu$ A for the sample with 80 nm Co<sub>3</sub>O<sub>4</sub> overlayer (inset of Figure 3.8). While both samples display the same trends in photocurrent decrease, the photocurrent value from the sample with 80 nm Co<sub>3</sub>O<sub>4</sub> is about 0.05  $\mu$ A higher in the wavelength range of 1200-1600 nm, but is 0.2  $\mu$ A higher in the wavelength range of 1800-2000 nm. The increased value of photocurrent in the film with the 80 nm Co<sub>3</sub>O<sub>4</sub> corresponds roughly to the d-d band absorption region of Co<sub>3</sub>O<sub>4</sub>. [73]



Figure 3.8: Photocurrent versus excitation wavelength for npp<sup>+</sup> GaAs samples with no  $Co_3O_4$  (blue) and 20 nm  $Co_3O_4$  (red) overlayer, obtained with 150 fs pulsed OPA output. Inset: zoom on wavelength region from 1200 to 2000 nm (left). Absorbance of a 10 nm  $Co_3O_4$  thin film on glass (right).

The importance of the particular illumination geometry was considered by comparing front illumination, back illumination, and a combination of front and back illumination with a 120 fs laser source on both np-GaAs and npp<sup>+</sup> GaAs samples (Figure 3.9). Back illumination at 0.4 mJ cm<sup>-2</sup> produces far less current than front illumination at the same fluence level, as was also seen in Figure 3.6 for the fs laser illuminated samples. However, illuminating both back and front sides with 0.4 mJ cm<sup>-2</sup> simultaneously does not produce more current than illuminating the front side alone. Current in the GaAs device thus reaches a saturation level that can be accessed at lower fluence levels when illuminating from the front of the device.



Figure 3.9: Photocurrent density of (a) np-GaAs with 80 nm  $\text{Co}_3\text{O}_4$  overlayer and (b) npp<sup>+</sup> GaAs with 80 nm  $\text{Co}_3\text{O}_4$  overlayer, illuminated at 0.4 mJ cm<sup>-2</sup> with 800 nm 150 fs pulsed laser illumination from the back (black), front (red), or both front and back (blue).

A thin film of  $\text{Co}_3\text{O}_4$  on glass does not generate photocurrent under any illumination method. The  $\text{Co}_3\text{O}_4$  TMO overlayer would thus not be expected to contribute to the photocurrent of the overall device, and there should be no dependence of the device photocurrent on the thickness of the film. Plotting the level of photocurrent for np-GaAs samples with varying levels of TMO thickness (from Figure 3.6a, b, c, and d) reveals that every combination of front and back side illumination and low (0.4 mJ cm<sup>-2</sup>) and high (5.4 mJ cm<sup>-2</sup>) power indeed displays no dependence of photocurrent on  $\text{Co}_3\text{O}_4$  thickness except in the case of high power and front side illumination, which shows a linear increase in the absolute value of photocurrent density at a rate of 11  $\mu$ A cm<sup>-2</sup> per nm of TMO film (Figure 3.10). Coupled with the higher photocurrent seen near the d-d band absorption region of the TMO in the xenon lamp spectra (Figure 3.8), this suggests that the TMO overlayer may be providing a boost to the device photocurrent via the d-states of the Co<sub>3</sub>O<sub>4</sub> film. However, the magnitude of the d-d state photocurrent boost in Figure 3.8 is small, and the increase in photocurrent

with TMO thickness is not reliably reproduced when illuminating with a continuous wave diode source (bottom plots of Figure 3.6). In addition, xenon lamp illumination shows the TMO film simply blocking light from reaching the GaAs rather than contributing its own current (Figure 3.7). Reproduction of the boost with high power femtosecond illumination would require measuring the photocurrent on a much larger, statistically significant number of samples with systematically varied TMO layer thickness. If a reproducible dependence of photocurrent on TMO thickness emerges for samples illuminated from the front, but not the back, then it can be stated that the TMO layer is contributing photocurrent to the overall device. With the data presented here, however, the effect is unproven and of a negligible magnitude.



Figure 3.10: Photocurrent density of np-GaAs samples with varying thicknesses of  $Co_3O_4$  overlayer for low (triangles) and high (circles) power and front (red) and back (black) illumination with a 150 fs laser. Linear lines are fits to the data for low power (dotted) and high power (solid) data.

#### 3.2.4 Device Quantum Efficiency

The number of photocarriers reaching the TMO can be calculated with a combination of absorbed fluence calculations and current-voltage data. The absorbed fluence is calculated as the incident fluence in mJ cm<sup>-2</sup> (for femtosecond measurements) or mW cm<sup>-2</sup> (for CW diode measurements) minus the fluences reflected from the surface for pump front and pump back geometries, absorbed by the TMO (for pump front geometry), and transmitted through the bulk of the device,

$$I_{abs} = (1 - R)(1 - A)(I_{inc} * (1 - 10^{-\alpha \ell}))$$
(3.6)

where R is the reflection coefficient, A is the calculated absorbance of the TMO layer,  $I_{inc}$  is the measured incident fluence,  $\alpha$  is the absorption coefficient of GaAs (13445 cm<sup>-1</sup>) [74],

and  $\ell$  is the device length (910 nm). This is converted to the density of absorbed photons within the excitation volume per second by dividing by the energy per photon (mJ) and the length of the device (cm) and multiplying by the repetition rate of the laser for femtosecond measurements to obtain a value with units of cm<sup>-3</sup> s<sup>-1</sup>:

$$P_{abs} = K * \frac{I_{abs}}{\ell} * \frac{\lambda}{hc}$$
(3.7)

where  $\lambda$ , h, and c, are the photon wavelength, Planck constant, and speed of light, respectively, and K is the repetition rate of the laser (1000 s<sup>-1</sup>) and is only included for pulsed measurements. The calculated variance in the density of absorbed photons for pulsed experiments, considering different reflectivity and absorbance values for front (in color) and back (in black) side illumination, is displayed in Figure 3.11.



Figure 3.11: Calculated absorbed photon density per pulse  $(cm^{-3})$  versus incident laser fluence  $(mJ cm^{-2})$  for pump front (in color) and pump back geometries (black) for all TMO types used in this study.

The quantum efficiency, or rate at which photons are converted to electrons and holes, can be determined by comparing the number of absorbed photons with photocurrent data for the GaAs junctions. The QE of the GaAs device is estimated here from np-GaAs with a 20 nm Co<sub>3</sub>O<sub>4</sub> overlayer (Figure 3.6b). The photocarrier density per second  $H_{photo}$  (cm<sup>-3</sup> s<sup>-1</sup>) is calculated from the photocurrent density  $A_{photo}$  (mA cm<sup>-2</sup>) in the negative bias region of Figure 3.6b, at -1.5 V, by

$$H_{photo} = \frac{A_{photo}}{\ell * q} \tag{3.8}$$

where q is the fundamental charge. The QE for the device can then be calculated as:

$$QE = \frac{H_{photo}}{P_{abs}} * 100 \tag{3.9}$$

QE values calculated from Eq. 3.7, 3.8, and 3.9 and Figure 3.6 are listed in Table 3.1.

laser	geometry	fluence	$H_{photo}(\mathrm{cm}^{-3} \mathrm{s}^{-1})$	$P_{abs} \ (\mathrm{cm}^{-3} \ \mathrm{s}^{-1})$	QE $(\%)$
fs	back	$0.4 \text{ mJ cm}^{-2}$	$1.2 * 10^{19}$	$1.1 * 10^{22}$	0.11
fs	back	$5.4 \text{ mJ cm}^{-2}$	$5.1 * 10^{19}$	$15 * 10^{22}$	0.034
fs	front	$0.4 \text{ mJ cm}^{-2}$	$3.9 * 10^{19}$	$1.0 * 10^{22}$	0.36
fs	front	$5.4 \text{ mJ cm}^{-2}$	$19 * 10^{19}$	$15*10^{22}$	0.13
diode	back	$20 \text{ mW cm}^{-2}$	$19 * 10^{19}$	$5.6 * 10^{20}$	33
diode	back	$200 \text{ mW cm}^{-2}$	$99 * 10^{19}$	$56 * 10^{20}$	18
diode	front	$20 \text{ mW cm}^{-2}$	$13 * 10^{19}$	$5.4 * 10^{20}$	23
diode	front	$200 \text{ mW cm}^{-2}$	$61 * 10^{19}$	$54 * 10^{20}$	11

Table 3.1: Quantum efficiencies for 20 nm  $Co_3O_4$  overlayer (from Figure 3.6b).

The ordering of quantum efficiency follows the ordering of current seen in Figure 3.6 — for femtosecond illumination, quantum efficiency is always higher in the pump front geometry. QE values are particularly high under CW diode illumination due to significantly higher current levels. Quantum efficiency decreases under higher fluence levels due to saturation of the absorptivity of the GaAs diode, as seen in Figure 3.9.

#### 3.2.5 Fitting and FFT adjustment procedure

Transient reflectivity spectra were fit to a linear combination of exponential decays and exponentially damped oscillatory components as follows:

$$fit = \sum_{1}^{n} A_{n} \exp\left(\frac{\sigma^{2}}{2\tau_{n}^{2}} - \frac{t}{\tau_{n}}\right) \operatorname{erfc}\left(\frac{\sigma^{2} - \tau_{n}t}{\sqrt{2}\sigma\tau_{n}}\right) + \sum_{1}^{m} A_{m} \exp\left(\frac{\sigma^{2}}{2\tau_{m}^{2}} - \frac{t}{\tau_{m}}\right) \operatorname{erfc}\left(\frac{\sigma^{2} - \tau_{m}t}{\sqrt{2}\sigma\tau_{m}}\right) \sin(k_{m}t + \phi_{m}) \quad (3.10)$$

where  $A, \tau, \sigma, k$ , and  $\phi$  are fitting parameters and t is time delay. The linear combination fit can be separated into its exponential decay (the first part of equation 3.10) and oscillatory (the second part of equation 3.10) components to isolate just the oscillatory part of the raw data. Figure 3.12a shows the raw data (black), the exponential component of the fit from equation 3.10 (red dotted), and the raw data minus the exponential fit, producing the oscillatory portion of the raw data (blue).



Figure 3.12: An explanation of the procedure used to generate FFT spectra. (a) Representative data of np-GaAs with  $IrO_2$  overlayer at 3.6 mJ cm<sup>-2</sup> (black), a linear combination of exponential decay functions as described in the text (dotted red), and the raw data minus the exponential fit (blue) to obtain just the damped oscillatory component of the raw data.

The effect of the oscillatory component extraction is shown in Figure 3.12b for np-GaAs with  $IrO_2$  overlayer at 3.6 mJ cm<sup>-2</sup> pump fluence, for pump back (black) and pump front (red) geometries. The left-most graph shows the FFT of the raw data. A noticeable background exists due to the exponential decay component of the transient reflectivity. The middle graph shows the FFT spectra for the extracted oscillatory component of the raw data. This isolates the frequencies of the oscillation without the background from the exponential decay component of the data. FFT spectra were then adjusted via Fresnel's equations to account for pump reflection losses at each interface (TMO/air, TMO/GaAs, InGaP/air, GaAs/InGaP) for pump front and pump back geometries as well as absorption of light by the TMO layer for pump front geometries (right-most graph of Figure 3.12b). The fraction of light reflected from a surface at normal incidence is calculated as

$$\mathbf{R} = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2 \tag{3.11}$$

where  $n_x$  denotes the refractive index of medium x. Pump front geometry calculations incorporate absorption of light by the TMO as  $A = 1 - e^{-d/m}$ , where d is the thickness of the TMO layer and m is the penetration depth of the pump light in the TMO layer, calculated

as  $m = \frac{\lambda}{4\pi k}$ , where  $\lambda$  is the pump wavelength and k is the imaginary component of the refractive index. Transmission calculated for pump front geometries considers reflection at the air/TMO and TMO/GaAs interfaces as well as absorption in the TMO film, as  $\%T = (1 - R_1)(1 - R_2)(1 - A) * 100$ . The calculations for pump back geometries consider reflection at the air/InGaP and InGaP/GaAs interfaces as  $\%T = (1 - R_1)(1 - R_2) * 100$ . Absorption of pump light at 800 nm is negligible in the InGaP layer and is not considered. The final %T values for each of the TMO types and excitation geometries are shown in Table 3.2.

geometry	TMO	d (nm)	InGaP n	GaAs n	TMO n	1-A	%T
back	all		3.33	3.68			71
front	ALD $Co_3O_4$	25		3.68	2.93	0.81	54
front	$PVD Co_3O_4$	80		3.68	2.93	0.50	33
front	$IrO_2$	15		3.68	1.70	0.64	52

Table 3.2: Light Transmitted to GaAs junction. [74–77]

Refractive index values were obtained from the references cited in the caption of Table 3.2 or, in the case of  $\text{Co}_3\text{O}_4$ , via experimental ellipsometry data for PVD  $\text{Co}_3\text{O}_4$  on glass. Fourier transform spectra were then adjusted to account for reflection losses so that all spectra are normalized to the same absorbed fluence. FFT spectra of transient reflectivity traces obtained with pump fluence values below 3.6 mJ cm<sup>-2</sup> were also adjusted to normalize for the varied pump fluences. The total adjustment equation used is

Adjusted FFT = 
$$\frac{\text{original FFT}}{\frac{\%T}{100} * \frac{\text{fluence used}}{3.6 \text{ mJ cm}^{-2}}}$$
 (3.12)

This procedure produces the right-most FFT spectra displayed in Figure 3.12b as well as all the FFT spectra reported in this chapter.

#### 3.3 Spectroscopic Results

In the following sections, spectroscopic results are described as using the "pump back" and "pump front" geometries. The former describes results with a pump beam incident on the back side of the device, and the latter results with a pump beam incident on the front side of the device, as defined in the first paragraph of section 3.2. All results use a pump beam with a wavelength of 800 nm. All data is collected with a probe beam incident on the front side of the device in reflectance.

#### 3.3.1 800 nm probe

Transient reflectivity spectra were first obtained by pumping through the back of the device with  $\lambda_{pump} = 800$  nm and probing in reflectance geometry from the front with  $\lambda_{probe} = 800$  nm. A full fluence dependence was conducted on all samples and is displayed in Figure 3.13: 3.13a and b display data from np-GaAs with no TMO overlayer, 3.13c and d data from np-GaAs with IrO<sub>2</sub> overlayer, 3.13e and f data from np-GaAs with 10 nm sputtered Co<sub>3</sub>O<sub>4</sub> overlayer, and 3.13g and h data from np-GaAs with 25 nm ALD Co<sub>3</sub>O<sub>4</sub> deposited at 300° C. The first plot in each pair displays the first 50 ps of the transient trace unnormalized, and the second plot of data shows the full time extent of the transient data with all fluence levels normalized to one value. Different fluence values in mJ cm<sup>-2</sup> are denoted by color in the plots; fluences noted in the first plot in a pair are valid for both plots.

Beginning with Figure 3.13a and b, it is noted that the decay of transient signal displays a transient absorption with a complex decay that relaxes back to equibrium in less than 100 ps. While the full decay is completed by 100 ps for all fluence levels, higher fluence levels display faster initial kinetics and a shoulder in the 5-15 ps time region changes from being a broad bump at the lowest fluence levels to a small shoulder at the highest fluence levels. The complex decay of signal shown for this sample suggests that pumping and probing at 800 nm detects photo-excited charge from all regions of the device. As charge flows through the n-p junction, holes flowing towards the probed region become more visible, while electrons flowing away from the probed region become less visible, resulting in a complex signal that undulates with the changing concentration of charge carriers being probed. Understanding the precise origin of the shoulder seen in the intermediate time region would require a more careful study of samples with varied doping and varied junction lengths to determine which photocarriers contribute to the signal and the importance of the magnitude of the junction electric field.

Depositing an overlayer on the np-GaAs sample changes the signal dramatically. Samples with IrO<sub>2</sub> overlayer (Figure 3.13c and d) still show decays that are non-monoexponential at all fluences. Signal decay becomes faster with fluence in the time region between 5-15 ps, and a small oscillation in signal is seen in the highest fluence data, foreshadowing results with  $\lambda_{probe} = 400$  nm described below. Samples with 10 nm sputtered Co<sub>3</sub>O<sub>4</sub> overlayer (Figure 3.13e and f) display a signal sign flip in the first 10 ps as fluence is raised. This build-in of positive signal matches the signal of the np-GaAs from Figure 3.13a and b and originates from the large number of photo-excited carriers drifting into the probing region under the impulse of the np-GaAs junction electric field. After 10 ps, the signal originating from the np-GaAs has relaxed, and signal at all fluence values returns to the same decay kinetics. Samples with  $IO_2$  overlayer, display the opposite trend with fluence – as fluence levels rise, kinetics become slower in the sub-20 ps time regime. However, the same faint oscillation becomes apparent at higher fluences.

Taken in full, the transient spectra with  $\lambda_{pump} = \lambda_{probe} = 800$  nm reveal the importance of the thickness and composition of the TMO layer. The thickest film (300° C 25 nm ALD



time delay (ps)

Figure 3.13: Pump-probe reflectivity spectra of np-GaAs (pumped from the back and probed from the front with  $\lambda_{pump} = \lambda_{probe} = 800$  nm) with (a and b) no TMO, (c and d) 4 nm Ir + 15 nm IrO<sub>2</sub>, (e and f) 10 nm sputtered Co<sub>3</sub>O<sub>4</sub>, and (g and h) 25 nm 300° C ALD Co<sub>3</sub>O<sub>4</sub> overlayers, displayed with unnormalized data (left column) against linear time delay and normalized data (right column) against time delay on a log scale. Pump fluence (mJ cm<sup>-2</sup>) for each row pair is noted in the figure.

 $Co_3O_4$ ) shows kinetics that are the most detached from the kinetics of the bare np-GaAs substrate, showing faster overall decay as well as showing the opposite trend with fluence. The thinnest film, on the other hand, shows kinetics that begin to map onto the kinetics of the np-GaAs substrate at higher pump fluence values. Each TMO film has characteristic differences from the others, allowing for identification of the TMO film based on the shape of the kinetic spectrum.



Figure 3.14: Pump-probe reflectivity spectra of np-GaAs (pumped from the back and probed from the front with  $\lambda_{pump} = \lambda_{probe} = 800$  nm) for two sets of purportedly identical samples with (a) 10 nm sputtered Co<sub>3</sub>O<sub>4</sub> and (b) 300° C ALD Co<sub>3</sub>O<sub>4</sub> overlayer. Solid lines: sample 1. Dotted lines: sample 2. Colors denote pump fluence levels.

Samples probed with 800 nm light, however, suffer from irreproducible spectra when data from multiple identical samples are compared. Figure 3.14 displays normalized transient reflectivity spectra for two purportedly identical samples of np-GaAs with 10 nm sputtered  $Co_3O_4$  overlayer (left) and two purportedly identical samples with 25 nm 300° C ALD  $Co_3O_4$ overlayer (right). At the same fluence, the two samples show very different kinetic shapes for both overlayer types. This suggest that results obtained with  $\lambda_{probe} = 800$  nm are both extremely sensitive to differences in fluence and spatially inhomogeneous even when the samples originated from the same TMO deposition. The etched area of the sample (the area pumped and probed), due to its  $\approx 1 \ \mu$ m thickness, mechanically buckles into a bulged shape that protrudes out from the plane of the sample surface. Depending on the area of the etched spot, the bulge out of plane will be different for each sample, resulting in a slightly different environment across samples subject to identical TMO depositions. A deeply penetrating probe beam will sample all of these inhomogeneities, resulting in inconsistent results across samples.

#### 3.3.2 400 nm probe

Transient reflectivity spectra were also obtained with  $\lambda_{probe} = 400$  nm in an attempt to avoid the reproducibility issues shown in Figure 3.14. The probe penetration depth at



Figure 3.15: Transient reflectivity for np-GaAs device pumped in the back at 800 nm with a fluence of 3.6 mJ cm<sup>-2</sup> (a) without TMO overlayer probed at 800 nm, (b) without TMO overlayer probed at 400 nm, (c) with 15 nm IrO<sub>2</sub> overlayer probed at 800 nm, and (d) with 15 nm IrO<sub>2</sub> overlayer probed at 400 nm.

400 nm in all TMO types considered in this study, calculated as  $\frac{\lambda}{4\pi n}$ , where *n* is the refractive index of the TMO, is under 15 nm, limiting the sampling depth to the TMO and TMO/GaAs region. [77] Figure 3.15 displays the effects of changing from an 800 nm probe to a 400 nm probe for both a bare np-GaAs substrate and an np-GaAs substrate with IrO<sub>2</sub> overlayer. Probing the np-GaAs junction without a TMO overlayer and deeply-penetrating 800 nm light results in an exponentially decaying signal that is attributable to recombination of photogenerated electron-hole pairs in the bulk GaAs junction (Fig. 3.15a). Switching the probe wavelength to 400 nm light (Fig. 3.15b), where the penetration depth in GaAs is reduced compared to 800 nm light, results in a signal that is much more surface sensitive. [74, 76] The

surface sensitivity is evidenced by the significantly lower signal of a smaller probed crosssection and a 7 ps exponential rise, which is also the transit time of holes for either drift or diffusion through the GaAs cell (see section 3.2.1). Signal from the GaAs junction with a TMO overlayer also shows the exponential decay of bulk charge carriers when probing with 800 nm light (Fig. 3.15c). However, with the TMO present (here, IrO<sub>2</sub>) and when probing with 400 nm light, large oscillations (typical magnitude ~  $\Delta R/R = 10^{-3}$ ) appear (Fig. 3.15d). The oscillatory component of the transient reflectance is larger by at least an order of magnitude than that induced by photo-generated strain waves in GaAs. [71, 78, 79] Previous experiments have shown that simply photo-exciting the TMO without the underlying p-GaAs/TMO interface does not generate coherent oscillations. [73]

The full fluence-dependent transient reflectivity kinetics are shown in Figure 3.16. All spectra shown in Figure 3.16 use the pump back geometry and a probe wavelength of 400 nm. In analogy to Figure 3.13, spectra are shown in pairs, with the left plot displaying earlytime-delay kinetics in an unnormalized plot and the right plot showing the full time kinetics normalized to one value. Spectra are shown for np-GaAs with no TMO overlayer (Figure 3.16a and b), 15 nm  $IrO_2$  overlayer (c and d), 10 nm sputtered  $Co_3O_4$  overlayer (e and f), and 25 nm 300° C ALD  $Co_3O_4$  overlayer (g and h). Like in Figure 3.13, the various TMO overlayer types display characteristic kinetic spectra. However, the spectra obtained with  $\lambda_{probe} = 400$  nm show no problems of irreproducibility and have the distinctive feature of characteristic oscillation magnitudes and frequencies. An increase in fluence has no effect on oscillation frequency but causes an increase in oscillation magnitude across all samples. While transient kinetics are unchanged by fluence for samples with  $IrO_2$  overlayer (Figure 3.16d), both cobalt-based samples show some dependence on fluence, with the 10 nm sputtered  $Co_3O_4$  sample showing a deviation only at low fluence values (Figure 3.16f) and the oscillation magnitude in the 25 nm  $300^{\circ}$  C ALD  $Co_3O_4$  sample comprising a greater fraction of the overall signal as fluence is increased (Figure 3.16h).

Since the oscillations are only present with the TMO overlayer and with a surface sensitive probe, the oscillatory component of the transient reflectance is suggested to originate from charge carriers at the p-GaAs/TMO interface. This is confirmed by the timing of reflected strain waves that propagate across the GaAs region, as shown in Figure 3.17. Strain waves propagate across the np-GaAs region by reflecting at the back (InGaP/air) interface and then returning to the probing region at the front (inset of Fig. 3.17). We refer to these recurring oscillations in the transient reflectance as echoes. A fine-resolution view of each echo is available in Figure 3.18. Notably, when pumping from the back, there are two echo types; minor echoes of smaller amplitude first appear at 215 ps, and major echoes of larger amplitude begin at 430 ps. Both echo types recur with a period of 430 ps. Pump back echoes show a high level of structure in their oscillations, particularly in the first appearance at 430 ps, with multiple peaks both positive and negative. This results from the propagation of the strain pulse through a round-trip length of the device – propagating strain pulses in GaAs have been shown to have similar dispersion when the pulse must move long distances



Figure 3.16: Pump-probe reflectivity spectra of np-GaAs (pumped from the back and probed from the front with  $\lambda_{pump} = 800$  nm and  $\lambda_{probe} = 400$  nm) with (a and b) no TMO, (c and d) 4 nm Ir + 15 nm IrO<sub>2</sub>, (e and f) 10 nm sputtered Co<sub>3</sub>O<sub>4</sub>, and (g and h) 25 nm 300° C ALD Co<sub>3</sub>O<sub>4</sub> overlayers, displayed with unnormalized data (left column) against linear time delay and normalized data (right column) against time delay on a log scale. Pump fluence (mJ cm<sup>-2</sup>) for each row pair is noted in the figure.



Figure 3.17: Transient reflectivity for np-GaAs with 25 nm 100° C Co<sub>3</sub>O<sub>4</sub> ALD overlayer in pump back (black) and pump front (red) geometries, with  $\lambda_{pump} = 800$  nm at 3.6 mJ cm<sup>-2</sup> and  $\lambda_{probe} = 400$  nm. Minor echoes begin at 215 ps in both geometries and major echoes begin at 430 ps in the pump back geometry; both types of echo repeat every 430 ps. Inset: Schematic of acoustic echo formation. Charge injection creates strain at each interface, which propagates through the device length.

before detection. [80] The propagation intervals are described by

$$T = \frac{2L}{\nu_s} \tag{3.13}$$

where L is the film thickness. Using the full length of the GaAs substrate, including InGaP layer, of L = 1010 nm and a period 430 ps,  $\nu_s$  is calculated to be  $4.7 \times 10^5$  cm s<sup>-1</sup>. This is consistent with previous studies. [81]. In order for two distinct echo types to appear in the probed region and phase delayed by half the round trip of the device, they have to be initially created at the two separate ends of the device. The minor echo arrives in the probed region at a 215 ps phase delay from the initial excitation and therefore originates from the back of the device. In the pump front geometry, the pumped volume is backed by the unetched SI-GaAs backing; the only visible echo is thus the first occurrence of the minor echo at 215 ps, which reflects off the front interface, is transmitted into the SI-GaAs layer, and does not return within the probing time window. The major echo is generated via the same charge injection at the p-GaAs/TMO interface that causes the oscillations visible in Figure 3.15d, then makes a round trip through the length of the GaAs device, reflecting from the InGaP/air interface and returning to the probing region at t = 430 ps and 430 ps intervals thereafter. The major echoes are visible across samples with diverse TMO overlayer types even when course time resolution is used. Minor echoes are small and only visible in spectra utilizing fine time resolution (Figure 3.19).



Figure 3.18: Zoom on echoes in transient reflectivity for np-GaAs with 100° C ALD overlayer for pump back (black) and pump front (red) geometries, from Figure 3.17. Major and minor echoes are displayed chronologically in the first and second row, respectively. First pump front minor echo is offset vertically for visual clarity.



Figure 3.19: Transient reflectivity for np-GaAs with TMO overlayers as noted in the legend, using the pump back geometry with  $\lambda_{pump} = 800$  nm at 3.6 mJ cm<sup>-2</sup> and  $\lambda_{probe} = 400$  nm. Major echoes appear even in samples with course time steps and recur in 415 ps intervals. IrO<sub>2</sub> spectrum is multiplied by -1; spectra are offset vertically for clarity. Dotted vertical lines denote appearance of major echoes.

Figure 3.20 shows the transient reflectivity spectra ( $\lambda_{probe} = 400 \text{ nm}$ ) for five different TMO overlayers along with corresponding fast Fourier transforms for each spectrum after subtraction of the exponentially decaying background (the subtraction procedure is detailed in section 3.2.5). Spectra obtained in the pump front and pump back geometries are displayed in red and black, respectively. The characteristic oscillations of each oxide are most prominent with back excitation. For the 15 nm  $IrO_2$  overlayer, the FFT shows a major component at 0.070 THz and a weaker component at 0.145 THz. For the sputtered 80 nm  $Co_3O_4$ overlayer, the major component is again 0.070 THz, with weaker components at 0.13 THz and at 0.18 THz. Two samples with 25 nm  $Co_3O_4$  overlayer deposited at 300° C display a singular peak that in one case matches the higher 0.145 THz frequency seen in the sample with  $IrO_2$  overlayer, but in the other case is redshifted to a value of 0.13 THz. The 25 nm  $Co_3O_4$  overlayer deposited at 100° C also only contains one peak in the FFT, but it is further redshifted to a frequency of 0.12 THz. Lastly, despite a clear oscillatory signal in the transient reflectivity, the 10 nm  $Co_3O_4$  sample yields a broad band of frequencies with little definition. With front excitation, frequencies above 0.1 THz in all overlayers are notable subdued or absent, while the magnitude of frequencies below 0.1 THz (notably in  $IrO_2$  and 80 nm  $Co_3O_4$  overlayers) are largely unaffected by the change in pump geometry. The magnitudes of the FFT spectra, whether exciting from the front or the back, have been scaled to represent a 3.6 mJ  $\rm cm^{-2}$  absorption in the GaAs junction (see section 3.2.5 for details on how the reflectivity and absorption of the TMO layer were taken into account). Table 3.3 displays a summary of all frequencies shown in Figure 3.20.

TMO	Frequencies (THz)			
IrO <sub>2</sub>	0.070	0.145		
$80 \text{ nm PVD } \text{Co}_3\text{O}_4$	0.070	0.13	0.18	
$300^{\circ}$ C ALD Co <sub>3</sub> O <sub>4</sub> sample 1		0.145		
$300^{\circ} \text{ C ALD } \text{Co}_3\text{O}_4 \text{ sample } 2$		0.13		
$100^{\circ} \text{ C ALD } \text{Co}_3\text{O}_4$		0.12		
$10 \text{ nm PVD } \text{Co}_3\text{O}_4$	indistinct			

Table 3.3: Prominent frequencies displayed in Figure 3.20

The origin of laser-induced signal oscillations in semiconductors can be traced to several physical processes, including electron/hole plasma oscillations, [82–86] optical phonons, [87, 88], optical phonon-plasma coupling, [89–91] thermoelasticity, [71] Gunn oscillations, [92] and acoustic phonons. [79, 93–106] The oscillations observed here exhibit a frequency well below the expected value for plasma oscillations [84] or optical phonons [107], and the frequency of oscillation is invariant with respect to pump fluence, further ruling out plasma oscillations or phonon-plasma coupling as the cause. Thermoelasticity mechanisms are far more prominent in metals than semiconductors, and calculations of the expected temperature rise in GaAs estimates only a few Kelvin under the fluence levels and photon energies used (section 3.2.1.2). [71, 108, 109] Gunn oscillations are precluded because the frequency of



Figure 3.20: Transient reflectivity spectra (left) with  $\lambda_{pump} = 800$  nm and  $\lambda_{probe} = 400$  nm for np-GaAs with all overlayers considered in this study (noted in the figure), with corresponding fluence-adjusted FFT spectra (right). Black: pump back. Red: pump front. Solid and dotted lines for 300° 25 nm ALD Co<sub>3</sub>O<sub>4</sub> represent spectra from two purportedly identical samples.

oscillation alters with probe wavelength (Figure 3.22 below) and Gunn diodes typically utilize highly doped n-GaAs rather than the lightly doped p-GaAs used here. Unlike electrons in n-GaAs, holes in p-GaAs do not exhibit a region of negative differential mobility, essential for Gunn oscillations. [67, 68, 110] Acoustic phonons are responsible for the signal oscillations, as the two recurring frequencies in the FFT spectra of 0.070 THz and 0.12-0.14 THz correspond to that expected for a coherent longitudinal acoustic phonon (CLAP) in TMO materials and GaAs, respectively. A CLAP induces a change in the index of refraction that travels with the sound velocity of the material, as depicted in Figure 3.21. An oscillation appears in the transient reflectivity as a result of the interference between the reflected probe beam and this refractive index change. The period of a CLAP oscillation is determined by:

$$T = \frac{\lambda_{probe}}{2\nu_s n} \tag{3.14}$$

where  $\nu_s$  and n are the sound velocity and the refractive index at the probe wavelength  $(\lambda_{probe})$ . [102, 104, 111] Using equation 3.14, the period of a CLAP in Co<sub>3</sub>O<sub>4</sub> is expected to be 13.4 ps where  $n_{400 nm}$  is 2.3 and  $\nu_s$  is  $7 \times 10^5$  cm s<sup>-1</sup>. [112–114] For IrO<sub>2</sub>, the period expected is similar at 14.3 ps, where  $n_{400 nm}$  is 2.3 and  $\nu_s$  is  $6 \times 10^5$  cm s<sup>-1</sup>. [115, 116]. On the other hand, the period expected in the GaAs layer is 9 ps, where  $n_{400 nm}$  is 4.5 and  $\nu_s$  is  $5 \times 10^5$  cm s<sup>-1</sup>. [74, 76, 81] The predicted TMO and GaAs frequencies roughly match those exhibited in Figure 3.20.



Figure 3.21: Schematic of CLAP detection at the np-GaAs/TMO interface. The incoming probe beam will reflect from the GaAs/air interface, the TMO CLAP, the GaAs/TMO interface, and the GaAs CLAP to varying degrees dependent on penetration depth of the probe beam. Movement of the CLAP waves and interference between the probe beam components results in the transient oscillations.

Figure 3.22a displays the change in observed oscillation period with probe wavelength for samples with 15 nm  $IrO_2$  and 25 nm 100° C ALD  $Co_3O_4$  overlayers along with predicted oscillation frequencies from equation 3.14. The predicted oscillation periods use literature values

for the refractive index and sound velocity of a sputtered  $IrO_2$  thin film and GaAs. [74, 76, 77, 81, 116] The oscillation period for the sample with 25 nm 100° C ALD  $Co_3O_4$  overlayer is seen to closely follow the predicted oscillation period for GaAs at all probe wavelengths. The oscillation period for the sample with  $IrO_2$  overlayer, on the other hand, displays three regions: from 700-550 nm, the oscillation period follows the predicted trend for GaAs, then from 550-425 nm, it enters a region in which the oscillation period crosses over to the predicted trend for an IrO<sub>2</sub> thin film, which it follows closely below 425 nm. Below 390 nm, the oscillatory component was a small fraction of the overall transient reflectance and a frequency could not be reliably determined. The crossover of oscillation frequency for samples with  $IrO_2$  overlayer from the GaAs predicted curve to the  $IrO_2$  predicted curve is accompanied by a change in sign in the transient reflectivity spectra, as seen in Figure 3.22c. All spectra obtained with a probe wavelength above 475 nm display a signal that is clearly negative. The signal moves in a positive direction below  $\lambda_{probe} = 475$  nm, oscillating near zero for spectra between 460-440 nm, then developing a clearly positive signal for spectra below  $\lambda_{probe} = 425$  nm. Oscillation magnitude decreases sharply below  $\lambda_{probe} = 400$  nm, disappearing completely below  $\lambda_{probe} = 485$  nm, resulting in the large frequency uncertainty seen in Figure 3.22a at  $\lambda_{probe} = 490$  nm. Oscillation periods displayed in Figure 3.22a were obtained from the results of a least-squares fit using a custom fitting function incorporating a sum of exponential decays and a single exponentially decaying sinusoidal oscillation (displayed as the black dotted lines in Figure 3.22b and c). Error bars in Figure 3.22a are derived from the standard deviation of the frequency fitting parameter. Full details of the custom fitting function are given in section 3.2.5.

The crossover of oscillation period in samples with the  $IrO_2$  overlayer can be explained by considering the penetration depth of the reflected probe light. The probe light penetrates well into the GaAs at longer wavelengths ( $\lambda = 550-700$  nm), detecting primarily the CLAP frequency associated with GaAs. At these longer wavelengths, the time scale with which the oscillation decays agrees with that expected for a traveling strain wave moving out of the probed region. As the probe penetration depth becomes shallower at shorter wavelengths, less of the GaAs region of the device is probed, causing the CLAP frequency stemming from the TMO film to become more prominent (crossover region,  $\lambda = 425-550$  nm). In the limit of a probe penetration depth that is shorter than the thickness of the TMO film, the CLAP frequency of the TMO is exclusively observed (below  $\lambda = 425$  nm). An estimate of this probe penetration depth for a thin, IrO<sub>2</sub> film on a transparent substrate is  $\lambda/4\pi n$  and is 15 nm, the thickness of the film, with  $\lambda = 425$  nm. As seen in Figure 3.22c, the crossover from the expected GaAs frequency to the expected  $IrO_2$  frequency is initiated along with a change in sign of the transient data. The deviation in the expected frequency, together with estimates of the probe penetration depth and the observed sign change, implies that the probed region markedly alters in the crossover region. While the 25 nm  $Co_3O_4$  film does not display this crossover, the thicker 80 nm  $Co_3O_4$  has its major FFT frequency at 0.070 THz, the expected frequency in the TMO for 400 nm probe light. The dependence on thickness further confirms that the probe penetration depth highlights one or the other CLAP oscillation. For a given thickness and TMO, the appearance of the CLAP in the



Figure 3.22: (a) Variation of observed oscillation period with probe wavelength for IrO<sub>2</sub> (red circles) and 100° C ALD Co<sub>3</sub>O<sub>4</sub> (blue diamonds) overlayers, pumping the front side of the device. The red and black lines are predicted oscillation periods for IrO<sub>2</sub> and GaAs, respectively, calculated as  $T = \frac{\lambda}{2\nu_s n}$ , where  $\nu_s$  is the sound velocity and n is the wavelength-dependent refractive index of the material. (b and c) Representative transient reflectivity traces for samples with (b) 100° C Co<sub>3</sub>O<sub>4</sub> ALD overlayer and (c) IrO<sub>2</sub> overlayer, pumping the front side of the device and probing with wavelength noted in the figure. Frequencies in (a) are obtained from fits (black dotted lines) to the data in (b) and (c) using a fitting function described in section 3.2.5. Error bars in the left figure are standard deviations of the frequency fitting parameter.

TMO will be determined by a combination of the probe penetration depth, the strength of the CLAP induced in the TMO, and the reflection coefficient for the sound wave at the GaAs/TMO interface. The latter dictates the number of bounces of the CLAP within the TMO layer and therefore its decay time in the transient reflectance.

#### 3.4 Mechanism

The formation of coherent acoustic phonons in semiconductors has been attributed to thermoelastic (TE), deformation potential (DP), and inverse piezoelectric effect (IPE) mechanisms. [71] As computed in section 3.2.1.2, the temperature rise in GaAs caused by the pump fluences used in this experiment is small. For pump photon energies close to the bandgap of the material, as used here, the effect of TE is negligible. [71, 108, 109] This section will thus consider the impact of the deformation potential and inverse piezoelectric effect mechanisms and discuss the likely source of the CLAP waves seen here.

Phonon generation by deformation potential occurs due to electron-hole pair creation. The transient change in charge density around the electron-hole pair causes a deformation to the semiconductor lattice and resultant phonon emission. For the case of excitation with photons near the bandgap energy, the resultant stress  $\sigma_{DP}$  can be determined as

$$\sigma_{DP} = -N(d_e + d_h) \tag{3.15}$$

where N is the density of photo-excited carriers and  $d_e$  and  $d_h$  are the deformation potentials for electrons and holes, respectively. The deformation potential in a material, given large enough values of  $d_e$  and  $d_h$ , is therefore dependent on the concentration of photogenerated electron-hole pairs. The inverse piezoelectric effect is a phenomenon in certain noncentrosymmetric materials in which a polarization in the electric field of a material causes a mechanical stress. The stress  $\sigma_{IPE}$  is coupled to the magnitude of the electric field E by the piezoelectric moduli of the material p:

$$\sigma_{IPE} = p * E \tag{3.16}$$

where p is a tensor incorporating the piezoelectric coupling constants for each crystallographic orientation of the crystal. The (100)-plane of GaAs is piezoelectrically active, making the IPE mechanism a possibility for electric fields in the device structure considered here. [117]

Acoustic oscillations in GaAs and other semiconductors have previously been reported to originate from both mechanisms, including reports of both mechanisms occuring simultaneously and reports of fluence-dependent dominance of one mechanism over the other. Young *et. al.* report DP as the mechanism in a sample of undoped SI-GaAs, notably lacking strong electric fields due to lack of doping. At a surface of p-GaAs, IPE is shown to be the dominant generation mechanism due to the ultrafast screening of the surface electric

field by photo-excited carriers. Oscillation magnitude is shown to plateau after the field has been completely screened. [79, 118] A similar study in n-GaAs, however, shows a fluencedependent hand-off between IPE and DP mechanisms, with IPE dominating at low fluence (as in the p-GaAs study) but DP becoming the dominant mechanism after the screening of the interfacial electric field is complete. This mechanism exchange occurs due to the sixtimes-larger deformation potential value of electrons versus holes in GaAs – the electrons are less confined to the surface of the sample in the n-doped case relative to the p-doped case and are thus free to exhibit their larger deformation ability. [96, 100].

In the np-GaAs device considered here, the CLAP oscillations originating from the n-GaAs/p-GaAs and p-GaAs/TMO interfaces could display separate mechanisms, so they will be considered separately here. IPE manifests when built-in electric fields are screened with photo-excited carriers and is proportional to the electric field size. The acoustic response of the system should therefore be proportional to the magnitude of the electric fields in the device if the mechanism is IPE. In the np-GaAs device considered here, the electric field at the n-GaAs/p-GaAs junction is calculated to have a magnitude of 32 kV/cm (section 3.2.1.1). The size of the electric field at the p-GaAs/TMO interface is not known, but other measurements of interfacial fields in GaAs range in the 100s or 1000s of kV/cm [71, 96]. The different size of the echoes originating from the two electric fields in the device (Fig. 3.17) suggests that the CLAP oscillations are sensitive to the electric field strength, giving evidence for the IPE mechanism at both interfaces.

As noted earlier, coherent acoustic phonons detected on n-GaAs interfaces have been reported to show a transition from IPE to DP mechanisms after the interfacial electric field is completely screened, and a similar experiment with p-GaAs showed a plateau in oscillation amplitude as the interfacial electric field is screened. [79, 96] To mimic this experiment and test the existence of a oscillation amplitude plateau on our devices with a TMO overlayer, transient reflectivity spectra for np-GaAs with 15 nm IrO<sub>2</sub> overlayer were obtained at high and low fluence values. The results, displayed in Figure 3.23, show a linear increase in oscillation amplitude between 0.37 and 20 mJ cm<sup>-2</sup>. The TMO CLAP oscillation is probed in the pump front geometry (analogous to the red curve in top plot of Figure 3.20). The fact that the oscillation magnitude does not plateau suggests that the interfacial electric field at the GaAs/TMO interface is not screened even at the highest fluences used. This is further evidence that the electric field at that interface is very large. In both the n-GaAs and p-GaAs cases stated above, the DP mechanism was negligible before the interfacial electric field was completely screened. [79, 96] Finding no evidence of electric field screening in Figure 3.23 is evidence for the dominance of the IPE mechanism of phonon formation.

A further test of the sensitivity of oscillation magnitude to electric field strength was conducted by obtaining preliminary transient reflectivity spectra of the np-GaAs/TMO structures in electrolyte solution. Because the TMO layer is so thin, the electric field at the p-GaAs/TMO interface will be strongly affected by the presence of a strong electric field and sizable depletion region at the TMO/electrolyte interface. Thinner TMO films should more strongly perturb the semiconductor/TMO interface, as the electric field at the TMO/electrolyte interface can stretch very close to or even overlap with the electric field at



Figure 3.23: (a) Transient reflectivity for n-p GaAs with 4 nm Ir + 15 nm IrO<sub>2</sub> overlayer in the pump front geometry under pump fluence intensity ranging from 0.37-20 mJ cm<sup>-2</sup>. (b) Extracted FFT amplitude from data in (a). Dotted line is linear guide to the eye.

the semiconductor/TMO interface. Spectra were obtained using the pump back geometry for np-GaAs samples with 300° C ALD  $Co_3O_4$  overlayer in air and 0.1 M NaOH electrolyte, and IrO<sub>2</sub> overlayer in air, DI water, and 0.1 M H<sub>2</sub>SO<sub>4</sub> electrolyte (Figure 3.24). The 25 nm thick 300° C ALD  $Co_3O_4$  samples display a small adjustment in the rise time of oscillations and a small increase in the amplitude of oscillation (Figure 3.24a). The thinner IrO<sub>2</sub> samples, however, display a large modulation in the amplitude of the signal oscillations, suggesting strong perturbation of the electric field at the GaAs/TMO interface (Figure 3.24b). The amplitude modulation is of similar magnitude for DI water and 0.1 M H<sub>2</sub>SO<sub>4</sub>, suggesting that the modulation effect is insensitive to specific counterions in solution; it is proposed here that the electric field at the TMO/electrolyte interface is equilibrating with the H<sub>2</sub>O/O<sub>2</sub> redox couple of the solution in both cases, causing a substantial change in the electric field at that interface, and by proximity, a change in the electric field at the p-GaAs/TMO interface. The phonon oscillations change their resultant magnitude due to the sensitivity of the IPE mechanism to electric field strength.

As each TMO film type possesses its own doping level and dielectric constant, the electric field at the TMO/electrolyte interface will change differently for each TMO type in the presence of electrolyte species. In addition, equilibration between the  $IrO_2$  surface and the  $H_2O/O_2$  redox couple would depend on a high density of surface states on  $IrO_2$ . [119] Determining the surface state density would require further electrochemical tests (see Chapter 4 for a description of such tests on n-GaN). Pinpointing the cause of the large amplitude modulation seen in Figure 3.24b therefore necessitates a study tuning the variables of TMO thickness, electrolyte species, and substrate doping density. A proposal for such a study is considered in section 3.5.1.

The presence of the large electric fields and the evidence-based argument above strongly



Figure 3.24: Pump-back transient reflectivity of np-GaAs with (a)  $300^{\circ}$  C ALD  $Co_3O_4$  overlayer in air (red) and 0.1 M NaOH (black) and (b) IrO<sub>2</sub> overlayer in air (red curve), DI water (blue), and 0.1 M H<sub>2</sub>SO<sub>4</sub> (black).

suggests but does not prove that IPE is the dominant mechanism for the creation of the CLAP oscillations seen in the transient reflectivity data. One common way in the literature to prove the IPE mechanism is to invert the crystal surface. This results in a  $\pi$  phase shift for oscillations caused by IPE but no phase shift for oscillations caused by DP. This is particularly easy for experiments on slabs of bulk  $GaAs(1\ 1\ 1)$ , which can simply be inverted to expose the opposite crystal face, GaAs(-1-1-1). [79, 96, 100] This technique is not possible in our case due to the asymmetrical multilayer structure of the sample and the usage of GaAs (1 0 0), which does not possess the same easy inversion antisymmetry. Another way to test the IPE mechanism is bias application. Reverse biasing increases the electric field size at the interface under consideration and has been shown to increase the size of acoustic oscillation produced by the IPE mechanism in GaN diode samples. [99] A proposed experiment for determining the effect of biasing on each electric field in the np-GaAs devices studied here is described in section 3.5.1. Finally, a careful adjustment of the doping at each interface could provide fine-tuning of the electric field strengths at the interface. This would have a resultant effect on the amplitude of IPE-based oscillations but should have a lesser impact on DP-based oscillations.

#### 3.5 Conclusion

#### **3.5.1** Proposed Future Experiments

The experiments described in this section have been successful at detecting charge carrier injection into the catalytic layer of a device. The technique is not, however, yet able to

quantitatively measure the density of photo-injected carriers or the strength of electric fields at the TMO surface. Both quantities would be immensely helpful for device optimization. Interface-specific counts of electron or hole injection would allow for each interface to be tuned for minimal recombination and maximal quantum efficiency. A quantitative measure of electric field strength could be used as an input to model the band structure of the interface, allowing for fine-tuned design of the optimal band structure for charge injection. In this section, future experiments towards these goals are proposed and described.

#### 3.5.1.1 Biasing for mechanism determination

It was noted in section 3.4 that reverse biasing the sample has been shown to cause larger signal oscillation magnitude in n-p GaN samples with acoustic phonons created by the IPE. [99] A similar effect may manifest in the np-GaAs samples in this study, helping prove the IPE mechanism. The entire device could be biased in a geometry like that shown in Figure 3.5a. The effect of the overall device bias could then be broken into the component effects of the biasing on each of the two major electric fields in the device by comparing the magnitude of the CLAP frequencies associated with the n-p GaAs junction (0.13 THz) and the p-GaAs/TMO junction (0.07 THz).

#### 3.5.1.2 Variables in electrolyte

As noted in Figure 3.24 and the surrounding text, the electric field at the p-GaAs/TMO interface is strongly perturbed by the presence of a liquid environment. The modulation of the transient reflectivity signal was stronger for an np-GaAs sample with  $IrO_2$  overlayer, yet it is not clear if the stronger perturbation in that film is due to the dielectric properties of the film or the thinner nature of the  $IrO_2$  film, or neither. Further experiments would first seek to determine the set of variables that cause the largest perturbation to the electric field at the p-GaAs/TMO interface for a single type of TMO. Electric field perturbation would be measured by examining the magnitude of the oscillations. The component frequencies of the oscillations would be used to determine the position of origin in the device, as in this thesis (Figure 3.20). The damping time of the oscillations gives information on the acoustic reflectivity of the various interfaces; damping time in these experiments would give information on the effect of the aqueous interface on CLAP lifetime.

The variables to test for the effects listed above include:

1. TMO thickness. The electric field formed at the TMO/electrolyte interface will have a stronger perturbation of the electric field at the p-GaAs/TMO interface if the two regions have a greater spatial overlap. Thinner films would therefore be expected to result in a larger perturbation of the electric field, and give the most oscillation magnitude changes relative to a sample in air. If the oscillation magnitude is entirely dependent on the p-GaAs/TMO interface and not on the TMO/electrolyte interface, an experiment on a very thick film would give an oscillation magnitude that is very
# CHAPTER 3. SPECTROSCOPIC PROBE OF COHERENT ACOUSTIC OSCILLATIONS ORIGINATING FROM BURIED INTERFACES

similar to the magnitude in air. On the other hand, the oscillation magnitude may be dependent on the stand-alone field at the TMO/electrolyte interface — in this case, the CLAP wave emitted would have the same frequency as the CLAP detected in the TMO, but may be phase-shifted by  $\pi$ , as it originates from the side of the TMO opposite the p-GaAs/TMO interface.

- 2. Electrolyte species. Although Figure 3.24b showed similar behavior for liquid environments containing water and 0.1 M H<sub>2</sub>SO<sub>4</sub>, it is not clear that this trend will hold for all electrolyte types. Each electrolyte species will introduce a new redox couple to which the electric field at the TMO/electrolyte interface will equilibrate. If the oscillation magnitude is sensitive to the counter-ions in solution, the size of the band bending, and electric field, at the interface will change. Testing the variance of the oscillation magnitude for a series of electrolyte species with progressively varied redox level positions, on a very thin film to maximize the potential electric field coupling between the p-GaAs/TMO and TMO/electrolyte fields, would likely provide the most effective comparison.
- 3. Electrolyte concentration. As noted in section 2.4, the charge density in the Helmholtz layer of a 0.1 M electrolyte approaches  $10^{20}$  cm<sup>-3</sup>. Increases in the concentration of the Helmholtz layer would therefore be unlikely to cause a significant change in the electric field on the semiconductor side of the interface, where the charge density will typically range from  $10^{15}$ - $10^{19}$  cm<sup>-3</sup>. This hypothesis is supported by the similarity of oscillation magnitude seen between water and 0.1 M H<sub>2</sub>SO<sub>4</sub> in Figure 3.24. A quick scan of concentration for one electrolyte type would show whether this hypothesis is correct, and no further concentration dependence studies are necessary, or if concentration variance is a meaningful variable for this system.
- 4. Varied TMO type. Once the variables that affect oscillation magnitude are isolated, various TMO types could be tested in electrolyte on only those variables. A series of TMO types could be assembled based on several characteristics: doping, dielectric constant, deposition quality (PVD vs. ALD, for example).

The possible variable space to explore is large. The experiments are important, as these devices mimic structures used in artificial photosynthesis, and the interfacial electric fields and charge behavior must be measured *in situ* for meaningful application to actual reaction conditions.

#### 3.5.1.3 All-optical quantification of electric fields

An ultimate goal of this research would be to demonstrate the ability to predict the size of a buried electric field with all-optical characterization of the CLAP oscillation magnitude. Ishioka *et. al.* have previously shown preliminary efforts to predict the band structure of buried Si/GaP interfaces based on signal oscillations originating from longitudinal optical

# CHAPTER 3. SPECTROSCOPIC PROBE OF COHERENT ACOUSTIC OSCILLATIONS ORIGINATING FROM BURIED INTERFACES

(LO) phonons and LO-plasmon coupling (LOPC). [91] The magnitude of the LOPC mode is compared to a calibrated set of LOPC oscillation amplitudes from well-characterized GaP thin film samples to obtain the Fermi level of the Si/GaP interface. The Fermi level estimation is then used as an input into modeling to determine the spatial band structure for Si/GaP interfaces containing different GaP morphologies. The LOPC mechanism used in their work depends on the screening of interfacial electric fields, much like the IPE mechanism used here. Similar work using the CLAP oscillations in the np-GaAs device here could be used to develop a calibration tool for determining the band structure of the buried np-GaAs/TMO interface for many TMO types, including prospective TMO electrocatalysts.

### 3.6 Conclusion

Model photoanodes for artificial photosynthesis have been found to generate large coherent acoustic oscillations upon photo-excitation that report on the strength of buried electric fields in the device. Acoustic pulses originating from the GaAs light absorber or TMO overlayer are selectively observed by pumping from the back or front of the device. The coherent oscillations change frequency with probe beam wavelength and are attributed to the inverse piezoelectric effect, a known cause for acoustic phonon emission in semiconductor samples. This is the first time acoustic oscillations of this magnitude have been attributed to charge carrier injection in a multilayer sample. With further development, the technique holds promise as a quantitative metric for the magnitude and position of buried electric fields in devices for artificial photosynthesis.

The observation of the CLAP oscillations for many different TMO types shows the versatility of the technique. A potential limiting factor is the use of GaAs (100). This substrate is piezoelectrically active, important for the creation of phonons by the inverse piezoelectric effect. GaAs is a popular choice for buried light absorbers, but other choices like silicon are also common. [27–29] For the technique to be developed as a measure of buried electric fields, the substrate must be susceptible to the creation of phonons by the IPE. Nevertheless, GaAs is a very popular choice of light absorber, and the continuation of this research holds great promise as it becomes more quantitative and expands to a wider array of substrates and TMO types.

### Chapter 4

## Transient Grating Spectroscopy as a Probe of Surface Hole Diffusivity

The first thing he learns is how to vary his index of refraction. He can choose anything between transparent and opaque. After the thrill of experimenting has worn off, he settles on a pale, banded onyx effect.

"It suits you," murmur his guides. "Now hurry."

Gravity's Rainbow THOMAS PYNCHON

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### 4.1 Introduction

After the initial processes of charge carrier separation and transport to the reactive interface, there remains the most important step of artificial photosynthesis: the actual reaction. A charge carrier finding itself at the interface must contend with a number of potential hindrances including:

- 1. recombination (surface and bulk)
- 2. surface trap states due to absent or improper surface passivation
- 3. disordered or damaged surfaces

- 4. Improper surface energetics for reaction
- 5. Poor spatial arrangement of reactants on the surface

Low recombination lifetimes are a common cause of device inefficiency. Fe<sub>2</sub>O<sub>3</sub>, for example, has excellent band alignment for water oxidation, but suffers from short charge carrier lifetimes that hamper its performance as a water oxidation catalyst. [26, 120] Short carrier lifetimes can be exacerbated by surface recombination centers, often stemming from material defects intrinsic to the material or caused by corrosive interaction with the electrolyte phase. [121–125] If a charge carrier avoids the issues of recombination and surface trapping, it still must have the proper oxidative (holes) or reductive (electrons) power required to complete the reaction, *i.e.* the band edges must align with the relevant redox couple in the electrolyte phase. Lastly, if a charge carrier arrives at a portion of the surface that is not sufficiently near a reactant on the electrolyte side of the interface, reaction cannot proceed. This could be particularly important for the water oxidation reaction, in which multiple steps exist that require concerted reaction of multiple holes and molecular surface intermediates. This chemical dance can only be successful with holes of the proper oxidative power and spatial positioning.

In this chapter, experiments are described in which transient grating spectroscopy (TGS) as well as pump-probe spectroscopies are used to investigate lateral hole diffusivity at the aqueous electrolyte interface of undoped GaN and n-GaN films. While TGS has been applied previously to determine lateral diffusivities at the air interface of semiconductors such as Si, GaAs, and GaN [126–130] and, additionally, at the TiO<sub>2</sub> or GaAs/electrolyte interface [131–135] to measure interfacial charge transfer, it has yet to extract diffusivities at the electrolyte interface. Results show that the lateral, interfacial hole diffusivity increases by a factor > 2 from air at the n-GaN/aqueous electrolyte interface for both pH = 1.4 (0.1 M HBr) and pH = 7 (0.1 M Na<sub>2</sub>SO<sub>4</sub>). This increase in diffusivity is not sensitive to defect centers, since the surface recombination velocity, also obtained from the TGS kinetics, differs by almost an order of magnitude between the two electrolytes. The origin of this increase in diffusivity in n-GaN is attributed to a new current pathway for surface holes due to the presence of mobile intermediates of the water oxidation reaction on the surface of the n-GaN.

The chapter closes with pump-probe results that demonstrate the power of TGS relative to pump-probe spectroscopy to measure the behavior of holes in GaN. TGS and pumpprobe spectra of n-GaN during voltage application reveal non-monoexponential kinetics and a rising offset with increased voltage, indicative of a damaged or disordered surface. Three potential fitting models are introduced to explain the data.

### 4.2 Transient Grating Spectroscopy

### 4.2.1 Formation of the transient grating

In general, light-matter interaction involves two steps: (1) the light produces a material excitation and (2) the optical properties of the material respond to the excitation. In a semiconductor, for example, above-bandgap excitation results in a change in the refractive index of the material due to a change in the conduction band density of electrons. When a sample of any type is inserted into the region of a pump beam, a change in some material property X is induced, as dictated by the beam intensity I [136]:

$$\Delta X = g(\lambda_{pump}) * \Delta I(\lambda_{pump}) \tag{4.1}$$

where g is the coupling constant between intensity I and the material property X. Examples of  $\Delta X$  range from scalar properties like temperature, to vectors like electric field, to tensor quantities that depend on the 3-dimensional orientation of atoms, like stress or strain. In this thesis, the most relevant relations involve the complex refractive index  $\tilde{n} = n + i\kappa$ , such that we will focus on the change in refractive index within the pumping region:

$$\Delta n = \left(\frac{\partial n}{\partial X}\right) \Delta X \qquad \Delta \kappa = \left(\frac{\partial \kappa}{\partial X}\right) \Delta X \qquad (4.2)$$

In transient grating spectroscopy, the refractive index is spatially modulated in a sinusoidal manner within the pumping region. This is accomplished by spatially and temporally overlapping two pump beams with wavevectors  $k_1$  and  $k_2$  on the sample with an angle  $<10^{\circ}$ between them. As shown in Figures 4.1 and 4.2, the beams form an interference pattern on the sample that is sinusoidally modulated in intensity in the plane of the beams and can be described by the grating wavevector  $q = \pm (k_1 - k_2)$ .

In a semiconductor, this creates a spatial modulation of electron-hole pairs and consequently also a sinusoidal modulation in the refractive index. The periodic change in the refractive index within the grating can be estimated using the Drude model, which models the conduction band electrons and valence band holes as oscillating as quasi-free carriers in the field of the light pulse. This yields:

$$\Delta n = \frac{-Ne^2}{2nm_{eh}\omega_{probe}^2\epsilon_0} = Nn_{eh} \qquad \Delta \kappa = \frac{Ne^2}{nm_{eh}\omega^2 c\tau\epsilon_0} = N\sigma_{eh} \tag{4.3}$$

where N is the density of photoexcited electron-hole pairs, e is the elementary charge,  $m_{eh}$  is the reduced effective mass of an electron-hole pair,  $\omega_{probe}$  is the angular frequency of the probe beam,  $\tau$  is the characteristic scattering time of electrons in the material, and  $n_{eh}$  and  $\sigma_{eh}$  are the refractive index and absorption coefficient change per volume element, respectively. The

CHAPTER 4. TRANSIENT GRATING SPECTROSCOPY AS A PROBE OF SURFACE HOLE DIFFUSIVITY



Figure 4.1: A graphic description of the interference of two Gaussian laser pulses for beams crossed at (a) small and (b) large angle  $\theta$ . Two pump beams overlapping in the xz-plane with wavevector  $k_1$  and  $k_2$  and wavelength peaks denoted by the red lines interfere constructively in places where the peaks overlap, *i.e.* where the red lines overlap. These overlap regions produce peaks in the plane of the sample (the xy coordinate plane) dictated by the wavelength and angle  $\theta$  of the beams in accordance with equation 4.4.



Figure 4.2: Wavevector description of the interference of two Gaussian pulses with wavevectors  $k_1$  and  $k_2$  resulting in grating wavevector  $q = \pm (k_1 - k_2)$ .

spatial modulation of the refractive index is called the "grating" and will decay in time due to processes described in section 4.2.3. The spacing between grating peaks  $\Lambda$  is controlled by the wavelength (equivalently, wavevector) of the pump pulse  $\lambda$  and the relative angle between the beams  $\theta$  as

$$\Lambda = \frac{2\pi}{q} = \frac{\lambda_{pump}}{2\sin\frac{\theta}{2}} \tag{4.4}$$

The most relevant parameter for the process of diffraction off of the grating is the change in the real part of the refractive index, as diffraction is a scattering process rather than an absorptive one. The sinusoidal distribution of photoexcited carriers and change in refractive index in the plane of the beams is shown for illustrative purposes in Figure 4.3 for an n-GaN sample pumped with above-bandgap and probed with below-bandgap light, using

equation 4.3 and a model that will be introduced in section 4.2.3. A photo-excitation in n-GaN of  $10^{18}$  carriers cm<sup>-3</sup> induces a change in the refractive index of  $\approx 10^{-10}$ . The sensitivity of TGS is superb and has been reported down to values of  $\Delta n = 10^{-16}$  using heterodyne detection [136], which will be discussed in section 4.2.5.



Figure 4.3: Left: calculation of the number of photoexcited charge carriers 25 nm into an n-GaN surface and 10 ps after pump excitation. Carrier density is modulated along the surface due to the interference of the pump beams. Right: The resultant change in refractive index as calculated using equation 4.3.

The change in refractive index can equivalently be related to a change in the dielectric constant or electric susceptibility of the material via the relation

$$\Delta \tilde{n} = \frac{\Delta \epsilon}{2\sqrt{\epsilon}} = \frac{\Delta \chi}{2(1+\chi)^{1/2}} \tag{4.5}$$

In the limit of  $\left(\frac{\partial n}{\partial X}\right) \to 0$  or  $\left(\frac{\partial \kappa}{\partial X}\right) \to 0$ , the grating is labeled as a pure amplitude or phase grating, respectively, meaning that only one component of the complex refractive index contributes to the change of optical properties in the material at the pump wavelength. For example, the transparent liquid carbon disulfide exhibits a pure phase grating over a wide frequency range and is frequently used as a calibration standard for transient grating setups (described in section 4.2.5). [137, 138]

### 4.2.2 Probing the transient grating

Once a grating has been formed by the pump beams, a spatially coincident but temporally delayed probe beam with wavevector  $k_3$  will diffract off of the transient grating at an angle dictated by Bragg diffraction, described by

$$\sin\phi_{\pm 1} = \sin\phi \pm \frac{\lambda_{probe}}{\Lambda} \tag{4.6}$$

where  $\phi_{\pm 1}$  refers to the angle of the  $\pm 1$  order of diffraction relative to the sample normal and  $\phi$  the incident angle of the probe relative to the sample normal. This produces a new signal beam (called the "diffracted" beam in this thesis) with wavevector  $k_{diff}$ . A description equivalent to equation 4.6 uses the language of wavevectors: the phase-matching condition  $k_{diff} = k_3 + q$  must be obeyed. The process of grating creation by two pump beams is displayed in Figure 4.4a and the diffraction of the signal beam from the grating is depicted in Figure 4.4b.



Figure 4.4: (a) Formation of the transient grating on the sample via the overlap of two Gaussian pump laser pulses. (b) A time-delayed laser pulse probes the grating region, producing a diffracted beam at an angle defined by equation 4.6.

Signal diffracting from the transient grating is proportional to the change in the complex refractive index and is measured as diffraction efficiency  $\eta$ , described by

$$\eta = \frac{I_{diff}}{I_{probe}} = \left(\frac{\pi \Delta \tilde{n}d}{\lambda_{probe}}\right)^2 = \left(\frac{\pi \Delta nd}{\lambda_{probe}}\right)^2 + \left(\frac{\Delta \kappa d}{4}\right)^2 \tag{4.7}$$

where  $I_x$  is the intensity (squared electric field  $E_x^2$ ) of beam x and d is the spatial depth of the grating. In the limit of  $\Delta \kappa \to 0$ , as in the case of a semiconductor probed with a below-bandgap probe, the second term is negligible and the diffraction efficiency responds solely to n, the real part of the refractive index.

#### 4.2.3 Decay of the transient grating

In a semiconductor sample, the transient grating will decay with time due to two main processes: (1) recombination of electrons and holes in the grating, and (2) diffusion of photocarriers laterally along the surface and into the bulk of the semiconductor. The temporal and spatial distribution of excited carrier density is described by:

$$\frac{\partial N(x,z,t)}{\partial t} + \frac{N(x,z,t)}{\tau_r} - D\frac{\partial^2 N(x,z,t)}{\partial x^2} = \frac{\gamma \kappa I(t)}{h\nu} [1 + \cos(2\pi x/\Lambda)]$$
(4.8)

where N(x, z, t) is the carrier density along the surface (x) and into the bulk (z),  $\gamma$  is the quantum efficiency of the semiconductor material for electron-hole pair creation,  $\kappa$  is the absorption coefficient at the pump wavelength, and I(t) is the intensity of the pump beam with respect to time. [136] The experiments described here use short pulses of pump light that act as a delta function at t = 0 with  $I = I_{pump}$ . The decay at all subsequent time points acts under the condition I(t > 0) = 0, leading to the simplified equation [130]

$$\frac{\partial N(x,z,t)}{\partial t} = D \frac{\partial^2 N(x,z,t)}{\partial x^2} - \frac{N(x,z,t)}{\tau_r}$$
(4.9)

with important boundary conditions

$$\left. \frac{\partial N(x,z,t)}{\partial z} \right|_{z=0} = \frac{S}{D} N(x,0,t) \tag{4.10}$$

and

$$N(x,\infty,t) = 0 \tag{4.11}$$

The first boundary condition displays the importance of and competition between surface recombination velocity S and diffusion constant D at the surface of the semiconductor. The second condition notes that the material excitation has finite depth.

Assuming S, D, and  $\tau_r$  are independent of carrier density, the solution to this equation is [130, 139]

$$N(x, z, t) = \left\{ 1 + \cos \frac{2\pi x}{\Lambda} \exp\left[ \left( -\frac{4\pi^2 D}{\Lambda^2} \right) t \right] \right\} \Phi(z, t)$$
(4.12)

where  $\Phi(z,t)$  is

$$\Phi(z,t) = \frac{N_0}{2} \exp\left(-\frac{t}{\tau_r}\right) \exp\left(-\frac{z^2}{4Dt}\right) \left\{ W\left(\alpha(Dt)^{\frac{1}{2}} - \frac{z}{2(Dt)^{\frac{1}{2}}}\right) + W\left(\alpha(Dt)^{\frac{1}{2}} + \frac{z}{2(Dt)^{\frac{1}{2}}}\right) - \frac{2\frac{S}{D}}{\frac{S}{D} - \alpha} \times \left[ W\left(\alpha(Dt)^{\frac{1}{2}} + \frac{z}{2(Dt)^{\frac{1}{2}}}\right) - W\left(\frac{S}{D}(Dt)^{\frac{1}{2}} + \frac{z}{2(Dt)^{\frac{1}{2}}}\right) \right] \right\}$$
(4.13)

with  $W(x) = \exp(x^2)\operatorname{erfc}(x)$ . Since N(x, z, t) is proportional to  $\Delta \tilde{n}$  (equation 4.3 and Figure 4.3) and the diffraction efficiency is proportional to  $\Delta \tilde{n}^2$  (equation 4.7), the diffraction efficiency  $\eta$  for a grating obeying equation 4.9 can be expressed with a carrier-density-dependent Bessel function as

$$\eta(t) = J_1^2 \left\{ \frac{\pi}{\lambda_{probe}} \frac{e^2}{2nm_{eh}^* \omega^2 \epsilon_0} \int_0^\infty \left[ N(\Lambda, z, t) - N\left(\frac{\Lambda}{2}, z, t\right) \right] dz \right\}$$
(4.14)

Plugging equation 4.12 into equation 4.14 yields the following solution as a model for the diffraction efficiency of the transient grating:

$$\eta(t) \propto \frac{\exp\left[\frac{-4\pi^2 Dt}{\Lambda^2} - \frac{t}{\tau_r}\right]}{\alpha} \left[ 1 + \frac{1}{\frac{S}{D} - \alpha} \left( \frac{S}{D} \exp(\alpha^2 Dt) \operatorname{erfc}(\alpha \sqrt{Dt}) - \frac{S}{D} - \alpha \exp\left( \left( \frac{S}{D} \right)^2 Dt \right) \operatorname{erfc}\left( \frac{S}{D} \sqrt{Dt} \right) + \alpha \right) \right]$$
(4.15)

This decay allows the modeling of the transient grating decays to produce insights into both diffusion and surface recombination. The integral in equation 4.14 extends infinitely deep into the bulk but considers the modulation of carriers in the x-direction along the surface. The diffraction efficiency and the measured diffusion constants in this thesis are therefore dependent on the surface-plane diffusion of carriers rather than diffusion of carriers into the bulk of the sample. [140]

The overall decay of the grating signal can be separated into recombination and diffusion components, as

$$\begin{aligned} \tau_g^{-1} &= \tau_r^{-1} + \tau_d^{-1} \\ &= \tau_r^{-1} + D \frac{4\pi^2}{\Lambda^2} \\ &= \tau_r^{-1} + Dq^2 \end{aligned} \tag{4.16}$$

where  $\tau_r$  and  $\tau_d$  are the recombination and diffusive decay constants, respectively, and  $\tau_d^{-1} = D \frac{4\pi^2}{\Lambda^2}$  is obtained by plugging equation 4.12 into equation 4.9. Figure 4.5a schematically displays grating decay processes due to diffusion and recombination. Recombination decreases charge carrier concentration at the peaks of the gratings, represented as downward arrows in Figure 4.5a, whereas diffusion causes the peak-to-valley concentration difference to diminish, represented as sideways arrows. The relative importance of the recombination and diffusive decays is material-specific and depends acutely on the grating period  $\Lambda$ . Materials with  $\tau_r \ll \tau_d$  will have grating decay entirely due to recombination and will exhibit identical decay kinetics at varied grating periods  $\Lambda$ . In contrast, materials with  $\tau_r \geq \tau_d$  will experience grating decays due to both recombination and diffusion of carriers and will exhibit decay kinetics that are faster at smaller values of  $\Lambda$ . Figure 4.5b shows transient grating decay curves for an n-GaN sample with  $\Lambda = 2.3 \ \mu m$  and  $\Lambda = 12 \ \mu m$ . The kinetics decay faster at 2.3 \mumber m. GaN.



Figure 4.5: (a) Mechanisms of grating decay on a semiconductor sample. (b) Example of TG decay of n-GaN, with faster decay for narrower grating period. Dotted lines denote single exponential fits following equation 4.33.

The extent to which TGS provides the ambipolar diffusion coefficient,  $D_a$ , or is a direct measurement of the hole diffusion coefficient,  $D_h$ , depends on the injected carrier concentrations ( $\Delta N_e$ ,  $\Delta N_h$ ), the electron and hole diffusion coefficient ( $D_e$ ,  $D_h$ , respectively) and the instrinsic doping concentration of sample ( $n_0$ ), and is given by [141]

$$D = \frac{(n_0 + \Delta N_e + \Delta N_h) D_e D_h}{[(n_0 + \Delta N_e) D_e + \Delta N_h D_h]}$$

$$\tag{4.17}$$

According to Scajev *et. al.*, two regimes exist for eq. 4.17 as noted by a steep sigmoidal relationship between D and injected carrier density for undoped GaN (Fig. 3a of Scajev *et. al.*). [126] The steep sigmoidal relationship implies that within an order of magnitude of tuning  $\Delta N$  or  $n_0$ , one of two regimes is accessed. For a moderate/high injection regime

where  $\Delta N_e = \Delta N_h \gg n_0$ , the carrier diffusivity behaves as ambipolar  $D_a \approx \frac{2D_h D_e}{D_h + D_e}$ . On the other hand when  $\Delta N_e = \Delta N_h \ll n_0$ , the low injection regime is reached and the carrier diffusivity D behaves as  $D_h$ .

### 4.2.4 Angle change in electrolyte

For samples in electrolyte solution, the angle of the pump beams changes when the beams transfer from air (n = 1) to the aqueous phase (n = 1.33) as depicted in Figure 4.6. This alters the grating period  $\Lambda$  according to equation 4.4. According to Snell's Law,

$$n_{air}\sin\left(\frac{\theta_{air}}{2}\right) = n_{water}\sin\left(\frac{\theta_{water}}{2}\right) \tag{4.18}$$

Therefore,

$$\theta_{water} = 2\sin^{-1}\left[\frac{n_{air}}{n_{water}}\sin\left(\frac{\theta_{air}}{2}\right)\right]$$
(4.19)

In order to correct for the refractive index change in electrolyte solution, the corrected  $\Lambda$ , calculated by plugging in  $\theta_{water}$  to equation 4.4, is

$$\Lambda = \frac{\lambda_{pump}}{2\frac{n_{air}}{n_{water}}\sin\left(\frac{\theta_{air}}{2}\right)} \tag{4.20}$$



Figure 4.6: Angle change of pump beams due to differing refractive indices of air and water phases.

#### 4.2.5 Heterodyne detection

Transient grating spectroscopy is a four-wave mixing technique, meaning three input frequencies yield one output frequency. In the most general case of TGS, two pump pulses with frequency  $\omega_{pump}$  mix with a probe pulse at  $\omega_{probe}$  to garner a signal pulse that also propagates with frequency  $\omega_{probe}$ .

$$\omega_{probe} = \omega_{probe} + \omega_{pump} - \omega_{pump} \tag{4.21}$$

The response of the system stems from the third-order polarization  $P^{(3)}$ , which is an expansion of the polarizability to incorporate the effect of high electric fields on the material properties of the system, such as dielectric constant, refractive index, and absorption coefficient: [142, chapter 11]

$$P = \epsilon_0 \chi E$$
  
=  $P^{(1)} + P^{(2)} + P^{(3)} + \cdots$   
=  $\epsilon_0 [\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \cdots]$  (4.22)

where  $\epsilon_0$  is the permittivity of free space, and  $\chi^{(j)}$  is the *j*-th order electric susceptibility of the material, which is related to dielectric constant  $\epsilon$  and the refractive index  $\tilde{n}$  as

$$\tilde{n}^2 = \epsilon = 1 + \chi \tag{4.23}$$

Using equation 4.22 and equation 4.23, we find that the dielectric constant  $\epsilon$  is related to the electric fields through the nonlinear susceptibilities and is dependent on the optical power:

$$\epsilon_r = 1 + \chi^{(1)} + \chi^{(2)}E + \chi^{(3)}E^2 + \cdots$$
(4.24)

Thus by applying high-power laser fields, we can cause non-linear changes to the dielectric constant, or, equivalently, the refractive index of the material under study [136, p. 35]. The second term  $P^{(2)}$  in equation 4.22 requires a combination of two input frequencies to create one output frequency, allowing only the sum or difference of the input frequencies. The output frequency in transient grating spectroscopy is the same as the input probe frequency, so the  $P^{(2)}$  term, and all even-order nonlinear contribution to P, cannot contribute to the signal. Thus, the relevant polarizability term for transient grating spectroscopy, and the focus of analysis in this thesis, is  $P^{(3)}$ .

Heterodyne detection extends the capabilities of the transient grating setup by introducing a reference beam (also known in the literature as a "local oscillator")  $k_{ref}$  that is overlapped with the diffracted probe beam  $k_{diff}$  on the detector. Whereas homodyne detection

measures the intensity  $I_{diff} = (E_{diff})^2$ , the measured quantity with heterodyne detection is the mixing between the diffracted and reference beams.

$$I_{het} = |E_{ref} + E_{diff}|^2 = E_{ref}^2 + E_{diff}^2 + 2E_{ref}E_{diff}\cos(\xi)$$
(4.25)

70

where  $\xi$  is the total phase difference between all beams.  $E_{diff}^2$  is negligibly small in this formulation, leaving a signal that has an offset of  $E_{ref}^2$  and an oscillatory component around the offset defined by the third term in equation 4.25. The third term can be expanded by expressing it in terms of the third-order polarizability [137, 143, 144] as follows:

$$E_{ref}E_{diff}\cos(\xi) = Re[E_{ref}^{*}(t)E_{diff}(t)]$$
  
=  $Im[E_{ref}^{*}(t)P^{(3)}]$   
=  $E_{ref}Im[e^{i\xi}P^{(3)}]$   
=  $E_{ref}[\cos(\xi)Im(P^{(3)}) + \sin(\xi)Re(P^{(3)})]$   
=  $E_{ref}E_{dic}(t)\cos(\xi) + E_{ref}E_{bir}(t)\sin(\xi)$   
(4.26)

where the first to second step follows because  $E_{diff}(t) \propto iP^{(3)}(t)$ , and  $E_{dic}(t)$  and  $E_{bir}(t)$  are the dichroic and birefringent responses of the system. The dichroic response corresponds to the imaginary part of the refractive index ( $\kappa$ ), while the birefringent response corresponds to the real part of the refractive index (n). Thus we see that by altering the system phase  $\xi$ , we can isolate signal that originates from processes corresponding to the real or imaginary part of the refractive index. This is not possible with pump-probe spectroscopy, where the phase of the signal electric field is passively locked to the phase of the probe electric field.

This brings the full heterodyned signal expression to:

$$I_{het} = E_{ref}^2 + 2E_{ref}E_{dic}(t)\cos(\xi) + 2E_{ref}E_{bir}(t)\sin(\xi)$$
(4.27)

The full phase of the heterodyned system  $\xi$  can be expanded into the component phases of each of the five relevant electric fields:

$$\begin{aligned} \xi &= \varphi_s + \xi_1 - \xi_2 - \xi_{ref} + \xi_{diff} \\ &= \varphi_s + \psi \end{aligned}$$
(4.28)

where  $\xi_1$  and  $\xi_2$  are the phases of the two pump beams,  $\xi_{ref}$  and  $\xi_{diff}$  the phases of the two probe beams, and  $\varphi_s$  the phase shift induced by diffraction from the sample.

For experiments requiring careful measurement of signal with total phase  $\psi$  equal to either  $\pi$  or  $\pi/2$ , accurate knowledge of  $\varphi_s$  is essential. This calibration can be achieved by using a reference sample such as carbon disulfide, toluene, or m-xylene [137, 138, 145], each of

which have small dichroic but large birefringent signals. The calibration can also be achieved interferometrically with a Mach-Zehnder interferometer [146–148], but this introduces added complexity and cost without greatly heightened phase stability. The system can be calibrated more simply by making the reference and probe beams identically powerful and measuring the heterodyne signal of both beams on two detectors simultaneously [149]. The phase difference between the two oscillatory signals is then simply  $2\varphi_s$  (Figure 4.7a), allowing for adjustment of the overall beam phase  $\xi$  to achieve  $\psi = \pi$  or  $\psi = \pi/2$ .



Figure 4.7: (a) Example of signal on both detectors showing TG/T,  $\Delta T/T$ , and  $\varphi_s$ . (b) Representative TG (decaying with time constant  $\tau_g$ ) and  $\Delta T/T$  signals on n-GaN with example single-exponential fit following equation 4.33.

In the formulation of Gedik and Orenstein [149], equation 4.27 is written for both signal beams as

$$\frac{\Delta I_{probe1}}{I_{eq}} = \left| \frac{\delta t}{t} \right| \left[ \cos(\varphi_s) + \epsilon \cos(\psi - \varphi_s) \right]$$

$$\frac{\Delta I_{probe2}}{I_{eq}} = \left| \frac{\delta t}{t} \right| \left[ \cos(\varphi_s) + \epsilon \cos(\psi + \varphi_s) \right]$$
(4.29)

where  $\frac{\Delta I_{probe}}{I_{eq}}$  is the pump-induced probe beam intensity change relative to its equilibrium value for probe beams 1 and 2,  $\frac{\delta t}{t}$  is the photo-induced change in the transmission coefficient,  $\epsilon$  is the ratio of the signal oscillation amplitude to the mean value of the signal oscillation, and all other symbols are as previously defined. Equation 4.29 can be fit to a function of the form

$$I = A + B \cos(k\theta + \beta) \tag{4.30}$$

to obtain the signal offset (A), amplitude (B), and phase ( $\beta$ ), with k being a conversion factor between signal phase  $\psi$  and the angle  $\theta$  of a rotatable coverslip inserted into one of

the probe beams (described in detail in section 4.2.6). Comparing equations 4.29 and 4.30 shows the following correspondences:

$$A = \frac{\delta t}{t} \cos(\varphi_s)$$
  

$$B = \frac{\delta t}{t} * \epsilon$$
  

$$\beta = \pm \varphi_s$$
(4.31)

Final values for offset, amplitude, and phase  $\varphi_s$  are found by averaging the offset and amplitude signals from each of the two detectors and subtracting the sample phase values:

$$\frac{A_2 + A_1}{2} = \frac{\Delta T}{T} (\%)$$

$$\frac{B_2 + B_1}{2} = \frac{TG}{T} (\%)$$

$$\frac{\beta_2 - \beta_1}{2} = \varphi_s$$
(4.32)

 $\frac{\Delta T}{T}$  measures the recombination decay of spatially uniform charge carriers in the grating.  $\frac{TG}{T}$  measures the diffraction efficiency of the grating and decays in time due to charge carrier recombination and diffusion with time constants  $\tau_r$  and  $\tau_d$ , as described in section 4.2.3. For the purposes of brevity,  $\frac{\Delta T}{T}$  results will sometimes be notated as "PP" in analogy to their equivalence with pump-probe results, and  $\frac{TG}{T}$  results will sometimes be abbreviated as "TG". Figure 4.7a displays example TG signal at t = 3 ps versus varied coverslip angle  $\theta$  for detectors 1 and 2. Signal oscillates with coverslip angle in accordance with equation 4.31 and the two detectors display a phase difference of  $2\varphi_s$  as shown in equation 4.29. The oscillation of signal is fit as described in equations 4.30, 4.31, and 4.32 to obtain  $\frac{\Delta T}{T}$ ,  $\frac{TG}{T}$ , and  $\varphi_s$ .

The procedure described in the preceding paragraphs requires obtaining the oscillation shown in Figure 4.7a for each time delay point in the spectrum. This is beneficial for the purposes of phase stability, as the drift in  $\psi$  is minimal within the time required to obtain the oscillation spectrum ( $\approx 1$  minute). However, a full spectrum over all time delays requires a time equal to (number of points in oscillation trace) × (number of time delay points) × (amount of time per data point), which can increase the time per full scan intolerably high. With a setup with superior phase stability, a faster procedure is possible by measuring the time delay trace at three distinct values of  $\psi$  (generally 0,  $\pi/2$ , and  $\pi$ ). The data at the three phase points for each time delay point is then fit to a modified equation 4.29 to solve for the three unknown variables  $\frac{\Delta T}{T}$ ,  $\frac{TG}{T}$ , and  $\varphi_s$ . [149–151] This procedure results in three phase points at each time delay rather than a minimum of six, halving the time necessary for data-taking.

#### 4.2.6 Extraction of TG signal

In the experiments described in this thesis, TG is measured at varied probe time delay. The signal oscillation portrayed in Figure 4.7a is induced by rotation of a 200  $\mu$ m thick glass or quartz coverslip inserted into one of the probe beams. One period of oscillation can be induced by rotation steps spanning 0.6°. After the signal oscillation is obtained at every probe beam delay time point on both probe beam detectors, the fitting procedure described in section 4.2.5 is applied to obtain PP and TG for each time delay point (Figure 4.7b).

TG signal will decay according to [152, 153]

$$\eta(t) = \eta_0 e^{\frac{-2t}{\tau_g}} \tag{4.33}$$

where  $\eta_0$  is the diffraction efficiency from equation 4.7 at probe time delay zero. The decay is fit with equation 4.33 to obtain a value for  $\tau_g$ , and the inverse of  $\tau_g$  is plotted against  $q^2$  per equation 4.16. This process is repeated for many values of  $q \ (= \frac{2\pi}{\Lambda})$ , as shown schematically in Figure 4.8. A linear fit to these data points will give  $\tau_r$  as the inverse of the y-intercept and D as the slope.



Figure 4.8: Schematic example plot of inverse grating lifetime  $\tau_g^{-1}$  versus grating wavevector  $q^2 = \frac{2\pi}{\Lambda}$ . The slope and intercept of a linear fit give the diffusion constant D and the inverse charge carrier recombination lifetime  $\tau_r^{-1}$ , respectively.

### 4.3 Experimental Setup

Successfully utilizing heterodyne detection in a transient grating setup requires excellent phase stability, particularly if measurements are to be obtained at a specific total phase  $\psi$ (equation 4.28). Slight jitter in an optic that one of the pump or probe beams passes through will cause phase oscillation that, if it exceeds  $\approx \Delta \psi = \pi/100$ , can drastically change the signal measured. If every beam follows a different beam path to the sample, these oscillations will multiply intolerably and make measurement impossible. To this end, it is advantageous to send the beams through as few optics as possible to minimize phase jitter.



Figure 4.9: Diagram of transient grating setup. Adapted with permission from Ref. [154].

This is achieved via a "boxcar" geometry and a diffractive optic (DO) to separate the beams. The boxcar and DO setup used in the experiments in this thesis is displayed in Figure 4.9. A pump and probe beam are focused onto a custom diffractive optic (Holoeve Inc., San Diego, CA), which is a slab of fused silica substrate with a series of 12 small  $(0.5 \times 0.5 \text{ cm}^2)$  diffraction gratings of varied slit spacing. The  $\pm 1$  orders of diffraction of the pump and probe beam are kept, turning the two beams (pump and probe) into four (two pump, two probe) beams. The beams are collected by a large collimating lens (CL), after which point they propagate parallel to each other with a cross-sectional pattern in which the beams are the corners of a square if  $\lambda_{pump} = \lambda_{probe}$  or trapezoid if  $\lambda_{pump} < \lambda_{probe}$ (Figure 4.10). The probe beams each pass through a 200  $\mu$ m thick glass coverslip, one of which is mounted on a piezoelectric rotation stage (Newport CONEX-AGP-PR100P) to allow fine rotation of the coverslip. The rotation of the coverslip causes the probe beam to travel a slightly longer or shorter beam path relative to the other probe beam, allowing for fine control over the beams' relative phase. The beams, collimated and traveling parallel to each other, are collected by a large focusing lens (FL), which focuses the beams to a single point. The focusing is verified with a 200  $\mu$ m pinhole next to and in the plane of the sample. By moving the pinhole horizontally and vertically through the beams and watching which beams appear and disappear in which order, the point of perfect overlap in the x-, y-, and z-directions can be determined. With pump beam spot size larger than probe beam spot size, perfect overlap in the xy-plane is signified by the following condition when moving the pinhole through the beams in the x-direction: the pumps appear simultaneously first, then the probes appear simultaneously, followed by the disappearance of the probes, then the pumps. Improper alignment of the pinhole in the z-direction is signified by the pumps (or the probes) appearing non-simultaneously – this shows that the pinhole is in front of or behind the beam overlap position, depending on which of the two pumps (or probes) appear first. The z-position of the sample is critical for maximizing signal and is controlled by a

motorized stage (Thorlabs Z825B). Once overlap is achieved on the pinhole, the sample is translated in the xy-plane into the beam overlap region.



Figure 4.10: Cross-sectional view of pump (lower) and probe (upper) beams in boxcar geometry between lenses CL and FL for (a) degenerate wavelengths  $\lambda_{pump} = \lambda_{probe}$  and (b) non-degenerate wavelengths  $\lambda_{pump} < \lambda_{probe}$ .

When using pump and probe wavelengths that differ, the angle of the beams out of the DO will be different for the pump and probe beams, as dictated by Bragg diffraction with a beam at normal incidence:

$$d\sin(\phi) = m\lambda \tag{4.34}$$

where d is the fringe spacing of the grating on the DO,  $\phi$  the diffracted angle of the beams, m the integer order of diffraction and  $\lambda$  the beam wavelength. Since no lens is perfectly achromatic, the beams will also experience different collimation and focusing lengths. For this reason, the lenses in the TG setup used here were bisected with a band saw and mounted on independent xyz stages for careful tuning. The top lenses (for the probe beams) and bottom lenses (for the pump beams) can be moved to the appropriate distance in the zdirection during alignment to assure complete overlap of all four beams. Beam movement in the x- and y-directions can be accomplished by moving the lenses in the x- and y-directions, but it is preferable and conducive to reproducibility to accomplish the same task simply by steering the beam entering the DO with a mirror placed prior to the setup.

The final grating period  $\Lambda$  on the sample compared to the DO fringe spacing d is calculated by plugging the angle out of the DO  $\phi$  of the first-order diffracted beam (equation 4.34) into equation 4.4 to obtain:

$$\Lambda = \frac{f_{FL}}{f_{CL}} * \frac{d}{2} \tag{4.35}$$

where  $f_{FL}$  and  $f_{CL}$  are the focal lengths of the focusing lens (FL in Figure 4.9) and collimating lens (CL in Figure 4.9) respectively. The experiments used in this thesis used lenses with 200 mm focal lengths for both CL and FL, giving a  $\Lambda$  value of d/2 in all cases.

The boxcar geometry ensures that the reference and diffracted beams will overlap regardless of input wavelength, since the pump and probe beams experience the same beam path length through the symmetrical TGS lens system. For a system with probe beams with angle  $\phi$  and  $-\phi$  relative to the surface normal, plugging in equation 4.4 to equation 4.6 shows that the diffracted beam angle will be

$$\sin(\phi_{-1}) = \sin(\phi) - \frac{2\lambda_{probe}\sin(\theta_{pump}/2)}{\lambda_{pump}}$$
(4.36)

Inserting equation 4.34 for pump and probe beams, where  $d = \Lambda$  and m = 1, equation 4.36 simplifies to

$$\sin(\phi_{-1}) = -\sin(\phi) \tag{4.37}$$

$$\phi_{-1} = -\phi \tag{4.38}$$

thus showing that the diffracted beam angle will overlap with the other probe beam for any combination of  $\lambda_{pump}$  and  $\lambda_{probe}$ .

Others have successfully used a boxcar geometry for heterodyne-detected transient grating experiments, sometimes using lenses [155–159], as described here, but often using large (5-10 inch diameter) spherical mirrors instead [137, 138, 144, 149, 160, 161]. The mirror setup offers several advantages: (1) A spherical mirror is naturally achromatic, eliminating the need for split lenses as described above. (2) A spherical mirror setup uses no transmissive optics, eliminating pulse dispersion, important for short pulse spectroscopy. (3) A spherical mirror setup often uses only one mirror, reducing the number of optical elements the beams encounter, and thus intrinsically reducing the phase jitter of the setup. This becomes particularly important if a specific value of phase  $\psi$  is needed during measurements (equation 4.28). In the experiments described here, the requirement for stable  $\psi$  is relaxed, since the TG quantity is only dependent on the amplitude of signal, not the phase. Lenses offer the advantage of being less bulky and more adaptable to a crowded laser table. A mirror with a huge diameter must be used to achieve the same beam angles on the sample that are obtainable with a smaller diameter lens system. The largest mirror currently commercially available with a suitable focal length is a 6" diameter mirror from Edmund Optics; the 3" diameter lenses used in this experiment are offered in stock by Thorlabs and Edmund Optics.

Transient grating measurements were performed with  $\sim 150$  fs laser pulses originating from a Ti:sapphire laser with a fundamental wavelength of 800 nm. 266 nm pump light was generated by reflecting a portion of the fundamental with a beam splitter and directing the beam onto multiple beta barium borate (BBO) crystals (kit from EKSMA Optics). The transmitted 800 nm probe beams were collected on Si photodiodes and recorded with a lockin amplifier using a Labview program that is detailed in Appendix A. The pump beam was mechanically chopped at 300 Hz for the purposes of lock-in detection. Further details on the experimental setup can be found in section 2.1.

### 4.4 Properties of gallium nitride

Gallium nitride (GaN) is a wide bandgap (3.4 eV) semiconductor most commonly exhibiting Wurtzite crystal structure (Figure 4.11). GaN is widely studied both experimentally and theoretically as a model for applications in catalysis because of its interesting surface chemistry. [162–165] Like other wide bandgap semiconductors such as  $TiO_2$  and  $SrTiO_3$  and unlike smaller bandgap semiconductors like GaAs and Si [166], GaN is resistant to corrosion in aqueous solution, making it an ideal candidate for photoelectrochemical studies that prioritize electrode stability.



Figure 4.11: (0001)-GaN unit cell displaying Wurtzite structure with Ga-polarity at the c-plane surface.

The bandgap of GaN can be better tuned to the solar spectrum by incorporating indium in place of gallium. Studies utilizing  $In_{x-1}Ga_xN$  have shown a bandgap tunable from 0.8 to 3.4 eV as x is varied from 0 to 1 [167]. The band edges of GaN straddle the water oxidation and reduction redox potentials [164, 168], and nano-structured or nanowire forms of GaN have been shown to enable photoelectrolysis of water as both anode and cathode. [169–175]

Although GaN is resistant to corrosion, photo-etching is possible in the presence of certain solutions (strong acid or base solutions like hydroxide or sulfuric acid) and illumination with above-bandgap light in a PEC cell. Etching speeds are faster on n-polar GaN and are proportional to the intensity of incident light. [176] In this study, pump fluences were kept low enough (0.06 mJ cm<sup>-2</sup>) to avoid photo-etching regimes. Corrosion of GaN in aqueous solutions occurs when the holes at the surface of the GaN transfer to the Ga/Ga<sup>3+</sup> redox couple, creating a Ga vacancy at the electrode surface as noted by equation 4.39. [168, 176–181]

$$2\operatorname{GaN}(s) + 6h^+ \to 2\operatorname{Ga}^{3+} + \operatorname{N}_2(g) \tag{4.39}$$

A carefully chosen aqueous electrolyte can impede this corrosion reaction by introducing a redox couple at a more favorable energetic level than the  $Ga/Ga^{3+}$  redox couple. Studies of the stability of GaN used in PEC cells with aqueous solution find that the use of hydrogen bromide (HBr) electrolyte increases the resistance of GaN to corrosion in comparison to other electrolytes such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) [182, 183]. This difference is due to the relative energetic placement of the redox couples in aqueous solution, as shown by Fig. 4.12. The Br<sup>-</sup> acts as a sacrificial reagent to accept the holes that would otherwise drive the gallium corrosion reaction.



Figure 4.12: n-GaN interface with aqueous electrolyte, displaying upward band bending at the interface and the position of relevant redox couples in acidic and neutral conditions. Black midgap band represents interfacial surface states formed during equilibration.

The undoped and Si-doped GaN (0001) films used in this study were purchased from MTI Corporation (Richmond, CA) and were grown nominally 5  $\mu$ m thick on C-plane sapphire by hydride vapour phase epitaxy (HVPE). Mott-Schottky plots yielded a doping density  $n_0$  of  $5 \times 10^{18}$  cm<sup>-3</sup>. A three-electrode customized Teflon electrochemical cell with CaF<sub>2</sub> optical windows was used to observe TGS dynamics *in situ*. Photoelectrochemical measurements were carried out at room temperature with Pt counter electrode and a Ag/AgCl reference electrode (MF-2052; Basi, West Lafayette, IN) using a CHI1140B Potentiostat (CH Instruments, Inc., Austin, TX) and constantly stirred. The electrolyte solution was 0.1 M HBr and 0.1 M Na<sub>2</sub>SO<sub>4</sub>. Ohmic contacts were made with Cu wire and InGa eutectic with Ag paste on n-GaN. Insulating lacquer covered the contact to only expose ~ 0.01 cm<sup>2</sup> of n-GaN.

#### 4.4.1 Electrochemical measurements

GaN features an array of midgap states that mediate catalysis via Fermi level pinning. [184, 185] This causes an array of water oxidation intermediates to be present on the surface of GaN in the dark. The equilibrated GaN surface at open circuit thus reproduces a surface environment like that of an active catalytic surface in a full 3-electrode cell, with a number of water intermediate species such as Ga=O or Ga-OH on the surface. [162, 186–188]



Figure 4.13: (a) Left: APCE (%) measured for n-GaN under xenon lamp illumination. Right: Absorbance vs. wavelength for n-GaN. Inset: Photocurrent density (mA cm<sup>-2</sup>) vs. Voltage (V vs. Ag/AgCl) used to calculate the xenon lamp APCE values. Different colors correspond to the various wavelengths tested. (b) APCE versus fluence for n-GaN under fs illumination (black) and xenon lamp illumination (black). Insets: CV curves used to calculate the fs illumination APCE values. Different colors represent different fluence values.

A series of electrochemical measurements establishes the degree to which Fermi-level pinning occurs, and the degree to which the surface environment at open circuit reproduces that of an active catalytic surface. First, the absorbed photon to current efficiency (APCE, measured as %) under illumination of a xenon lamp is displayed in Figure 4.13a. The APCE is a measure of the photo-catalytic activity of a material, calculated by

$$APCE = \frac{j_{photo} \cdot N_a \cdot h \cdot c}{\lambda \cdot \beta \cdot F}$$

$$(4.40)$$

where  $j_{photo}$  is photocurrent,  $N_a$  is Avogadro's constant, h is Planck's constant, c is the speed of light,  $\lambda$  is the excitation wavelength,  $\beta$  is the absorbed power, and F is Faraday constant. The APCE under xenon lamp illumination (Figure 4.13a) increases similarly to the absorbance as photon energy increases due to the greater absorbance of above-bandgap photons. The current-voltage (CV) curves used to generate the APCE data are shown in

the inset. The dependence of APCE on xenon lamp and femtosecond laser fluence was also measured and is displayed in Figure 4.13b. APCE drops off at higher fluence values due to greater electron-hole pair recombination. Both xenon lamp and fs illumination produces similar diode-like current turn-on behavior and APCE > 20% (insets of Figure 4.13), suggesting that the charge dynamics measured by ultrafast TGS measurements may also apply in continuous, broadband conditions such as a simulated solar spectrum.

The flatband potential  $V_{fb}$  and dopant density  $N_d$  can be calculated from capacitance measurements using the Mott-Schottky equation:

$$\frac{1}{C^2} = \frac{1}{C_H^2} \left\{ 1 + \frac{2C_H^2}{e_0 \epsilon \epsilon_0 N_d} \left( V - V_{fb} - \frac{k_B T}{e_0} \right) \right\}$$
(4.41)

Where C is the total capacitance,  $C_H$  is the capacitance of the Helmholtz layer,  $e_0$  is the elementary charge, and V is the applied voltage. Capacitance measurements were obtained with both xenon lamp (Figure 4.14) and 150 fs pulsed laser illumination (Figure 4.15) for 0.1 M electrolyte solutions of HBr, HCl, NaCl, and Na<sub>2</sub>SO<sub>4</sub>. Flatband voltages obtained from the x-intercept Mott-Schottky data in Figure 4.14 and Figure 4.15 (right column) display little difference in light and dark conditions. In addition, capacitance measurements taken under femtosecond illumination (Figure 4.15, left column) also show little effect of illumination at the fluence levels used in this study. This shows that no new surface states are created by the laser illumination, and TGS probes dark states created during the equilibration of the n-GaN surface with water.

The equilibrium open circuit potential (OCP) was measured as a function of time for each of the electrolyte species (Figure 4.16a). The open-circuit photovoltage  $(V_{ph})$  shows a linear dependence on the redox potential  $(V_{redox})$  of the solution with a slope of ~0.6 (Figure 4.16b). A slope of 1 implies no Fermi-level pinning. [64]. The OCP was also measured as a function of laser fluence with a pulsed fs laser source. The plateau displayed in Figure 4.16c above  $\approx 0.05 \text{ mJ cm}^{-2}$  is a direct measure of the potential drop in the semiconductor (band bending,  $V_{sc}$ ).

The values obtained from the electrochemical measurments described above can be used to estimate the surface charge and voltage of the GaN surface at equilibrium in the dark [59, 189]. The charge  $q_{sc}$  stored in the depletion layer, defined by the Schottky approximation, can be calculated from  $V_{sc}$  and  $N_d$  as:

$$q_{sc} = \sqrt{2\epsilon\epsilon_0 |e_0| N_d \left( V_{sc} - \frac{k_B T}{|e_0|} \right)} \tag{4.42}$$

where  $\epsilon$ ,  $\epsilon_0$ ,  $e_0$ , and  $N_d$  are the permittivity, vacuum permittivity, electric charge, and doping density respectively. The charge due to the Schottky approximation,  $q_{sc}$  (cm<sup>-2</sup>), and the surface charge at the interface,  $q_{ss}$  (cm<sup>-2</sup>) together determine the potential drop across the Helmholtz layer according to:

CHAPTER 4. TRANSIENT GRATING SPECTROSCOPY AS A PROBE OF SURFACE HOLE DIFFUSIVITY



Figure 4.14: Mott-Schottky plots in dark (blue trace) and under 266 nm xenon lamp illumination (red trace) with linear best fit line following equation 4.41, for n-GaN in the denoted 0.1 M electrolytes.

$$V_H = \frac{q_{sc} + q_{ss}}{C_H} \tag{4.43}$$

For a highly doped semiconductor, as considered in the present case, the measured capac-

itance depends on both the depletion layer and Helmholtz capacitances, i.e.  $\frac{1}{C} = \frac{1}{C_{sc}} + \frac{1}{C_H}$ . The relationship of the flatband potential  $(V_{fb})$  and the x-intercept  $(U_{C^{-2}=0})$  of the Mott-Schottky plot is derived from equation 4.41:

$$V_{C^{-2}=0} = V_{fb} + 0.059 \times (PZC - pH) + \frac{k_BT}{e_0} - \frac{e_0\epsilon\epsilon_0 N_d}{2C_H^2}$$
(4.44)

In the above, the flatband potential is corrected for the small dipole induced by a pH away from the point of zero charge (PZC), approximately pH = 6 in GaN. At open circuit,



Figure 4.15: A.C. voltammetry (left column) and Mott-Schottky (right column) plots in dark (black or blue traces) and under 266 nm pulsed laser illumination (red trace), for n-GaN in the denoted 0.1 M electrolyte.

CHAPTER 4. TRANSIENT GRATING SPECTROSCOPY AS A PROBE OF SURFACE HOLE DIFFUSIVITY



Figure 4.16: (a) OCP versus time measured for n-GaN in four different 0.1 M electrolyte species. (b) The equilibrium photovoltage values determined from (a) display a slope of 0.6, indicating partial Fermi level pinning. (c) OCP measurements as a function of pulsed 267 nm laser fluence for the various 0.1 M electrolytes.

$$V_{redox} - V_{fb} = V_H + V_{sc} \tag{4.45}$$

since the only voltage drop across the semiconductor/electrolyte junction is  $|V_{redox} - V_{fb}|$ .

Inserting equations 4.43 and 4.44 into equation 4.45 and setting  $C_H = 20 \ \mu F/cm^2$ , we determine  $V_H$  and  $q_{ss}$  for the different interfaces. Experimental inputs are the intercept of the Mott-Schottky plots in the dark  $(V_{C^{-2}=0})$  and the photovoltage  $(V_{sc})$  for each electrolyte. The surface charge  $(q_{ss})$  along with the voltage drop across the full junction,  $V_{fb}$ , the depletion width of the semiconductor,  $V_{sc}$ , and the Helmholtz layer,  $V_H$  are in shown in Table 4.1 for each electrolyte.

CHAPTER 4. TRANSIENT GRATING SPECTROSCOPY AS A PROBE OF SURFACE HOLE DIFFUSIVITY

Interface	$V_{redox}$ (V)	$V_{fb}$ (V)	$V_{sc}$ (V)	$V_H$ (V)	$q_{ss}$ (charge cm <sup>-2</sup> )	$\frac{V_H}{V_{fb}}(\%)$
GaN/HBr	0.94	-1.22	0.47	1.7	$5.3 \times 10^{14}$	78
$GaN/Na_2SO_4$	0.61	-1.28	0.48	1.41	$4.4 \times 10^{14}$	74

Table 4.1: Surface charge and potential distribution

### 4.5 Results

#### 4.5.1 Surface diffusivity of holes in GaN

Figure 4.17 demonstrates the variation in the interfacial diffusivity at undoped GaN and n-GaN interfaces with air and electrolyte. Based on the linear fit of  $\tau_g^{-1}$  vs.  $q^2$ , undoped GaN has a D of  $1.4 \pm 0.1 \text{ cm}^2 \text{ s}^{-1}$  in air, as shown in Fig. 4.17a. For undoped GaN,  $n_0 \sim 10^{15} \text{ cm}^{-3}$ and  $\Delta N \sim 10^{19} \text{ cm}^{-3}$ . Therefore, the moderate/high excitation regime of eq. 4.17 is accessed. Since  $D_h \ll D_e$  for GaN, TGS measures  $D_a \approx 2D_h$ . [190]  $D_a$  is comparable to previous values obtained by TGS experiments on GaN. [126, 127, 140] From  $D_h$ , the hole mobility determined by Einstein's relation,  $\mu_h = D_h(\frac{k_BT}{e})^{-1}$ , is 27 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. For comparison, the reported bulk value for undoped and n-GaN ranges from 300 - 5 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> [191–194]; a bulk  $\mu_h$  of ~10 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> has been found for majority holes in p-doped GaN. [195, 196]

When undoped GaN is introduced to an electrolyte environment, *e.g.* 0.1 M HBr, no significant change in diffusivity was observed. As shown in Fig 4.17a,  $D_a$  remains  $1.4 \pm 0.6 \text{ cm}^2 \text{ s}^{-1}$ . The inset shows the kinetics do not change between air and 0.1 M HBr for both the largest and smallest  $\Lambda$  used. Importantly, the data exhibits no substantial difference in kinetics for the range of grating periods measured, as can be seen by comparing Fig. 4.17c to Fig. 4.17d.

For n-GaN in air, D is found to be  $0.8 \pm 0.1 \text{ cm}^2 \text{ s}^{-1}$  (Fig. 4.17b) from the linear fit. Unlike in undoped GaN, the TGS of n-GaN approaches the low injection limit due to the increased  $n_0$ . [126] Although the calculated injection density at the earliest time scales,  $\Delta N$  ( $10^{19} \text{ cm}^{-3}$ ) is similar to  $n_0$  ( $5 \times 10^{18} \text{ cm}^{-3}$ ), two experimental considerations suggest a low injection limit. First, the effective injected carrier density at times where the diffusive decay manifests, namely around 200-400 ps, can be 5-10 times lower than the initial  $\Delta N$  reported for GaN because of changes to the carrier density profile by diffusion and recombination into the bulk. [130, 197, 198] Second, the TGS kinetics are independent of pump fluences which should change the carrier injection by an order of magnitude (Figure 4.18). Additionally, the diffusivity obtained experimentally for n-GaN is nearly equivalent to the  $D_h$  obtained for undoped GaN, which is the expected value of the low injection limit (*i.e.* half the ambipolar diffusivity). Taken together, the experimental considerations and the measured values of the carrier diffusivity demonstrate the TGS of n-GaN directly probes the hole carrier diffusivity ( $D \sim D_h$ ).

A significant increase in  $D_h$  to  $2.1 \pm 0.3 \text{ cm}^2 \text{ s}^{-1}$  is observed at the n-GaN/0.1 M HBr electrolyte interface, based on the linear fit of  $\tau^{-1}$  vs  $q^2$  (Fig. 4.17b). The change in kinetics



Figure 4.17: TGS spectrum decays at varied  $q^2$  values, as explained in Figure 4.8 and equation 4.16, for (a) undoped GaN and (b) n-GaN in air and electrolyte as noted. Inset: kinetic decays at the highest (solid) and lowest (dotted) grating periods  $\Lambda$  for each chemical environment (air vs. HBr) as noted by the color. (c)-(g) TGS kinetic decays plotted and modeled with equation 4.15. Curves offset vertically for clarity.



Figure 4.18: Inverse kinetic decay  $\tau_g^{-1}$  versus  $q^2$  for n-GaN in air (as in Figure 4.17b) at varied pump fluence levels. kinetic decays match closely to values expected for  $D_h$ , rather than  $2D_h$ , as dictated by equation 4.17 in the low injection limit.

between air and 0.1 M HBr environments is highlighted at the smallest and largest grating period in the inset of the Fig. 4.17b. The data over a range of grating periods shows significantly faster kinetics in electrolyte (Fig. 4.17f, g) compared to air (Fig. 4.17e). Taken together, the data and analysis show that  $D_h$  increases at the 0.1 M HBr interface by a factor of 2.6 from the air interface.

The increased hole diffusivity at the n-GaN/aqueous interface is not unique to an HBr electrolyte at pH = 1.4, but also occurs with an Na<sub>2</sub>SO<sub>4</sub> electrolyte at pH = 7, as shown in Fig. 4.17g. For 0.1 M Na<sub>2</sub>SO<sub>4</sub>,  $D_h$  is  $1.8 \pm 0.3$  cm<sup>2</sup> s<sup>-1</sup>, a factor of 2.2 increase from air. While the addition of the Br<sup>-</sup>/Br<sub>3</sub><sup>-</sup> redox potential and a change in pH does affect the interfacial hole diffusivity, it is not substantially altered. That is, in both cases, equilibration to the H<sub>2</sub>O/O<sub>2</sub> redox potential is what creates the unique n-GaN/aqueous electrolyte interface that changes the lateral diffusivity. The lack of a pronounced difference between the two electrolytes in terms of the overall surface composition is reflected in the similar behavior of the photovoltage (Fig. 4.16a) and that both interfaces lead to  $q_{ss} \sim 10^{14}$  cm<sup>-2</sup>.

Sample	$S\left(\frac{cm}{s}\right)$	$D_h\left(\frac{cm^2}{s}\right)$	$\tau_r \ (\mathrm{ps})$	$L_p (\mathrm{nm})$
GaN	$4.0 \times 10^{3}$	0.7	407	169
GaN (HBr)	$7.0 \times 10^{3}$	0.7	389	165
n-GaN	$1.6 \times 10^{4}$	0.8	1000	283
n-GaN (HBr)	$5.0 \times 10^{3}$	2.1	505	326
n-GaN (Na <sub>2</sub> SO <sub>4</sub> )	$2.5{ imes}10^4$	1.8	703	356

Table 4.2: Variables obtained from fits using diffraction efficiency model (eq. 4.15)

While it is expected that the dominant composition of the surface in the presence of

aqueous electrolytes will be a mixture of surface water species, the two electrolyte interfaces could have substantially different defect densities. Using the full TGS differential equation model mentioned in section 4.2.3 and equation 4.15 (shown as fits on the TGS kinetics of Fig 4.17c-g), this defect density can be quantified by the surface recombination velocity, S, reported in Table 4.2. A surface that is well passivated, *i.e.* low defect density, has a low S while a surface with many recombination centers has a high S. For undoped GaN,  $S = 4 \times 10^3$  cm s<sup>-1</sup> which agrees with previous experiments. [199] No change is observed when an aqueous electrolyte environment is introduced. For n-GaN/HBr, the aqueous electrolyte environment causes significant surface passivation, leading to almost an order of magnitude decrease in S from  $\sim 10^4$  cm s<sup>-1</sup> in air to  $\sim 10^3$  cm s<sup>-1</sup>. On the other hand, for the n- $GaN/Na_2SO_4$  aqueous interface, the S remains similarly high as at the air interface. This suggests that, while the defect density and surface recombination velocity are sensitive to the specific counter ions and pH of the aqueous electrolyte, the interfacial hole diffusivity is not. The substantially lower S determined for HBr is likely related to the lower photo-corrosion observed during catalysis, as compared to  $Na_2SO_4$ . The lower S suggests HBr mediates reactions that avoid trapping holes in defect sites of GaN, thought to create Ga<sup>3+</sup>. [177, 178, 200

The increase in the lateral hole diffusivity occurs uniquely at the n-GaN/aqueous electrolyte interface, which leads to insights into its origin. When the n-GaN/aqueous electrolyte interface equilibrates with the water oxidation reaction, a surface charge develops simultaneously with a depletion layer in the semiconductor and a Helmholtz screening layer at the interface. On the other hand, at the n-GaN/air interface, a depletion layer and at the undoped GaN/electrolyte interface, a Helmholtz screening layer, will develop separately and without a substantial surface charge. However, at both interfaces, the hole diffusivity remains ~0.7-0.8 cm<sup>2</sup> s<sup>-1</sup> (Table 4.2). Therefore, the change in the hole diffusivity that occurs at the n-GaN/aqueous interface is attributed to a surface charge that modifies the composition of surface water species. This finding is further substantiated by the fact that the interfacial hole diffusivity is sensitive to the overall composition of surface water species, and not specific defect centers, since S changes largely between the two electrolytes and D does not.

The suggested origin for the increase in interfacial hole mobility is depicted schematically in Fig. 4.19. The surface charge generated at the n-GaN/aqueous interface should modify surface water species by creating reaction intermediates and changing the distribution of hydroxylated and water adsorbed sites. A GaN (0001) surface with a monolayer of adsorbed water, calculated by DFT, leads to a distribution of Ga-OH and Ga-H<sub>2</sub>O sites. [162, 186] During equilibration at the n-GaN/aqueous interface, the distribution of these surface water species will alter, and could contain a significant population of Ga-OH and Ga-O<sup>\*</sup>, as suggested by ambient pressure photoemission of the n-GaN (0001) surface exposed to water [187] and by calculation of time scale evolutions of excited holes at different GaN surfaces. [188] At 300 K, phonon-assisted charge carrier hopping accompanied by PCET is expected between sites. [201]. Therefore, the equilibrated surface, which includes both localized charge in the form of reaction intermediates and neighboring sites to which the



Figure 4.19: GaN(0001) surface with Ga sites terminated by  $H_2O$ , OH, and O<sup>\*</sup> after equilibration with an aqueous 0.1 M HBr electrolyte. Holes from the nitrogen valence band hop on the surface (solid arrows), accompanied by proton release and capture (dotted arrows), before returning to the bulk.

charge can easily hop (e.g. Ga-OH), should increase surface hopping mobility. In the energy band description of this interface, equilibration increases the density of surface states and broadens the mid-gap band [202, 203] of the n-GaN/aqueous interface, in contrast to the undoped GaN/air, undoped GaN/aqueous, and n-GaN/air interfaces. Surface hopping could affect carrier mobility for many lattice lengths into the bulk for two reasons: (1) The surface states form a narrow, mid-gap band such that energy shifts in the photoluminescence reflect their filling with pH, as observed on GaN [185] and (2) Diffusion lengths are  $\sim 200$  nm in GaN (Table 4.2).

The increased interfacial carrier mobility can be considered one step in the catalytic process that creates a current pathway at the solid-liquid interface. One way to quantify the opening of this current pathway is through the mean square displacement of the charge carrier profile from the average position of the initial profile,  $\langle x^2 \rangle$  (t), along the air vs. electrolyte interface. The mean square displacement, according to  $\langle x^2 \rangle \sim Dt$ , increases by the same factor as the diffusivity, or by 2.6 at the n-GaN/HBr interface. The standard deviation ( $\sqrt{\langle x^2 \rangle}$ ) of the carrier profile is 60% higher and hence, a 60% larger interfacial distance is traversed at the electrolyte interface. Another way to quantify the opening of the current pathway, especially important for photo-catalysis, is the hole diffusion length,  $L_p = \sqrt{D_h \tau_r}$ . The hole diffusion lengths for the different interfaces are shown in Table 4.2. For undoped GaN in air and in aqueous electrolyte,  $L_p$  is ~200 nm in agreement with previous experiments. [194]  $L_p$  increases by ~100 nm for n-GaN, but mostly due to the increased recombination time  $\tau_r$ . On the other hand, an additional ~50 nm is observed when an aqueous electrolyte is introduced to the n-GaN surface and is due to the increased diffusivity, since  $\tau_r$  lowers. This demonstrates that at the n-GaN/electrolyte interface, photo-holes will

diffuse longer distances before recombining as a direct result of the increased diffusivity.

### 4.5.2 Kinetic Voltage Dependence

The effect of voltage application on the pump-probe and TG kinetic spectra on n-GaN was also considered. Samples of n-GaN were immersed in 0.1 M HBr and spectra were obtained as described previously while applying a fixed voltage in a three electrode cell at values ranging from -0.3 V to +1.2 V vs Ag/AgCl (Pt counter-electrode). Voltages were chosen to match with prominent voltage regions in the current-voltage curves shown in the inset of Figure 4.13b. Positive voltage application corresponds to an increase in the band bending of the n-GaN, as shown in Figure 4.12, while negative voltage application moves towards a flattening of the semiconductor bands.



Figure 4.20: (a) TGS kinetic traces of n-GaN with  $\Lambda = 5.6 \ \mu m$  and (b) pump-probe kinetic traces of n-GaN with applied voltages as noted.

Pump-probe spectra (Figure 4.20a) display low overall signal, which matches the trend of low PP component signal for all GaN samples measured in this study (*e.g.* Figure 4.7b). Although spectral kinetics is unchanged among the various voltages, a complete quenching of signal occurs as voltage moves from open circuit and negative voltages towards positive voltage application. Previous voltage-dependent transient infrared spectroscopic studies of n-GaN have noted that because of the large discrepancy between the effective mass of electrons and holes in GaN, pump-probe spectra are only capable of generating photo-generated electron, not hole, dynamics. [47] As the band bending in the n-GaN is increased (positive voltage application) all photo-generated electrons are swept away from the surface and out of the probing region, explaining the decrease in signal.

The TG data, in contrast, *is* capable of detecting the dynamics of photoexcited holes, as described in section 4.5.1. Two main changes in the TGS spectra (Figure 4.20b) are observed:

- 1. As voltage application increases, the spectral shape departs from a mono-exponential shape, changing into a multi-exponential decay, which coincides with the start of significant current flow in Figure 4.13b and other published reports [168, 174]. The initial decay constant shortens to a value < 10 picoseconds.
- 2. An offset with a lifetime of tens of nanoseconds or greater appears starting above +0.25 V and grows in until a plateau in around a value of +1 V vs Ag/AgCl.

These changes at positive voltages occur simultaneously with changes in the surface structure of the GaN, which is easily detectable by eye as a darkening of the surface. The spectral changes, then, are proposed here to result from (1) the increase in charge transfer at the surface along with (2) a simultaneous degradation of the surface caused by the infusion of a greater number of surface photoholes.

The first cause of spectral change (the increase in charge transfer) is shown by the coincident increase in current in the inset of Figure 4.13b and decrease in the lifetime of the first component of the kinetic decay in Figure 4.20b. This signal decay and current correspond to holes transferring to water as part of the water oxidation reaction. The second cause of spectral change (the appearance of an offset at higher positive voltage, attributed to surface damage) follows due to the greater oxidizing power of photoholes at this voltage. Although the tests are conducted in HBr to inhibit the photocorrosion of the GaN surface, voltage application combined with photoexcitation is known to cause etching on GaN (section 4.4). [176] The increase in corrosion at the GaN surface will create a high density of gallium vacancies which can act as traps for holes at the surface of the GaN. Since the electrons are swept away from the surface and HBr inhibits surface recombination, the holes are able to live for tens of nanoseconds, well beyond the time that can be probed by the delay stage in this experiment. An experiment on a microsecond to millisecond time scale could provide a better decay estimate for the long-lived offset.

One consequence of the multi-exponential spectral shape with applied voltage is the inability to determine a diffusion constant using the single exponential fit equation 4.16 given on page 66. Fitting the data with a single exponential decay curve gives passable results at negative or low positive voltage application (Figure 4.21a), but provides a poor fit at voltages greater than or equal to +0.25V (fit shown at +1.2 V in Figure 4.21b), underestimating the rate of decay at early time delays but overestimating at later time delays. A double exponential fit works well for all voltage levels and makes intuitive sense given the two-event decay process described in the previous paragraph. One intriguing possibility is the use of a stretched exponential fitting function. Stretched exponentials  $(\frac{\Delta T}{T} = A \exp[-t/\tau]^{\beta}$ , where dispersion parameter  $\beta$  is between 0 and 1) are primarily used to describe diffusion in disordered systems, including many semiconductor systems [204] such as amorphous silicon [205] and porous silicon [206, 207], as well as silicon nanocrystallites. [208–210] In a semiconductor, the dispersive diffusion process is frequently charge carrier hopping or trapping. The distinction between hopping and trapping is defined simply by the energetic depth of the trap and the probability of charge carrier tunneling to the next trap site. [211,



time delay (ps)

Figure 4.21: Comparison of single exponential  $(\frac{\Delta T}{T} = A \exp[-t/\tau])$ , double exponential  $(\frac{\Delta T}{T} = A_1 \exp[-t/\tau_1] + A_2 \exp[-t/\tau_2])$ , and stretched exponential  $(\frac{\Delta T}{T} = A \exp[-t/\tau]^{\beta}$ , where  $0 < \beta < 1$ ) fitting procedures on TGS kinetic data with  $\Lambda = 5.6 \ \mu m$  at (a) -0.3 V applied bias and (b) +1.2 V applied bias.

212] A stretched exponential arises when a diffusion process occurs without a homogeneous rate, but rather with an array of independent rates that can be expressed as a sum of exponential decays. [213] A value of  $\beta$  closer to zero represents a greater dispersion in the diffusion rates. At the surface of GaN, augmented by the oxidative potential of positive voltage, surface traps could be formed with an array of spatial arrangements and energetic positions in the bandgap, causing surface holes in those traps to move along the surface or hop between trapping sites at speeds independent of the other trapped holes and causing an array of independent decay rates described by a stretched exponential decay. This would be indicated by a lower value of  $\beta$  at higher voltages.

A summary of the most important parameters of the voltage-dependent TG decay fits for the three fit methods described here is shown in Figure 4.22. Higher voltages invariably show higher offset values  $y_0$  and lower decay lifetime  $\tau$  in all fit methods. Single exponential and stretched exponential fits display a transition at V = +0.5 V in all parameters, reflecting the rise in current shown at that voltage level in the inset of Figure 4.13b. The double exponential fit shows a decrease in  $\tau_1$  and an increase in  $\tau_2$  as voltage increases, reflecting the two-part decay kinetics seen in Figure 4.20b. The  $\beta$  parameter of the stretched exponential fit decreases as voltage is increased, reflecting the decrease in homogeneity of the surface as photo-assisted degradation processes work on the GaN surface.

### 4.6 Next Steps

The success of TGS to measure hole diffusivity on n-GaN in open-circuit conditions is promising but leaves many avenues of further research open, including:



Figure 4.22: A summary of the most important parameters of the fits to the data summarized in Figure 4.21. Higher voltages invariably show higher offset values  $y_0$  and lower decay lifetime  $\tau$ . Single exponential and stretched exponential fits display a transition at V = +0.5 V in all parameters. Double exponential fit shows a decrease in  $\tau_1$  and an increase in  $\tau_2$  as voltage increases, reflecting the two-part decay kinetics seen in Figure 4.20b.

- 1. Diffusivity measurements on n-GaN surfaces with a co-catalyst metal oxide layer deposited.
- 2. Diffusivity measurements of other promising electrode and catalyst materials.
- 3. Usage of heterodyne detection to separate dynamics that respond selectively to real or imaginary components of the TGS signal.
- 4. Diffusivity measurements of n-GaN anodes in operando in a full three-electrode cell

This section will briefly consider these experiments in order.
#### 4.6.1 TGS on n-GaN with cocatalysts

Many device architectures use a light absorber coupled to a catalytic component. The catalytic overlayer reduces the overpotential needed for reaction and can also provide a passivation and corrosion inhibition effect. Depositing a catalytic overlayer on the surface of n-GaN would mimic such a setup and could provide unique insights into the various functions of the overlayer. One interesting variable to study would be the thickness of the overlayer. With a very thin film deposited at open circuit, if charge transfer into the catalyst is facile, the catalytic overlayer may maintain the same layer of water oxidation intermediates seen on n-GaN in aqueous electrolyte and may see the same diffusivity enhancement observed on n-GaN. However, if the overlayer causes a Schottky barrier or recombination centers to form, the diffusivity values observed may change radically from the bare n-GaN case.

With a progressively thicker layer, the degree of coupling between electrode and catalytic overlayer could be tested. At the limit of a very thick layer, the catalytic overlayer may be completely uncoupled from the electrode if charge transfer into the catalytic overlayer is impeded, leading to diffusivity measurements that match the values obtained from the film alone, rather than the electrode/overlayer composite system. Facile charge transfer into and throughout the thick catalyst film, however, may produce values that match those obtained in the limit of a very thin catalytic overlayer, thus providing insight into the charge transfer into and throughout cataltyic films in real devices. A thick catalytic film would allow a control study of the importance of the mid-gap states of n-GaN, which were implicated in this work for the observed diffusivity increase. A comparison of two overlayers, one with significant surface charge, and one without significant surface charge, would give another gauge on the importance of surface reactivity on charge carrier diffusivity at a surface.

With a wide array of overlayer compositions, thicknesses, and morphologies (i.e. thin film, nanoparticle, amorphous or epitaxial), the potential experimental space is rich. Preliminary experiments in this direction were undertaken by sputtering a  $Co_3O_4$  overlayer onto n-GaN and performing TGS spectroscopy. A reliable diffusivity measurement was not achieveable due to overlayer degradation, as seen in Figure 4.23. The bare n-GaN film (Figure 4.23a) shows a terraced surface without heterogeneity (the large angular structures are surface debris). After  $Co_3O_4$  deposition (Figure 4.23b), streaks representing  $Co_3O_4$  domains with a size of tens of microns appear in directions that cut directly and diagonally across the n-GaN terraces. These streaks disappear, however, after exposure to 0.1 M HBr, suggesting dissolution of the overlayer film in the experimental conditions (Figure 4.23c). Small remnants of the films are visible hugging close under the edge of terraces in (Figure 4.23c), but most of the overlayer film is gone. The dissolution was also visible by eye as a slight change in opacity of the n-GaN in the area of the sample that was exposed to the electrolyte, when compared to an area that was protected by lacquer. A first step in this experimental direction, then, would be finding robust overlayers that can withstand many hours of exposure to electrolyte. both in the dark and while illuminated.

CHAPTER 4. TRANSIENT GRATING SPECTROSCOPY AS A PROBE OF SURFACE HOLE DIFFUSIVITY



Figure 4.23: SEM images of n-GaN with (a) no overlayer deposited, (b) 5 nm of  $Co_3O_4$  deposited via sputtering, and (c) the same film as (b) after approximately 1 hour exposure to to 0.1 M HBr electrolyte.

#### 4.6.2 TGS on other catalyst and electrode materials

There are many possible applications of TGS other than probing the effect of surface reactivity on charge carrier diffusivity, as in this work. The natural first step would be probing other materials used in artificial photosynthesis, both as composite devices as described in section 4.6.1 or as stand-alone systems. The limitation on material choices is the range of diffusivities in the materials. n-GaN, with diffusivities of about  $1 \text{ cm}^2 \text{ s}^{-1}$ , worked well in this study, in which  $\Lambda$  exhibited a range of 2-15  $\mu$ m. For materials with extremely large or extremely small diffusivity values, this range may not be sufficient. For example, a material with an extremely large diffusivity may cause diffusive decay to dominate the transient grating decay (section 4.2.3 and equation 4.16), causing no change in the measured diffraction efficiency even at large values of  $\Lambda$ . Experimentally, this would require a setup that allowed an extremely small angle  $\theta$  between the pump beams. The maximum value of  $\Lambda$  is ultimately limited by the diameter of the pump beam used. A material with an extremely small diffusivity, on the other hand, may not exhibit any diffusive decay even at the smallest values of  $\Lambda$ , causing the transient grating decay to be entirely dictated by recombination decay (eq. 4.16). Measuring such tiny diffusivities would require a very large angle  $\theta$  between the incident pump beams, which would require abandoning the boxcar geometry employed here (section 4.3), or using lenses or mirrors with an enormous diameter. An extreme example described by Eichler, Günter, and Pohl utilizes anti-parallel pump beams with  $\theta = 180^{\circ}$ . This would require abandoning the boxcar geometry of heterodyne detection, instead developing some other creative method of heterodyning (section 4.2.5). Such methods abandoning the boxcar setup are reported to allow values of  $\Lambda$  between 0.1 and 100  $\mu$ m. [136, p. 16]

#### 4.6.3 Heterodyne-dependent experiments

Calibration of a TGS setup allows for experiments with a fixed and defined value of beam phase  $\psi = \pi$  or  $\pi/2$ , accessing exclusively the birefringent or dichroic components of the transient grating signal (equation 4.27). This allows insights into excited state system

# CHAPTER 4. TRANSIENT GRATING SPECTROSCOPY AS A PROBE OF SURFACE HOLE DIFFUSIVITY

relaxation that pump-probe spectroscopy, in which the signal and probe beams are intrinsically phase-locked, cannot provide, as demonstrated in section 4.5.2. Many groups have utilized this capacity to probe dynamics selectively in a wide array of systems. [137, 138, 144–146, 151, 160, 161, 214–218] In this work, the beam phase  $\psi$  was tuned through at each time delay position and the amplitude of signal was measured. Measuring the time kinetics of signal at fixed phase points instead would be a way to measure the system's response to real versus imaginary components of the refractive index, providing more and different information than that presented in this study.

The boxcar setup used in this study is virtually identical to setups used for photon echo spectroscopy and 2-D IR spectroscopy. A slight change in the setup involving different levels of control over the various beam phases in the setup would allow for those experiments as well. [219–221]

#### 4.6.4 TGS in full 3-electrode setup

A potentially culminating experiment would be to combine experiments 4.6.1 and 4.6.2 to study catalysts, electrodes, or multi-component devices while in circuit and performing water oxidation in a three-electrode cell. The experiments reported in section 4.5.2 were subject to applied bias in a closed circuit, but damage issues hindered the determination of diffusivity, and the results reported in section 4.5.1 only considered charge on the surface at open circuit. This charge was present both on the semiconductor side of the interface and on surface intermediate species adsorbed onto the semiconductor. On a working photoanode, the intermediate species would be reacting continuously and desorbing as oxygen gas, taking the charge with them. This may introduce a new pathway for grating decay in the form of charge used in reaction, causing equation 4.16 to be altered to incorporate a reaction decay component  $\tau_{rxn}$ :

$$\tau_q^{-1} = \tau_r^{-1} + \tau_d^{-1} + \tau_{rxn}^{-1} \tag{4.46}$$

A plot of inverse decay time constants  $\tau_g^{-1}$  at varied values of  $q^2$  (Figure 4.8) would remain linear if  $\tau_{rxn}$  remains constant at all grating periods  $\Lambda$ . Since the reaction rate should proceed independent of the size of  $\Lambda$ , this is a valid assumption in the absence of factors that introduce disorder or damage to the surface, as described in section 4.5.2. The effect of  $\tau_{rxn}$ , then, would be to lower the y-intercept of Figure 4.8. In the event that  $\tau_{rxn}$  is extremely high, the combined recombination and reaction decay of the grating could dwarf  $\tau_d$ , making determination of diffusivity impossible. In this case, smaller values of  $\Lambda$  would need to be accessed.

# CHAPTER 4. TRANSIENT GRATING SPECTROSCOPY AS A PROBE OF SURFACE HOLE DIFFUSIVITY

## 4.7 Conclusion

Transient grating spectroscopy has been shown to be sensitive to changes in hole diffusivity in n-GaN. This ability distinguishes TGS from pump-probe spectroscopy, which is not sensitive to holes at the surface of GaN. Equilibrium hole diffusivity at the surface of GaN was found to increase by over two times only in the case of n-doped GaN in an aqueous environment, reflecting the presence of many water oxidation intermediates stemming from surface charge and the equilibration process with water. Charge is able to hop between surface intermediates that are mobile themselves, creating a new charge pathway for holes at the surface. These measurements are the first conclusively linking surface reactivity to an increase in charge carrier speed at the interface.

Further studies explored the role of voltage on the GaN electrodes in a three-electrode cell. Diffusivity values were unable to be resolved due to the appearance of non-monoexponential kinetics. However, the relative insensitivity of the biased system to pump-probe spectroscopy and the large signal obtained from TGS validated the use of TGS as a unique probe for holes at the surface of GaN. Changes in TGS signal were linked to an increase in surface damage and fitted with three potential fitting functions to explain the kinetic changes.

Proposed future experiments include the introduction of co-catalysts onto the electrode, the study of full buried junction model devices, and the introduction of a full three-electrode cell for studies of the system *in operando*.

## Appendix A

# TGS processing code and Labview programs

The TGS data collection process involves obtaining signal from at least six coverslip oscillation points at each time delay point in the transient data scan, on both detectors A and B, as described in sections 4.2.6 and 4.3. Ultimately, the amplitude of the oscillation represented by the data points at those six coverslip angles must be measured to obtain the quantity  $\frac{TG}{T}$  (equation 4.32). This appendix describes the Labview programs used to collect data as well as Igor processing scripts used to automate data processing. All program names are correct as of the publication date of this thesis.

### A.1 Main TGS data collection Labview program

The Labview program used to collect TGS data is called "TG\_TwoLockIn\_Draft.vi". There are six key buttons in the program. "Setup APT Motor" engages the Thorlabs software used to control the motor (Thorlabs Z825B) on the z-direction of the sample stage. "Setup Rotation Motor" opens a sub-VI to control the Newport CONEX-AGP-PR100P rotation stage that holds the rotating coverslip in one of the probe beams. "Setup Delay Stage Motor" opens a sub-VI to control the Newport FMS300CC delay stage. "Setup delays" and "Setup rotation" open an interface that allows the user to program the positions and step intervals for the delay stage and rotation stage respectively. Typical TGS scans used 100-200 delay stage points and 6 rotation points at each delay stage position. Finally, "Setup Lock-in" buttons initialize each of the lock-in detectors, notated as "lock-in A" and "lock-in B". A detailed description of the code supporting each of the buttons and the function of the overall program can be found by analyzing the block diagram for the VI.

Two\_LockIn\_Draft.vi creates one data column for each coverslip point (e.g. six signal columns, one for each coverslip angle setting). The number of rows (number m, say) corresponds to the number of time delay points, giving a matrix of m rows and 6 columns. To measure the amplitude of the oscillation, those columns must be transposed to get one

oscillation per time delay point, giving 6 rows and m columns. Plotting each column (in Igor, a "wave") against an x-axis of the coverslip angle in degrees or, more usefully, radians, gives a plot like that seen in Figure 4.7a. Via the batch curve fitting function in Igor, all of the n waves can be loaded and fit with a fitting function like that described in equation 4.30, *i.e.*  $A + B \cos(k\theta + \beta)$ . The parameters from the batch curve fit, A, B, and  $\beta$ , can then be used to calculate  $\frac{\Delta T}{T}$ ,  $\frac{TG}{T}$ , and  $\varphi_s$ . Details on transposition code and batch curve fitting are given in section A.3.

## A.2 Other useful Labview VIs

In addition to the main data collection program, a number of support VIs are useful and described below.

#### A.2.1 Signal oscillation at fixed time delay

It is frequently useful to monitor the amplitude of the signal oscillation in real time to verify that the sample is in the optimal z-axis position for overlap between pump and probe beams. This can be done quickly and simply by manually moving the coverslip and estimating the signal change on the lock-in detector over the course of an oscillation period change of  $\pi$ . It is occasionally necessary to plot the oscillation more formally. This could be for a more concrete visualization of oscillation magnitude, or multiple scans can be compared to measure the phase drift of signal over time.

The Labview VI "TG\_fixed\_timedelay\_vary\_coverslip\_Phasecheck.vi" allows recording of the oscillation in signal. The time delay stage is fixed at a chosen value and the coverslip rotation stage is scanned through a programmed itinerary of positions. The data results in an oscillatory signal such as that displayed in Figure 4.7a. As currently written, the program is unable to record signal from both detectors at once. Recording both detectors simultaneously is possible in "TG\_TwoLockIn\_Draft.vi" and that program could be used as a model if twodetector input is incorporated into "TG\_fixed\_timedelay\_vary\_coverslip\_Phasecheck.vi" in the future.

#### A.2.2 Kinetic decays at fixed coverslip angle

The inverse of "TG\_fixed\_timedelay\_vary\_coverslip\_Phasecheck.vi" is provided by the VI titled "TG\_fixed\_coverslip\_vary\_timedelay\_Phasecheck.vi". This program records signal over a user-inputted set of time delay stage positions with the coverslip rotation stage fixed at a particular angle. This program is not currently used in data collection but, given excellent beam phase stability, could be incorporated into a data collection scheme that collects three full scans of time delay stage at pre-determined fixed coverslip positions, as described in the last paragraph of section 4.2.5.

# A.2.3 Signal over absolute time at fixed coverslip angle and time delay position

Another measure of phase stability can be obtained by fixing the coverslip angle and delay stage positions at a given point and measuring the signal on the detector over absolute chronological time (not time delay). A setup exhibiting excellent phase stability will maintain a fairly constant signal value, whereas a setup exhibiting phase drift will show a moving signal value, and a setup with high phase jitter will show a high level of noise. This can be measured with the Labview program titled "TG\_Signal\_over\_Time\_fixedCoverslip\_fixedTimeDelay.vi". The program simply plots the signal on the detector versus time.

#### A.2.4 Signal versus sample z-axis position at fixed coverslip angle and time delay position

Lastly, it is important to align the sample surface at the overlap of all four beams for maximum signal. This is usually achievable by simply aligning the beams to a pinhole that is in the plane of the sample, then translating the sample in the xy-plane into the beams. The correct position can then be verified by manually moving the coverslip angle and monitoring the signal oscillation amplitude by noting the values displayed on the lock-in detector. A more formal way to find the optimal position, or a way to measure the sensitivity of signal to z-axis sample position, is available with the VI named "TG\_fixed\_timedelay\_vary\_zaxisAPTstage\_Phasecheck.vi". This program uses user-inputted positions to vary the z-axis position of the sample stage (controlled with a Thorlabs Z825B motor). The time delay stage and coverslip rotation stage positions are fixed.

## A.3 Igor scripts for TGS processing

The following is a description and repository of code I developed within Igor Pro to greatly decrease the manual processing needed to analyze TGS data. The code works with data collected using the Labview VI "TG\_TwoLockIn\_Draft.vi". Future researchers using the same setup, Labview code, and Igor Pro may find it useful to replicate or copy the code in this appendix for their work. I give full permission to all other researchers to use the code verbatim or in parts. The code can also be downloaded from my Dropbox for as long as the file stays in my Dropbox and Dropbox remains in business [222]. Computer scientists would cringe at my organization and coding style; this is something I was learning as I went, and a careful reader may notice style improvement in later code blocks. Plugging this code into the Procedure window in Igor will trigger some helpful color-coding. Also included in the Dropbox folder are two raw data files (one signal file and one choppered probe file) to test the code with. The names and number of waves in one data file is detailed in Table A.1.

With the root folder selected in an Igor experiment, the order in which the functions are run is the following:

Column name	number of columns	Description
X_mm	1	Each time delay point on the delay stage in mm
X_fs	1	Each time delay point on the delay stage in fs
X_Xav	2n	Lock-in signal magnitude for the current scan
X_Xse	2n	Variance on lock-in signal magnitude for the current scan
X_Phase	2n	Lock-in signal phase for the current scan
X_Av_Xav	2n	Lock-in signal magnitude running average for all scans
X_Av_Xse	2n	Variance on lock-in signal magnitude running average for all scans
X_Av_Phase	2n	Lock-in signal phase running average for all scans

Table A.1: TGS Labview program (TG\_TwoLockIn\_Draft.vi) data for 2 detectors and n coverslip angle points

- 1. MFP(), short for "move files phase", initiates open file sequences for a signal data file and a choppered probe data file. All the waves in the signal file are loaded, and a menu allows selection of the waves desired from the choppered probe file. All waves except one X\_Av wave and one X\_Phase wave for each detector A and B (four waves in total) should be skipped. The function then creates folders and organizes the waves, and turns raw data into  $\Delta R/R$ , the transient reflectivity change (or equivalently, the transient transmittance change), by incorporating phase from the lock-in for the signal and choppered probe data files. Full details can be determined by examining the code within the function.
- 2. Tp(), short for "transpose", transposes m columns and n rows into n columns and m rows and puts the new transposed waves into one folder for each of the A and B detectors. This gives one wave of six data points for each time delay point for each detector.
- 3. Batch Curve Fitting is an Igor applet that allows many waves to be fit using the same fitting function. It is found in the Analysis menu under Packages. A new batch should be made in the folder containing the transposed waves and titled either "A" or "B" depending on which detector is used this titling is important for the function used in the next step. In "Batch Data Setup", select "Y from a set of 1D waves, X from a single 1D wave". Choose all the transposed waves in the Y section and the Radian wave in the X column, then proceed to Functions and Coefficients. Using the cosFit fitting function (included with the code) for GaN, frequency is generally fixed at 650 (this value can be tested on individual transposed waves), with other values free to move and set initially to values of 0.1. The batch is then run and the results undergo a cursory inspection before the next step. An ambitious next step for a future researcher

would be to automate this process within the rest of the code, so that this step and the next may be combined.

4. wf(), short for "wave fitting", moves the Batch Curve Fitting results for each detector A and B to the root folder, then runs exdata(), which uses the fitting results to calculate TG,  $\Delta R/R$ , and  $\varphi_s$ , along with a few other quantities.

A further useful applet is PlotPanel, which displays the signal oscillation waves for both A and B detectors against the radian value of the coverslip oscillation. PlotPanel can be used after step 1 above. After the code given in this section is compiled, PlotPanel is found in the Panel Macros submenu of the Windows Menu. Selection of PlotPanel may initially give an error because the variable used to index the graphs is not defined; select Quit Macro, then enter makenumwaves() into the Command Window. This function initializes the counter in PlotPanel to run from 0 up to one less than the number of waves in the data folder "PerRefl\_T\_A\_BS". Now when the arrows next to the counter on the PlotPanel window are clicked, a graph is displayed showing the A and B detector oscillation curves for the time-delay point selected. This can be used to find phase-determination errors in the automated script MFP(), which can then be fixed manually by editing the wave containing the offending point.

The code is reproduced below and at the link cited here. [222]

```
#include <Kill Waves>
```

```
Function MFP() //large script that does many things. 1: creates folders
        // and places files into them. 2. divides data waves by choppered probe
        // wave to obtain deltaR/R. 3. Subtracts background from the waves. The
        // final product is six waves for each detector, in units of deltaR/R (%),
        // each representing a different coverslip angle.
        NewDataFolder root:A
        NewDataFolder root:B
        NewDataFolder root:Raw
        NewDataFolder root:A:Raw
        NewDataFolder root:A:PerRefl_A
        NewDataFolder root:A:PerRefl_A_BS
        NewDataFolder root:A:PerRefl_T_A_BS
        NewDataFolder root:A:Raw:PhaseSubtr
        NewDataFolder root:A:Raw:Phase_adjust
        NewDataFolder root:B:Raw
        NewDataFolder root:B:PerRefl_B
        NewDataFolder root:B:PerRefl_B_BS
        NewDataFolder root:B:PerRefl_T_B_BS
        NewDataFolder root:B:Raw:PhaseSubtr
        NewDataFolder root:B:Raw:Phase_adjust
        SetDataFolder root: //open data wave and its CP wave
        OpenFunc()
        CP()
        OpenFuncCP()
        SetDataFolder root:
        //establishing variables and strings...
        String waves = WaveList("*",";","")
        String wave0
```

```
String PhaseSubtrA
String PhaseAdjustA
String PhaseSubtrB
String PhaseAdjustB
Variable i=0
Variable j=0
Variable m = ItemsInList(WaveList("*",";",""))
for (i=0; i < m; i+=1) //This for loop organizes the raw waves into
                      //their correct folders.
        wave0=StringFromList(i, waves)
        Wave SortWave = $wave0
        Variable sm1 = StringMatch(wave0, "X_Av*")
        Variable sm2 = StringMatch(wave0, "X_Xse*")
        if (sm1 = 1 || sm2 = 1)
                MoveWave SortWave, root:Raw:
        endif
        Variable sm3 = StringMatch(wave0, "X_Xav_A*")
        Variable sm4 = StringMatch(wave0, "X_Phase_A*")
        if (sm3 = 1 || sm4 = 1)
                MoveWave SortWave, root:A:Raw:
        endif
        Variable sm5 = StringMatch(wave0, "X_Xav_B*")
        Variable sm6 = StringMatch(wave0, "X_Phase_B*")
        if (sm5 = 1 || sm6 = 1)
                MoveWave SortWave, root:B:Raw:
        endif
endfor
SetDataFolder root: CP: // establishing more variables and strings ...
String wavesCP = WaveList("*",";","")
String waveCP
String wavel
String Aphase
String Bphase
String AXav
String BXav
String filestring CP = "root: CP:"
String filestringARaw = "root:A:Raw:"
String filestringBRaw = "root:B:Raw:"
String filestringARaw_phaseadj = "root:A:Raw: Phase_adjust:"
String filestringBRaw_phaseadj = "root:B:Raw: Phase_adjust:"
String filestringAPer_Refl = "root:A:PerRefl_A:"
String \ filestring BPer\_Refl = "root:B:PerRefl\_B:"
Variable n = ItemsInList(WaveList("*",";","))
for (i=0; i<=n; i+=1) //this for loop gives all the CP data full file
                       //path names so it can be used from other folders.
        waveCP=StringFromList(i, wavesCP)
if (StringMatch(waveCP, "X_Xav_A_*") ==1)
                AXav = filestring CP + wave CP
                Wave A_Xav =  AXav
        elseif (StringMatch(waveCP, "X_Xav_B_*") ==1)
                BXav = filestring CP + wave CP
                Wave B_Xav = BXav
        elseif (StringMatch(waveCP, "X_Phase_A_*") ==1)
```

APhase = filestringCP + waveCP Wave A\_Phase = \$APhase

```
elseif (StringMatch(waveCP, "X_Phase_B_*") ==1)
BPhase = filestringCP + waveCP
Wave B_Phase = $BPhase
```

endif

```
endfor
i=0 //This block of code subtracts CP phase data from actual
        //phase data for the A waves. It also creates waves that
        //are 1 or -1 for negative/positive phase adjustments.
SetDataFolder root:A:Raw:
for (i=0; i <=m; i+=1)
        wave0=StringFromList(i,waves)
        if (StringMatch(wave0, "X_Phase_A_*") == 1)
                PhaseSubtrA = filestringARaw + wave0 + "_PhaseSubtr"
                PhaseAdjustA = filestringARaw + wave0 + "_PhaseAdjust"
                Wave numprtsref = wave0
                Make/N=(numpnts(numpntsref)) $PhaseSubtrA
                Wave PhasesubA = PhaseSubtrA
                wave1 = filestringARaw + wave0
                         //wavel is the full file path string
                         //for the current loop wave
                Wave waveone = wave1
                         //make a wave for the full file path
                         //of the current loop wave
                PhasesubA = waveone - A_Phase
//subtract CP phase from A wave phase
                Make/N=(numpnts(numpntsref)) $PhaseAdjustA
                Wave PhaseadjA = PhaseAdjustA
                for (j=0; j < numpnts (PhasesubA); j+=1)
                         //if less than 90, put a 1 in the
                         //phase adjustment wave, else -1
                         if (abs(PhasesubA[x2pnt(PhasesubA,j)])<90)
                                 PhaseadjA[x2pnt(PhaseadjA, j)] = 1
                         else
                                 PhaseadjA[x2pnt(PhaseadjA, j)] = -1
                         endif
                endfor
                MoveWave PhasesubA, root:A:Raw:PhaseSubtr:
                         //move it into correct folder
                MoveWave PhaseadjA, root:A:Raw:Phase_adjust:
        endif
endfor
i = 0
j=0 //This block of code subtracts CP phase data from actual
        //phase data for the B waves. It also creates waves that
        //are 1 or -1 for negative/positive phase adjustments.
SetDataFolder root:B:Raw:
for (i=0; i <=m; i+=1)
        wave0=StringFromList(i,waves)
        if (StringMatch(wave0, "X_Phase_B_*") == 1)
                PhaseSubtrB = filestringBRaw + wave0 + "_PhaseSubtr"
                PhaseAdjustB = filestringBRaw + wave0 + "_PhaseAdjust"
                Wave numprtsref = wave0
                Make/N=(numpnts(numpntsref))  $PhaseSubtrB
                Wave PhasesubB = PhaseSubtrB
                wave1 = filestringBRaw + wave0
                         //wavel is the full file path string
                         //for the current loop wave
```

```
Wave waveone = wave1
                         //make a wave for the full file path
                         //of the current loop wave
                PhasesubB = waveone - B_Phase
                         //subtract CP phase from A wave phase
                Make/N=(numpnts(numpntsref)) $PhaseAdjustB
                Wave PhaseadjB = PhaseAdjustB
                for(j=0; j<numpnts(PhasesubB); j+=1)</pre>
                         //\,\mathrm{if} less than 90, put a 1 in the
                         // phase adjustment wave, else -1
                         if (abs(PhasesubB[x2pnt(PhasesubB,j)])<90)
                                 PhaseadjB[x2pnt(PhaseadjB, j)] = 1
                         else
                                 PhaseadjB[x2pnt(PhaseadjB, j)] = -1
                         endif
                endfor
                MoveWave PhasesubB, root:B:Raw:PhaseSubtr:
                         //move it into correct folder
                MoveWave PhaseadjB, root:B:Raw:Phase_adjust:
        endif
endfor
//The following block of code takes the raw Xav waves for A,
//divides them by CP_A wave, multiplies by the phase correction
//number (-1 or 1) wave, and multiplies by 100.
//Gives percent reflectance change for A waves.
String PerRefl_A
SetDataFolder root:A:Raw:
String fullwaveXavA
String fullwavePadjA
String waveXavA
String wavePadjA
String wavesXAvA = WaveList("X_Xav*",";","")
Variable itemsA = ItemsInList(wavesXAvA)
SetDataFolder root:A:Raw: Phase_adjust:
String wavesPhaseadjA = WaveList("X_Phase*",";","")
for (i=0; i \le i \le i \le A; i+=1)
        waveXavA=StringFromList(i, wavesXAvA)
        SetDataFolder root:A:Raw:
        Wave numpntsref_refl = $waveXavA
        Variable wavestrlenA = strlen(waveXavA)
        String numlwA = waveXavA[wavestrlenA -7, wavestrlenA -6]
        String num2wA = waveXavA [wavestrlenA -4]
        wavePadjA=StringFromList(i, wavesPhaseadjA)
        Variable phasestrlenA = strlen(wavePadjA)
        String numlpA = wavePadjA[phasestrlenA - 19, phasestrlenA - 18]
        String num2pA = wavePadjA[phasestrlenA -16]
        Variable stA1 = StringMatch(waveXavA,"X-Xav-A-"+num1wA+"-"+num2wA+"*")
        Variable stA2 = StringMatch (wavePadjA, "X_Phase_A_"+num1pA+"_"+num2pA+"*")
        if (stA1 = 1 \&\& stA2 = 1)
                fullwaveXavA= filestringARaw + waveXavA
```

```
fullwavePadjA = filestringARaw\_phaseadj + wavePadjA
PerRefl_A = filestringARaw + waveXavA + "PerRefl_A"
Wave fullpathXavA = $fullwaveXavA
Wave fullpathPadjA = fullwavePadjA
```

```
//Make/O $PerRefl_A
```

```
Wave A_PerRefl = PerRefl_A
```

```
A_PerRefl = fullpathXavA*100*fullpathPadjA/A_Xav
```

```
//A_PerRefl = fullpathXavA*100/A_Xav
```

endif

i = 0

MoveWave A\_PerRefl, root:A:PerRefl\_A:

endfor

//The following block of code takes the raw Xav waves for B,  $//\,{\rm divides}$  them by CP\_B wave, multiplies by the phase correction //number (-1 or 1) wave, and multiplies by 100. //Gives percent reflectance change for B waves. i = 0String PerRefl\_B SetDataFolder root:B:Raw: String fullwaveXavB String fullwavePadjB String waveXavB String wavePadjB String wavesXAvB = WaveList("X\_Xav\*",";","") Variable itemsB = ItemsInList(wavesXAvB) SetDataFolder root:B:Raw:Phase\_adjust: String wavesPhaseadjB = WaveList("X\_Phase\*",";","") for  $(i=0; i \le itemsB; i+=1)$ waveXavB=StringFromList(i, wavesXAvB) SetDataFolder root:B:Raw Wave numpntsref\_refl = \$waveXavB Variable wavestrlenB = strlen(waveXavB) String num1w = waveXavB[wavestrlenB-7, wavestrlenB-6]String num2w = waveXavB[wavestrlenB-4] wavePadjB=StringFromList(i, wavesPhaseadjB) Variable phasestrlenB = strlen(wavePadjB)String num1p = wavePadjB[phasestrlenB-19, phasestrlenB-18]String num2p = wavePadjB[phasestrlenB -16] Variable stB1 = StringMatch (waveXavB, "X\_Xav\_B\_"+num1w+"\_"+num2w+"\*") Variable stB2 = StringMatch (wavePadjB, "X\_Phase\_B\_"+num1p+"\_"+num2p+"\*") if (stB1 = 1 && stB2 = 1)fullwaveXavB = filestringBRaw + waveXavBfullwavePadjB = filestringBRaw\_phaseadj + wavePadjB  $PerRefl_B = filestringBRaw + waveXavB + "PerRefl_B"$ Wave fullpathXavB =\$fullwaveXavB Wave fullpathPadjB =fullwavePadjB Wave  $B_PerRefl = PerRefl_B$  $B_PerRefl = fullpathXavB*100*fullpathPadjB/B_Xav$  $//B_PerRefl = fullpathXavB*100/B_Xav$ endif MoveWave B\_PerRefl, root:B:PerRefl\_B: endfor //The following block of code averages the first  $// \, three$  values of the PerRefl\_A wave and subtracts //that value from the wave, creating the background //subtracted wave PerRefl\_A\_BS i = 0j=0String PerReflA\_BS Variable PointcounterA Variable AverageA SetDataFolder root:A:PerRefl\_A: Variable p = ItemsInList(WaveList("\*",";",")) String PerReflA\_waves = WaveList ("\*",";","") AverageA=0 for (i=0; i < p; i+=1)wave0=StringFromList(i, PerReflA\_waves) Wave  $PerReflA_wave0 =$ \$wave0 for (j=0; j <=3; j+=1) $PointcounterA = PerReflA_wave0(j)$ 

```
AverageA += PointcounterA
                endfor
        endfor
        AverageA/=(4*p)
        print "Background A: " + num2str(AverageA)
        i = 0
        for (i=0; i < p; i+=1)
                wave0=StringFromList(i,PerReflA_waves)
                Wave PerReflA_wave1 = $wave0
                PerReflA_BS = filestringAPer_Refl + wave0 + "_BS"
                Duplicate PerReflA_wave1, $PerReflA_BS
                Wave BS_PerReflA = PerReflA_BS
                BS_PerReflA-=AverageA
                MoveWave BS_PerReflA, root:A:PerRefl_A_BS:
        endfor
        //The following block of code averages the first
        //three values of the PerRefl_B wave and subtracts
        //that value from the wave, creating the background
        //subtracted wave PerRefl_B_BS
        i = 0
        j=0
        String PerReflB_BS
        Variable PointcounterB
        Variable AverageB
        SetDataFolder root:B:PerRefl_B:
        p = ItemsInList(WaveList("*",";",""))
        String PerReflB_waves = WaveList("*",";","")
        AverageB=0
        for (i=0; i < p; i+=1)
                wave0=StringFromList(i,PerReflB_waves)
                Wave PerReflB_wave0 = $wave0
                for (j=0; j <=3; j+=1)
                         PointcounterB = PerReflB_wave0(j)
                         AverageB+=PointcounterB
                endfor
        endfor
        AverageB/=(4*p)
        print "Background B: " + num2str(AverageB)
        i = 0
        for (i=0; i < p; i+=1)
                wave0=StringFromList(i,PerReflB_waves)
                Wave PerReflB_wave1 = $wave0
                PerReflB_BS = filestringBPer_Refl + wave0 + "_BS"
                Duplicate PerReflB_wave1, $PerReflB_BS
                Wave BS_PerReflB = PerReflB_BS
                BS\_PerReflB-=AverageB
                MoveWave BS_PerReflB, root:B:PerRefl_B_BS:
        endfor
Conrad()
dispAwaves()
dispBwaves()
Function ConRad() //Converts X_deg wave into radians
                  //and deletes superfluous zero points.
        SetDataFolder root:
        Wave X_deg
        Duplicate X_deg, Radian //make radian wave same as X_deg
        Variable minnum
```

End

minnum = wavemin(X\_deg) //minimum value of X\_deg

```
Radian = (X_deg-minnum)*(pi/180) //convert to radians
        Variable i=0
        for (i=0; i \le numpnts (Radian); i+=1)
                 //loop through the points in the wave. When a zero
                 //is encountered, delete it and all the points following.
                 if (Radian [x2pnt(Radian, i)]==0)
                          DeletePoints i, numpnts (Radian), Radian
                 endif
        endfor
        Duplicate Radian, Radian0
        //create two extra copies for transfer to T_BS folders
        Duplicate Radian, Radian1
        MoveWave \ Radian0 \ , \ :A \colon PerRefl_T_A_BS : Radian
        MoveWave Radian1, :B:PerRefl_T_B_BS:Radian
End
// displays all six time delay waves from detector A,
// so that any obviously wrong phase determinations
// by the lock-in can be corrected by hand
Function dispAwaves()
        SetDataFolder root:
        Wave X_fs
        SetDataFolder \ root:A:PerRefl_A_BS
        String Awaves = WaveList("*",";","")
        Variable numAwaves = ItemsInList(Awaves)
        Variable i = 0
        String currentWave
        Display
        Make/N=6 red = \{0, 65535, 0, 65535, 0, 0\}
        Make/N=6 green = {0,45535,65535,0,65535,0}
        Make/N=6 blue = \{0, 0, 65535, 0, 20000, 65535\}
        for (i = 0; i < numAwaves; i +=1)
                 currentWave = StringFromList(i,Awaves)
                 Wave currWave = $currentWave
                 AppendToGraph currWave vs root:X_fs
                 ModifyGraph lsize = 2
                 ModifyGraph rgb($currentWave) = (red[i], green[i], blue[i])
        endfor
        ModifyGraph zero(left)=1
        KillWaves /A/Z
End
// displays all six time delay waves from detector B,
// so that any obviously wrong phase determinations // by the lock-in can be corrected by hand
Function dispBwaves()
        SetDataFolder root:
        Wave X_fs
        SetDataFolder root:B:PerRefl_B_BS
        String Bwaves = WaveList("*",";","")
        Variable numBwaves = ItemsInList(Bwaves)
        Variable i = 0
        String currentWave
        Display
        Make/N=6 red = \{0, 65535, 0, 65535, 0, 0\}
        Make/N=6 green = \{0, 45535, 65535, 0, 65535, 0\}
        Make/N=6 blue = \{0, 0, 65535, 0, 20000, 65535\}
        for (i = 0; i < numBwaves; i +=1)
                 currentWave = StringFromList(i, Bwaves)
                 Wave currWave = $currentWave
                 AppendToGraph currWave vs root: X_{fs}
                 ModifyGraph lsize = 2
                 ModifyGraph rgb($currentWave) = (red[i], green[i], blue[i])
```

endfor ModifyGraph zero(left)=1 KillWaves /A/Z

#### End

Function Tp()

```
transposeA()
transposeB()
makenumwaves()
```

#### End

```
Function transposeA()
        SetDataFolder root:A:PerRefl_A_BS:
        String Awaves = Wavelist("X_Xav_A*",";","")
        String firstwave = stringfromlist (0, Awaves)
        Wave wave1 = $firstwave
        Variable wavelen = numpnts(wave1) //number of time delay point waves
        Variable wavelistlen = ItemsInList(Awaves) //number of coverslip point waves
        Variable i = 0
        Variable j = 0
        for (i = 0; i < wavelen; i += 1)
                 //for each time delay point
                 for (j = 0; j < wavelistlen; j += 1)
                         //for each coverslip point within that time delay point
String Twavename = "PerRefl_T_A_BS_" + num2str(i)
                                  //transposed wave names
                         Make/O/N=(wavelistlen) $Twavename
                                  //make the transposed waves
                         Wave Twave = Twavename
                                  //make it manipulable
                         String currWave = StringFromList(j, Awaves)
                                  //get name of jth coverslip wave
                         Wave currentWave = $currWave //make it manipulable
                         Variable wavePnt = currentWave[i]
                                  //get the ith value from that wave
                         Twave[j] = wavePnt //put the ith value into the
                                              //jth spot of the transposed wave.
                 endfor
                 MoveWave Twave, :: PerRefl_T_A_BS: //move to the correct folder
```

#### End

endfor

```
Function transposeB()
          SetDataFolder root:B:PerRefl_B_BS:
          String Bwaves = Wavelist("X_Xav_B*",";","")
          String firstwave = stringfromlist (0, Bwaves)
          Wave wave1 = $firstwave
          \label{eq:Variable wavelen} \begin{array}{l} \mbox{Variable wavelen} = \mbox{numpris}(\mbox{wavel}) \ //\mbox{number of time delay point waves} \\ \mbox{Variable wavelistlen} = \mbox{ItemsInList}(\mbox{Bwaves}) \ //\mbox{number of coverslip point waves} \end{array}
          Variable i = 0
          Variable j = 0
          for (i = 0; i < wavelen; i += 1)
                    //for each time delay point
                    for (j = 0; j < wavelistlen; j += 1)
                              //for each coverslip point within that time delay point
                              String Twavename = "PerRefl_T_B_BS_" + num2str(i)
                                         //transposed wave names
                              Make/O/N=(wavelistlen) $Twavename
                                         //make the transposed waves
                              Wave Twave = $Twavename //make it manipulable
                              String currWave = StringFromList(j, Bwaves)
                                         //get name of jth coverslip wave
                              Wave currentWave = $currWave //make it manipulable
```

```
Variable wavePnt = currentWave[i]
                                //get the ith value from that wave
                        Twave[j] = wavePnt //put the ith value into the
                                           //jth spot of the transposed wave.
                endfor
                MoveWave Twave, :: PerRefl_T_B_BS: //move to the correct folder
        endfor
End
Function MakenumWaves() //When executed from the command window, this makes a
                        //wave that counts from 0 to the total number of A waves.
                        //The counter is then set to be that value.
        SetDataFolder root:A: 'PerRefl_T_A_BS ':
        Make/O/N=(ItemsInList(WaveList("*",";","))) numWaves=x
        setVariable setvar0, value=numWaves
End
Window PlotPanel() : Panel
                                       // building window...
        PauseUpdate; Silent 1
        NewPanel /W=(997, 186, 1140, 235)
        ShowTools/A
        SetVariable setvar0, pos = \{14, 15\}, size = \{110, 16\}, proc=SetVarProc, title="Select Wave"
        SetVariable setvar0, limits = {0,151,1}, value= root:A: 'PerRefl T A BS':numWaves[0]
EndMacro
Function wf()
        SetDataFolder root:A:PerRefl_T_A_BS:WMBatchCurveFitRuns:A:
        wfA()
        SetDataFolder root:B:PerRefl_T_B_BS:WMBatchCurveFitRuns:B:
        wfB()
        exdata()
End
Function wfA() //This moves the ResultsMatrix for B waves to the root folder.
               //Start with the directory containing WMResultsMatrix
               //as the working directory
        Wave WMBatchResultsMatrix
        Duplicate WMBatchResultsMatrix, WMBatchResultsMatrix_moverA
        End
Function wfB()//This moves the ResultsMatrix for B waves to the root folder.
              //Start with the directory containing WMResultsMatrix
              //as the working directory
        Wave WMBatchResultsMatrix
        Duplicate \ WMB atchResultsMatrix , \ WMB atchResultsMatrix\_moverB
        MoveWave WMBatchResultsMatrix_moverB, root:WMBatchResultsMatrix_B
End
Function exData()
        //\mathrm{This} function takes the results of batch curve fitting
        //and removes the relevant data, giving each its own wave.
        //The relevant data is TG, deltaR, phi_s, and a couple
        //other ancillary functions, DELTA and epsilon, which
        //were initally thought useful but were ultimately not.
        //"exdata" is short for "extract data".
        //part one: pull individual results waves from ResultsMatrix
        SetDataFolder root:
        Wave WMBatchResultsMatrix_A
```

```
Wave WMBatchResultsMatrix_B
\label{eq:constraint} Duplicate/R= \ [] \ [0 \ , 0] \ WMBatchResultsMatrix_A \ , \ offset_A
Redimension/N=-1 offset_A
//Redimension takes the matrix wave and makes it a single column wave
Duplicate/R= [] [0,0] WMBatchResultsMatrix_B, offset_B
Redimension/N=-1 offset_B
Duplicate/R= [] [1,1] WMBatchResultsMatrix_A, amplitude_A
Redimension/N=-1 amplitude_A
Duplicate/R= [] [1,1] WMBatchResultsMatrix_B, amplitude_B
Redimension/N=-1 amplitude_B
Duplicate/R= [] [3,3] WMBatchResultsMatrix_A, phase_A
Redimension/N=-1 phase_A
Duplicate/R= [] [3,3] WMBatchResultsMatrix_B, phase_B
Redimension/N=-1 phase_B
Variable j=0 //Make amplitude waves positive and adjust
             //corresponding point in phase waves by Pi
for (j=0; j<numpnts(amplitude_A); j+=1)
        if (amplitude_A[x2pnt(amplitude_A,j)] <0)
                 amplitude_A [x2pnt(amplitude_A, j)] *= -1
                 phase_A[x2pnt(phase_A, j)] += Pi
        endif
endfor
Variable i=0
for (i=0; i < numpnts (amplitude_B); i+=1)
        if (amplitude_B[x2pnt(amplitude_B, i)] <0)
                 amplitude_B[x2pnt(amplitude_B, i)] *= -1
                 phase_B[x2pnt(phase_B, i)] += Pi
        endif
endfor
Duplicate amplitude_A, TG // Create TG wave as average of adjusted amplitude waves
TG = (amplitude_A + amplitude_B)/2
Duplicate offset_A , deltaR
deltaR = (offset_A + offset_B)/2 //Create deltaR wave as average of offset waves
Variable k=0 //Adjust outlier values in phase waves. It's a loop that says,
              //" if the value of the point is greater than 2*Pi, subtract
             //2Pi until it is less than 2*Pi. Or if the value of the point
             // is less than 0, add 2Pi until it is greater than 0.
             //In this way, all points coalesce to the range 0<x<2*Pi
for (k=0; k < numpnts (phase_A); k+=1)
        do
                 if (phase_A [x2pnt(phase_A, k)] \ge 0)
                         break
                 endif
                 phase_A[x2pnt(phase_A, k)] += 2*Pi
        while (phase_A [x2pnt(phase_A, k)] < 0)
endfor
k=0
for (k=0; k< numpnts(phase_A); k+=1)
        do
                 if (phase_A [x2pnt(phase_A, k)] \le 2*Pi)
                         break
                 endif
                 phase_A[x2pnt(phase_A, k)] -= 2*Pi
        while (phase_A [x2pnt(phase_A, k)] > 2*Pi)
endfor
k=0
for (k=0; k< numpnts(phase_B); k+=1)
        do
```

```
if (phase_B[x2pnt(phase_B, k)] \ge 0)
                                   break
                          endif
                          phase_B[x2pnt(phase_B, k)] += 2*Pi
                 while (\text{phase}_B [x2\text{pnt}(\text{phase}_B, k)] < 0)
        endfor
        k=0
        for (k=0; k< numpnts(phase_B); k+=1)
                 do
                          if (phase_B[x2pnt(phase_B, k)] \le 2*Pi)
                                   break
                          endif
                          phase_B[x2pnt(phase_B, k)] -= 2*Pi
                 while (phase_B [x2pnt (phase_B, k)] > 2*Pi)
        endfor
        {\tt Duplicate\ phase\_A}\ ,\ {\tt phi\_s}\ //\,{\tt create\ phi\_s}\ {\tt wave\ as\ average\ of\ phase\ waves}
        phi_s = (phase_B - phase_A)/2
        Duplicate TG, TGcosphi_s //compare sign of TGphi_s to deltaR point by point.
        //If TGphi-s is positive but deltaR negative, counter TGpos +=1. If TGphi-s
        // is negative but deltaR positive, counter TGneg +=1. If either of these
        //counters exceeds half the total points of the scan, adjust phase_A or
        //phase_b by adding 2*Pi.
        TG cosphi_s = TG*(cos(phi_s))
        k=0
        Variable TGpos = 0
        Variable TGneg = 0
Variable TG_deltaR_same = 0
        for (k=0; k<numpnts(TGcosphi_s); k+=1)</pre>
                 Variable signTG = sign(TGcosphi_s[x2pnt(TGcosphi_s, k)])
                 Variable signR = sign(deltaR[x2pnt(deltaR, k)])
                 if (signTG = 1 \&\& signR = -1)
                          TGpos+=1
                 elseif (signTG == -1 && signR == 1)
                          TGneg+=1
                 else
                          TG_deltaR_same +=1
                 endif
        endfor
        if (TGpos \ge (TGpos+TGneg+TG_deltaR_same)/2)
                 phase_B+=2*Pi
                 phi_s = (phase_B - phase_A)/2
                 TGcosphi_s = TG*(cos(phi_s))
         elseif (TGneg >= (TGpos+TGneg+TG_deltaR_same)/2)
                 phase_A+=2*Pi
                 phi_s = (phase_B - phase_A)/2
                 TGcosphi_s = TG*(cos(phi_s))
        endif
        Duplicate deltaR, DELTA //\,{\tt create} delta wave
        DELTA = deltaR / (cos(phi_s))
        Duplicate TG, epsilon //create epsilon wave
        epsilon = TG/DELTA
Function cosFit(w,x) : FitFunc
        Wave w
        Variable x
```

End

```
//CurveFitDialog/ These comments were created by the Curve Fitting dialog.
//CurveFitDialog/ Altering them will make the function less convenient
//CurveFitDialog/ to work with in the Curve Fitting dialog.
//CurveFitDialog/ Equation:
//CurveFitDialog/ f(x) = offset + amplitude*cos(frequency*x + phase)
//CurveFitDialog/ End of Equation
//CurveFitDialog/ Independent Variables 1
//CurveFitDialog/ x
//CurveFitDialog/ x
//CurveFitDialog/ w[0] = offset
//CurveFitDialog/ w[1] = amplitude
//CurveFitDialog/ w[2] = frequency
//CurveFitDialog/ w[3] = phase
```

return  $w[0] + w[1] * \cos(w[2] * x + w[3])$ 

End

## Bibliography

- UN Department of Economic and Social Affairs, Population Division. World Population Prospects: The 2015 Revision., https://esa.un.org/unpd/wpp/, custom data acquired via website; accessed 5-October-2016.
- (2) Scripps Inst. of Oceanography. Note on Reaching the Annual Low Point., https: //scripps.ucsd.edu/programs/keelingcurve/2016/09/23/note-on-reachingthe-annual-low-point/, accessed 5-October-2016.
- (3) Schwartz, J. A Milestone for Carbon Dioxide in the Atmosphere., http://www. nytimes.com/2016/10/04/science/atmospheric-carbon-dioxide-400-ppm. html, accessed 5-October-2016.
- (4) The Intergovernmental Panel on Climate Change. Climate Change 2013: The Physical Science Basis; tech. rep., online at https://www.ipcc.ch/report/ar5/wg1/. Accessed 5-October-2016; The Intergovernmental Panel on Climate Change, 2013.
- (5) Herbert, G. J.; Iniyan, S.; Sreevalsan, E.; Rajapandian, S. A review of wind energy technologies. *Renewable and Sustainable Energy Reviews* **2007**, *11*, 1117–1145.
- (6) Kaldellis, J. K.; Zafirakis, D. The wind energy (r)evolution: A short review of a long history. *Renewable Energy* **2011**, *36*, 1887–1901.
- (7) Saxena, R.; Adhikari, D.; Goyal, H. Biomass-based energy fuel through biochemical routes: A review. *Renewable and Sustainable Energy Reviews* **2009**, *13*, 167–178.
- (8) Berndes, G.; Hoogwijk, M.; van den Broek, R. The contribution of biomass in the future global energy supply: a review of 17 studies. *Biomass and Bioenergy* 2003, 25, 1–28.
- (9) Field, C. B.; Campbell, J. E.; Lobell, D. B. Biomass energy: the scale of the potential resource. *Trends in Ecology & Evolution* **2008**, *23*, 65–72.
- (10) Lund, J. W.; Boyd, T. L. Direct utilization of geothermal energy 2015 worldwide review. *Geothermics* **2016**, *60*, 66–93.
- (11) Jean, J.; Brown, P. R.; Jaffe, R. L.; Buonassisi, T.; Bulović, V. Pathways for solar photovoltaics. *Energy & Environmental Science* 2015, 8, 1200–1219.
- (12) Spiro, T. G.; Stigliani, W. M. In; Prentice Hall: Upper Saddle River, NJ, 2003; Chapter 1, p 9.

- (13) Dunn, B.; Kamath, H.; Tarascon, J.-M. Electrical Energy Storage for the Grid: A Battery of Choices. *Science* 2011, 334, 928–935.
- (14) Wang, Y.; Chen, K. S.; Mishler, J.; Cho, S. C.; Adroher, X. C. A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research. *Applied Energy* **2011**, *88*, 981–1007.
- (15) Edwards, P.; Kuznetsov, V.; David, W.; Brandon, N. Hydrogen and fuel cells: Towards a sustainable energy future. *Energy Policy* 2008, *36*, Foresight Sustainable Energy Management and the Built Environment Project, 4356–4362.
- (16) Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* 1972, 238, 37–38.
- (17) Yoneyama, H.; Sakamoto, H.; Tamura, H. A Photo-electrochemical Cell with Production of Hydrogen and Oxygen by a Cell Reaction. *Electrochim. Acta* 1975, 20, 341–345.
- (18) Kainthla, R.; Zelenay, B.; Bockris, J. Significant Efficiency Increase in Self-Driven Photoelectrochemical Cell for Water Photoelectrolysis. J. Electrochem. Soc. 1987, 134, 841–845.
- (19) Khaselev, O.; Turner, J. A. A Monolithic Photovoltaic-Photoelectrochemical Device for Hydrogen Production via Water Splitting. *Science* **1998**, *280*, 425–427.
- (20) Licht, S.; Wang, B.; Mukerji, S.; Soga, T.; Umeno, M.; Tributsch, H. Efficient Solar Water Splitting, Exemplified by RuO<sub>2</sub>-Catalyzed AlGaAs/Si Photoelectrolysis. J. Phys. Chem. B 2000, 104, 8920–8924.
- (21) Khaselev, O.; Bansal, A.; Turner, J. High-efficiency integrated multijunction photovoltaic/electrolysis systems for hydrogen production. *International Journal of Hydrogen Energy* 2001, 26, Third International Symposium on New Materials, Renewable Energy and Environment, 127–132.
- (22) Reece, S. Y.; Hamel, J. A.; Sung, K.; Jarvi, T. D.; Esswein, A. J.; Pijpers, J. J.; Nocera, D. G. Wireless solar water splitting using silicon-based semiconductors and earth-abundant catalysts. *Science* **2011**, *334*, 645–648.
- (23) Ager, J. W.; Shaner, M. R.; Walczak, K. A.; Sharp, I. D.; Ardo, S. Experimental demonstrations of spontaneous, solar-driven photoelectrochemical water splitting. *Energy Environ. Sci.* 2015, 8, 2811–2824.
- (24) Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. Chemical Society Reviews **2009**, *38*, 253–278.
- (25) Chen, L.; Alarcón-Lladó, E.; Hettick, M.; Sharp, I. D.; Lin, Y.; Javey, A.; Ager, J. W. Reactive Sputtering of Bismuth Vanadate Photoanodes for Solar Water Splitting. *The Journal of Physical Chemistry C* 2013, 117, 21635–21642.

- (26) Kay, A.; Cesar, I.; Grätzel, M. New Benchmark for Water Photooxidation by Nanostructured α-Fe<sub>2</sub>O<sub>3</sub> Films. Journal of the American Chemical Society 2006, 128, PMID: 17147381, 15714–15721.
- (27) Cox, C. R.; Winkler, M. T.; Pijpers, J. J. H.; Buonassisi, T.; Nocera, D. G. Interfaces between water splitting catalysts and buried silicon junctions. *Energy Environ. Sci.* **2013**, 6, 532–538.
- (28) Winkler, M. T.; Cox, C. R.; Nocera, D. G.; Buonassisi, T. Modeling integrated photovoltaic–electrochemical devices using steady-state equivalent circuits. *Proceed*ings of the National Academy of Sciences **2013**, 110, E1076–E1082.
- (29) Sun, K.; Saadi, F. H.; Lichterman, M. F.; Hale, W. G.; Wang, H.-P.; Zhou, X.; Plymale, N. T.; Omelchenko, S. T.; He, J.-H.; Papadantonakis, K. M.; Brunschwig, B. S.; Lewis, N. S. Stable solar-driven oxidation of water by semiconducting photoanodes protected by transparent catalytic nickel oxide films. *Proceedings of the National Academy of Sciences* **2015**, *112*, 3612–3617.
- (30) Zhong, D. K.; Cornuz, M.; Sivula, K.; Grätzel, M.; Gamelin, D. R. Photo-assisted electrodeposition of cobalt–phosphate (Co–Pi) catalyst on hematite photoanodes for solar water oxidation. *Energy & Environmental Science* **2011**, *4*, 1759–1764.
- (31) Herlihy, D. M.; Waegele, M. M.; Chen, X.; Pemmaraju, C.; Prendergast, D.; Cuk, T. Detecting the oxyl radical of photocatalytic water oxidation at an n-SrTiO<sub>3</sub>/aqueous interface through its subsurface vibration. *Nature chemistry* 2016.
- (32) Waegele, M.; Chen, X.; Herlihy, D.; Cuk, T. How Surface Potential Determines the Kinetics of the First Hole Transfer of Photo-Catalytic Water Oxidation. J. Am. Chem. Soc. 2014, 136, 10632–10639.
- (33) Li, Y.-F.; Liu, Z.-P.; Liu, L.; Gao, W. Mechanism and Activity of Photocatalytic Oxygen Evolution on Titania Anatase in Aqueous Surroundings. *Journal of the American Chemical Society* **2010**, *132*, PMID: 20738085, 13008–13015.
- (34) Zhang, Y.; Zhang, H.; Ji, H.; Ma, W.; Chen, C.; Zhao, J. Pivotal Role and Regulation of Proton Transfer in Water Oxidation on Hematite Photoanodes. J. Am. Chem. Soc. 2016, 138, 2705–2711.
- (35) Zhang, M.; Frei, H. Towards a Molecular Level Understanding of the Multi-Electron Catalysis of Water Oxidation on Metal Oxide Surfaces. *Catal. Lett.* 2015, 145, 420– 435.
- (36) Brimblecombe, R.; Dismukes, G. C.; Swiegers, G. F.; Spiccia, L. Molecular wateroxidation catalysts for photoelectrochemical cells. *Dalton Trans.* **2009**, 9374–9384.
- (37) Man, I. C.; Su, H.-Y.; Calle-Vallejo, F.; Hansen, H. A.; Martínez, J. I.; Inoglu, N. G.; Kitchin, J.; Jaramillo, T. F.; Nørskov, J. K.; Rossmeisl, J. Universality in Oxygen Evolution Electrocatalysis on Oxide Surfaces. *ChemCatChem* **2011**, *3*, 1159–1165.

- (38) Katz, J. E.; Gingrich, T. R.; Santori, E. A.; Lewis, N. S. Combinatorial synthesis and high-throughput photopotential and photocurrent screening of mixed-metal oxides for photoelectrochemical water splitting. *Energy Environ. Sci.* 2009, *2*, 103–112.
- (39) Greeley, J.; Jaramillo, T. F.; Bonde, J.; Chorkendorff, I.; Nørskov, J. K. Computational high-throughput screening of electrocatalytic materials for hydrogen evolution. *Nature materials* 2006, 5, 909–913.
- (40) Moulton, P. F. Spectroscopic and laser characteristics of Ti:Al<sub>2</sub>O<sub>3</sub>. J. Opt. Soc. Am. B Jan. 1986, 3, 125–133.
- (41) Zewail, A. H. Laser Femtochemistry. Science 1988, 242, 1645–1653.
- (42) Loh, Z.-H.; Leone, S. R. Capturing Ultrafast Quantum Dynamics with Femtosecond and Attosecond X-ray Core-Level Absorption Spectroscopy. *The Journal of Physical Chemistry Letters* **2013**, *4*, PMID: 26283437, 292–302.
- (43) Pendlebury, S. R.; Barroso, M.; Cowan, A. J.; Sivula, K.; Tang, J.; Grätzel, M.; Klug, D.; Durrant, J. R. Dynamics of photogenerated holes in nanocrystalline α-Fe<sub>2</sub>O<sub>3</sub> electrodes for water oxidation probed by transient absorption spectroscopy. *Chemical Communications* **2011**, 47, 716–718.
- (44) Willis, R. L.; Olson, C.; O'Regan, B.; Lutz, T.; Nelson, J.; Durrant, J. R. Electron dynamics in nanocrystalline ZnO and TiO<sub>2</sub> films probed by potential step chronoamperometry and transient absorption spectroscopy. *The Journal of Physical Chemistry* B 2002, 106, 7605–7613.
- (45) Cherepy, N. J.; Liston, D. B.; Lovejoy, J. A.; Deng, H.; Zhang, J. Z. Ultrafast studies of photoexcited electron dynamics in  $\gamma$ -and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> semiconductor nanoparticles. *The Journal of Physical Chemistry B* **1998**, *102*, 770–776.
- (46) Furube, A.; Asahi, T.; Masuhara, H.; Yamashita, H.; Anpo, M. Charge carrier dynamics of standard TiO<sub>2</sub> catalysts revealed by femtosecond diffuse reflectance spectroscopy. *The Journal of Physical Chemistry B* **1999**, *103*, 3120–3127.
- (47) Yamakata, A.; Yoshida, M.; Kubota, J.; Osawa, M.; Domen, K. Potential-Dependent Recombination Kinetics of Photogenerated Electrons in n- and p-Type GaN Photoelectrodes Studied by Time-Resolved IR Absorption Spectroscopy. J. Am. Chem. Soc. 2011, 133, 11351–11357.
- (48) Hoffmann, R. How Chemistry and Physics Meet in the Solid State. Angewandte Chemie International Edition in English **1987**, 26, 846–878.
- (49) Xu, Y.; Schoonen, M. A. The absolute energy positions of conduction and valence bands of selected semiconducting minerals. *American Mineralogist* 2000, 85, 543– 556.
- (50) Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S. Solar Water Splitting Cells. *Chemical Reviews* **2010**, *110*, PMID: 21062097, 6446–6473.

#### BIBLIOGRAPHY

- (51) Streetman, B. G., *Solid State Electronic Devices (6th Ed.)* Prentice-Hall, Inc.: Upper Saddle River, NJ, USA, 1995.
- (52) Debbar, N.; Biswas, D.; Bhattacharya, P. Conduction-band offsets in pseudomorphic  $In_xGa_{1-x}As/Al_{0.2}Ga_{0.8}As$  quantum wells ( $0.07 \le x \le 0.18$ ) measured by deep-level transient spectroscopy. *Phys. Rev. B* July 1989, 40, 1058–1063.
- (53) Yu, E. T.; McCaldin, J. O.; McGill, T. C. In, Ehrenreich, H., Turnbull, D., Eds.; Solid State Physics, Vol. 46; Academic Press: 1992, pp 1–146.
- (54) Moniz, S. J.; Shevlin, S. A.; Martin, D. J.; Guo, Z.-X.; Tang, J. Visible-light driven heterojunction photocatalysts for water splitting–a critical review. *Energy & Envi*ronmental Science **2015**, *8*, 731–759.
- (55) Calow, J.; Deasley, P.; Owen, S.; Webb, P. A review of semiconductor heterojunctions. Journal of Materials Science 1967, 2, 88–96.
- (56) Bard, A.; Faulkner, L., *Electrochemical Methods Fundamentals and Applications*, 2nd; John Wiley and Sons Ltd.: New York City, New York, 2002.
- (57) Hodes, G., *Electrochemistry of nanomaterials*; John Wiley & Sons: 2008.
- (58) Nozik, A. J.; Memming, R. Physical chemistry of semiconductor-liquid interfaces. *The Journal of Physical Chemistry* **1996**, *100*, 13061–13078.
- (59) Uosaki, K.; Kita, H. Effects of the Helmholtz Layer Capacitance on the Potential Distribution at Semiconductor/Electrolyte Interface and the Linearity of the Mott-Schottky Plot. J. Electrochem. Soc. 1983, 130, 895–897.
- (60) Bard, A.; Bocarsly, A.; Fan, F.-R.; Walton, E.; Wrighton, M. The Concept of Fermi Level Pinning at Semiconductor/Liquid Junctions. Consequences for Energy Conversion Efficiency and Selection of Useful Solution Redox Couples in Solar Devices. J. Am. Chem. Soc. 1980, 102, 3671–3677.
- (61) Quarto, F. D.; Bard, A. J. Semiconductor electrodes. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry 1981, 127, 43–58.
- (62) Cardon, F.; Gomes, W. On the determination of the flat-band potential of a semiconductor in contact with a metal or an electrolyte from the Mott-Schottky plot. *Journal of Physics D: Applied Physics* **1978**, *11*, L63.
- (63) Oskam, G.; Hoffmann, P. M.; Schmidt, J. C.; Searson, P. C. Energetics and kinetics of surface states at n-type silicon surfaces in aqueous fluoride solutions. *The Journal* of Physical Chemistry **1996**, 100, 1801–1806.
- (64) Nagasubramanian, G.; Wheeler, B.; Fan, F.-R.; Bard, A. XLII. Evidence for Fermi Level Pinning from Shifts in the Flatband Potential of p-Type Silicon in Acetonitrile Solutions with Different Redox Couples. J. Electrochem. Soc. **1982**, 129, 1742–1745.
- (65) Hu, S.; Shaner, M. R.; Beardslee, J. A.; Lichterman, M.; Brunschwig, B. S.; Lewis, N. S. Amorphous TiO<sub>2</sub> coatings stabilize Si, GaAs, and GaP photoanodes for efficient water oxidation. *Science* **2014**, *344*, 1005–1009.

- (66) Tilley, S. D.; Cornuz, M.; Sivula, K.; Grätzel, M. Light-Induced Water Splitting with Hematite: Improved Nanostructure and Iridium Oxide Catalysis. Angewandte Chemie 2010, 122, 6549–6552.
- (67) Dalal, V. L. Hole Velocity in p-GaAs. Applied Physics Letters 1970, 16, 489–491.
- (68) Dalal, V. L.; Dreeben, A. B.; Triano, A. Temperature Dependence of Hole Velocity in p-GaAs. *Journal of Applied Physics* **1971**, *42*, 2864–2867.
- (69) Quay, R.; Moglestue, C.; Palankovski, V.; Selberherr, S. A temperature dependent model for the saturation velocity in semiconductor materials. *Materials Science in Semiconductor Processing* 2000, 3, 149–155.
- (70) Blakemore, J. S. Semiconducting and other major properties of gallium arsenide. Journal of Applied Physics **1982**, 53, R123–R181.
- (71) Ruello, P.; Gusev, V. Physical mechanisms of coherent acoustic phonons generation by ultrafast laser action. *Ultrasonics* **2015**, *56*, 21–35.
- (72) Williams, R. E., Modern GaAs processing methods; Artech House Publishers: 1990.
- (73) Waegele, M.; Doan, H.; Cuk, T. Long-lived photoexcited carrier dynamics of d-d excitations in spinel ordered Co<sub>3</sub>O<sub>4</sub>. J. Phys. Chem. C **2014**, 118, 3426–3432.
- (74) Aspnes, D. E.; Kelso, S. M.; Logan, R. A.; Bhat, R. Optical properties of  $Al_xGa_{1-x}As$ . Journal of Applied Physics **1986**, 60, 754–767.
- (75) Schubert, M.; Gottschalch, V.; Herzinger, C. M.; Yao, H.; Snyder, P. G.; Woollam, J. A. Optical constants of Ga<sub>x</sub>In<sub>1-x</sub>P lattice matched to GaAs. *Journal of Applied Physics* 1995, 77, 3416–3419.
- (76) Jellison, G. Optical functions of GaAs, GaP, and Ge determined by two-channel polarization modulation ellipsometry. *Optical Materials* **1992**, *1*, 151–160.
- (77) Liao, P. C.; Ho, W. S.; Huang, Y. S.; Tiong, K. K. Characterization of sputtered iridium dioxide thin films. *Journal of Materials Research* May 1998, 13, 1318–1326.
- (78) Wright, O. B.; Perrin, B.; Matsuda, O.; Gusev, V. E. Ultrafast carrier diffusion in gallium arsenide probed with picosecond acoustic pulses. *Phys. Rev. B* Aug. 2001, 64, 081202.
- (79) Babilotte, P.; Ruello, P.; Vaudel, G.; Pezeril, T.; Mounier, D.; Breteau, J.-M.; Gusev, V. Picosecond acoustics in p-doped piezoelectric semiconductors. *Appl. Phys. Lett.* 2010, *97*, 174103.
- (80) Young, E.; Akimov, A.; Campion, R.; Kent, A.; Gusev, V. Picosecond strain pulses generated by a supersonically expanding electron-hole plasma in GaAs. *Physical Re*view B 2012, 86, 155207.
- (81) McSkimin, H. J.; Jayaraman, A.; Andreatch, P. Elastic Moduli of GaAs at Moderate Pressures and the Evaluation of Compression to 250 kbar. *Journal of Applied Physics* 1967, 38, 2362–2364.

- (82) Voßebürger, M.; Roskos, H.; Wolter, F.; Waschke, C.; Kurz, H.; Hirakawa, K.; Wilke, I.; Yamanaka, K. Radiative decay of optically excited coherent plasmons in a twodimensional electron gas. JOSA B 1996, 13, 1045–1053.
- (83) Kersting, R.; Unterrainer, K.; Strasser, G.; Gornik, E. Few-cycle THz emission from cold plasma oscillations. *Phys. Rev. Lett.* **1997**, *79*, 3038–3041.
- (84) Kersting, R.; Heyman, J.; Strasser, G.; Unterrainer, K. Coherent plasmons in n-doped GaAs. *Physical Review B* 1998, 58, 4553.
- (85) Sha, W.; Smirl, A. L.; Tseng, W. Coherent plasma oscillations in bulk semiconductors. *Physical review letters* **1995**, *74*, 4273.
- (86) Irmer, G.; Wenzel, M.; Monecke, J. Light scattering by a multicomponent plasma coupled with longitudinal-optical phonons: Raman spectra of p-type GaAs: Zn. *Physical Review B* 1997, 56, 9524.
- (87) Papalazarou, E.; Faure, J.; Mauchain, J.; Marsi, M.; Taleb-Ibrahimi, A.; Reshetnyak, I.; Van Roekeghem, A.; Timrov, I.; Vast, N.; Arnaud, B., et al. Coherent phonon coupling to individual Bloch states in photoexcited bismuth. *Physical review letters* 2012, 108, 256808.
- (88) Kutt, W. A.; Albrecht, W.; Kurz, H. Generation of coherent phonons in condensed media. *IEEE journal of quantum electronics* 1992, 28, 2434–2444.
- (89) Cho, G.; Dekorsy, T.; Bakker, H.; Hövel, R.; Kurz, H. Generation and relaxation of coherent majority plasmons. *Physical review letters* **1996**, *77*, 4062.
- (90) Ishioka, K.; Brixius, K.; Höfer, U.; Rustagi, A.; Thatcher, E. M.; Stanton, C. J.; Petek, H. Dynamically coupled plasmon-phonon modes in GaP: An indirect-gap polar semiconductor. *Physical Review B* **2015**, *92*, 205203.
- (91) Ishioka, K.; Brixius, K.; Beyer, A.; Rustagi, A.; Stanton, C. J.; Stolz, W.; Volz, K.; Höfer, U.; Petek, H. Coherent phonon spectroscopy characterization of electronic bands at buried semiconductor heterointerfaces. *Applied Physics Letters* 2016, 108 051607, DOI: http://dx.doi.org/10.1063/1.4941397.
- (92) Nurmikko, A.; Schwartz, B.; Jamison, S.; Enstrom, R. Infrared field induced Gunn oscillations in GaAs. Solid-State Electronics 1978, 21, 241–245.
- (93) Joshya, R.; Ptak, A.; France, R.; Mascarenhas, A.; Kini, R. Coherent acoustic phonon generation in GaAs<sub>1-x</sub>Bi<sub>x</sub>. Appl. Phys. Lett. **2014**, 104, 091903–4.
- (94) Lim, D.; Averitt, R. D.; Demsar, J.; Taylor, A. J.; Hur, N.; Cheong, S. W. Coherent acoustic phonons in hexagonal manganite LuMnO3. *Applied Physics Letters* 2003, 83, 4800–4802.
- Liu, R.; Sanders, G.; Stanton, C.; Kim, C.; Yahng, J.; Jho, Y.; Yee, K.; Oh, E.; Kim, D. Femtosecond pump-probe spectroscopy of propagating coherent acoustic phonons in In<sub>x</sub>Ga<sub>1-x</sub>N/GaN heterostructures. *Phys. Rev. B* 2005, *72*, 195335.

- (96) Babilotte, P.; Ruello, P.; Pezeril, T.; Vaudel, G.; Mounier D.and Breteau, J.-M.; Gusev, V. Transition from piezoelectric to deformation potential mechanism via photogeneration in n-doped GaAs semiconductors. J. Appl. Phys. 2011, 109, 064909.
- (97) Babilotte, P.; Mounier, D.; Pezeril, T.; Vaudel, G.; Edely, M.; Breteau, J.-M.; Gusev, V.; Blary, K. Femtosecond laser generation and detection of high-frequency acoustic phonons in GaAs semiconductors. *Phys. Rev. B* **2010**, *81*, 245207.
- (98) Wen, Y.-C.; Chern, G.-W.; Lin, K.-H.; Yeh, J. J.; Sun, C.-K. Femtosecond optical excitation of coherent acoustic phonons in a piezoelectric *p-n* junction. *Phys. Rev. B* Nov. 2011, 84, 205315.
- (99) Chen, C.-C.; Huang, H.-M.; Lu, T.-C.; Kuo, H.-C.; Sun, C.-K. Magnitude-tunable sub-THz shear phonons in a non-polar GaN multiple-quantum-well p-i-n diode. Applied Physics Letters 2012, 100 201905, DOI: http://dx.doi.org/10.1063/1. 4718524.
- (100) Vaudel, G.; Pezeril, T.; Lomonosov, A.; Lejman, M.; Ruello, P.; Gusev, V. Laser generation of hypersound by a terahertz photo-Dember electric field in a piezoelectric GaAs semiconductor. *Phys. Rev. B* July 2014, *90*, 014302.
- (101) Bosco, C.; Azevedo, A.; Acioli, L. Laser-wavelength dependence of the picosecond ultrasonic response of a NiFe/NiO/Si structure. *Phys. Rev. B* **2002**, *66*, 125406.
- (102) Bozovic, I.; Schneider, M.; Xu, Y.; Sobolewski, R.; Ren, Y.; Lupke, G.; Demsar, J.; Taylor, A.; Onellion, M. Long-lived coherent acoustic waves generated by femtosecond light pulses. *Phys. Rev. B* 2004, *69*, 132503.
- (103) Grahn, H. T.; Maris, H. J.; Tauc, J. Picosecond ultrasonics. *IEEE Journal of Quantum Electronics* Dec. 1989, 25, 2562–2569.
- (104) Xu, Y.; Qi, J.; Miller, J.; Cho, Y.-J.; Liu, X.; Furdyna, J.; Shahbazyan, T.; Tolk, N. Pump-probe studies of traveling coherent longitudinal acoustic phonon oscillations in GaAs. *Phys. Stat. Sol. C* **2008**, *8*, 2632–2636.
- (105) Mizoguchi, K.; Hase, M.; Nakashima, S.; Nakayama, M. Observation of coherent folded acoustic phonons propagating in a GaAs/AlAs superlattice by two-color pumpprobe spectroscopy. *Phys. Rev. B* Sept. 1999, 60, 8262–8266.
- (106) Yamamoto, A.; Mishina, T.; Masumoto, Y.; Nakayama, M. Coherent oscillation of zone-folded phonon modes in GaAs-AlAs superlattices. *Physical review letters* 1994, 73, 740.
- (107) Lockwood, D.; Yu, G.; Rowell, N. Optical phonon frequencies and damping in AlAs, GaP, GaAs, InP, InAs and InSb studied by oblique incidence infrared spectroscopy. *Solid State Communications* **2005**, *136*, 404–409.
- (108) Gusev, V. E. Generation of Picosecond Acoustic Pulses by Laser Radiation in Piezosemiconductors. *physica status solidi* (b) **1990**, *158*, 367–381.

#### BIBLIOGRAPHY

- (109) Akhmanov, S. A.; Gusev, V. É. Laser excitation of ultrashort acoustic pulses: New possibilities in solid-state spectroscopy, diagnostics of fast processes, and nonlinear acoustics. *Soviet Physics Uspekhi* 1992, 35, 153.
- (110) Požela, J.; Reklaitis, A. Electron transport properties in GaAs at high electric fields. Solid-State Electronics 1980, 23, 927–933.
- (111) Thomsen, C.; Grahn, H.; Maris, H.; Tauc, J. Surface generation and detection of phonons by picosecond light pulses. *Phys. Rev. B* **1986**, *34*, 4129–4138.
- (112) Gallant, D.; Pezolet, M.; Simard, S. Optical and physical properties of cobalt oxide films electrogenerated in bicarbonate aqueous media. *The Journal of Physical Chemistry B* 2006, 110, 6871–6880.
- (113) Uchida, N.; Saito, S. Elastic Constants and Acoustic Absorption Coefficients in MnO, CoO, and NiO Single Crystals at Room Temperature. *The Journal of the Acoustical Society of America* **1972**, *51*, 1602–1605.
- (114) Ohtsuka, T.; Satio, N. S. Anodic oxide film on cobalt in weakly alkaline solution. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry 1983, 147, 167–179.
- (115) Goel, A. K.; Skorinko, G.; Pollak, F. H. Optical properties of single-crystal rutile RuO<sub>2</sub> and IrO<sub>2</sub> in the range 0.5 to 9.5 eV. *Phys. Rev. B* Dec. 1981, 24, 7342–7350.
- (116) Deligoz, E.; Colakoglu, K.; Ciftci, Y. O. A first principles study of cubic IrO<sub>2</sub> polymorph. Eur. Phys. J. B 2007, 60, 477–481.
- (117) Fricke, K. Piezoelectric properties of GaAs for application in stress transducers. *Journal of Applied Physics* **1991**, *70*, 914–918.
- (118) Wen, Y.-C.; Ko, T.-S.; Lu, T.-C.; Kuo, H.-C.; Chyi, J.-I.; Sun, C.-K. Photogeneration of coherent shear phonons in orientated wurtzite semiconductors by piezoelectric coupling. *Physical Review B* **2009**, *80*, 195201.
- (119) Doan, H. Q.; Pollock, K. L.; Cuk, T. Transient optical diffraction of GaN/aqueous interfaces: Interfacial carrier mobility dependence on surface reactivity. *Chemical Physics Letters* 2016, 649, 1–7.
- Braun, A.; Sivula, K.; Bora, D. K.; Zhu, J.; Zhang, L.; Grätzel, M.; Guo, J.; Constable, E. C. Direct Observation of Two Electron Holes in a Hematite Photoanode during Photoelectrochemical Water Splitting. *The Journal of Physical Chemistry C* 2012, 116, 16870–16875.
- (121) Gutsche, C.; Niepelt, R.; Gnauck, M.; Lysov, A.; Prost, W.; Ronning, C.; Tegude, F.-J. Direct Determination of Minority Carrier Diffusion Lengths at Axial GaAs Nanowire p-n Junctions. *Nano Lett.* **2012**, *12*, 1453–1458.
- (122) Ma, J.; Lee, W.; Bae, J.; Jeong, K.; Oh, S.; Kim, J.; Kim, S.-H.; Seo, J.-H.; Ahn, J.-P.; Kim, H.; Cho, M.-H. Carrier Mobility Enhancement of Tensile Strained Si and SiGe Nanowires via Surface Defect Engineering. *Nano Lett.* **2015**, *15*, 7204–7210.

- (123) Gunawan, O.; Sekaric, L.; Majumdar, A.; Rooks, M.; Appenzeller, J.; Sleight, J.; Guha, S.; Haensch, W. Measurement of Carrier Mobility in Silicon Nanowires. *Nano Lett.* 2008, *8*, 1566–1571.
- (124) Niquet, Y.-M.; Delerue, C.; Krzeminski, C. Effects of Strain on the Carrier Mobility in Silicon Nanowires. *Nano Lett.* 2012, 12, 3545–3550.
- (125) Fonoberov, V.; Balandin, A. Giant Enhancement of the Carrier Mobility in Silicon Nanowires with Diamond Coating. *Nano Lett.* **2006**, *6*, 2442–2446.
- (126) Šcăjev, P.; Jarašiunas, K.; Okur, S.; Özgür, Ü.; Morkoç, H. Carrier Dynamics in Bulk GaN. J. Appl. Phys. 2012, 111, 023702–8.
- Malinauskas, T.; Jarašiunas, K.; Miasojedovas, S.; Juršenas, S.; Beaumont, B.; Gibart,
   P. Optical Monitoring of Nonequilibrium Carrier Lifetime in Freestanding GaN by
   Time-Resolved Four-Wave Mixing and Photoluminescence Techniques. Appl. Phys.
   Lett. 2006, 88, 202109–3.
- (128) Sjodin, T.; Li, C.-M.; Petek, H.; Dai, H.-L. Ultafast Transient Grating Scattering Studies of Carrier Dynamics at a Silicon Surface. *Chem. Phys.* **2000**, *251*, 205–213.
- (129) Jarasiunas, K.; Lovergine, N. Characterisation of Bulk Crystals and Structures by Light-Induced Transient Grating Technique. *Mater. Sci. Eng.* 2002, *B91-92*, 100– 104.
- (130) Hoffman, C.; Jarašiunas, K.; Gerritsen, H.; Nurmikko, A. Measurement of Surface Recombination Velocity in Semiconductors by Diffraction from Picosecond Transient Free-Carrier Gratings. *Appl. Phys. Lett.* **1978**, *33*, 536–539.
- (131) Kasinski, J.; Gomez-Jahn, L.; Faran, K.; Gracewski, S.; Dwayne Miller, R. Picosecond Dynamics of Surface Electron Transfer Processes: Surface Restricted Transient Grating Studies of the n-TiO<sub>2</sub>/H<sub>2</sub>O Interface. J. Chem. Phys. **1989**, 90, 1253–1269.
- (132) Morishita, T.; Hibara, A.; Sawada, T.; Tsuyumoto, I. Ultrafast Charge Transfer at TiO<sub>2</sub>/SCN<sup>-</sup> (aq) Interfaces Investigated by Femtosecond Transient Reflecting Grating Method. J. Phys. Chem. B 1999, 103, 5984–5987.
- (133) Nakabayashi, S.; Komuro, S.; Aoyagi, Y.; Kira, A. Transient Grating Method Applied to Electron-Transfer Dynamics at a Semiconductor/Liquid Interface. J. Phys. Chem. 1987, 91, 1696–1698.
- (134) Gomez-Jahn, L.; Min, L.; Dwayne Miller, R. In Situ Picosecond Studies of Surface Reaction Dynamics at GaAs(100) Interfaces. *Mol. Cryst. Liq. Cryst.* 1991, 194, 181– 190.
- (135) Wang, D.; Buontempo, J.; Li, Z.; Miller, R. Picosecond Surface Restricted Grating Studies of n-GaAs (100) Liquid Junctions. Evidence for Interfacial Charge Transfer Approaching Adiabatic Limits. *Chem. Phys. Lett.* **1995**, *232*, 7–15.
- (136) Eichler, H.; Günter, P.; Pohl, D., *Laser-Induced Dynamic Gratings*; Springer Series in Optical Sciences; Springer Berlin Heidelberg: 1986.

- (137) Xu, Q.-H.; Ma, Y.-Z.; Fleming, G. Heterodyne Detected Transient Grating Spectroscopy in Resonant and Non-Resonant Systems using a Simplified Diffractive Optics Method. *Chem. Phys. Lett.* **2001**, *338*, 254–262.
- (138) Scholes, G. D.; Kim, J.; Wong, C. Y. Exciton spin relaxation in quantum dots measured using ultrafast transient polarization grating spectroscopy. *Phys. Rev. B* May 2006, 73, 195325.
- (139) Eichler, H. J.; Massmann, F. Diffraction efficiency and decay times of free carrier gratings in silicon. *Journal of Applied Physics* **1982**, *53*, 3237–3242.
- (140) Aleksiejunas, R.; Sudžius, M.; Malinauskas, T.; Vaitkus, J.; Jarašiunas, K.; Sakai, S. Determination of Free Carrier Bipolar Diffusion Coefficient and Surface Recombination Velocity of Undoped GaN Epilayers. *Appl. Phys. Lett.* **2003**, *83*, 1157–1159.
- (141) Schetzina, J.; McKelvey, J. Ambipolar Transport of Electrons and Holes in Anisotropic Crystals. *Phys. Rev. B* **1970**, *2*, 1869–1874.
- (142) Fox, M., *Optical Properties of Solids*; Oxford Master Series in Physics; OUP Oxford: 2010.
- (143) Xu, Q.-H.; Ma, Y.-Z.; Fleming, G. R. Different real and imaginary components of the resonant third-order polarization revealed by optical heterodyne detected transient grating spectroscopic studies of crystal violet: model and experiment. *The Journal* of Physical Chemistry A 2002, 106, 10755–10763.
- (144) Khalil, M.; Demirdöven, N.; Golonzka, O.; Fecko, C. J.; Tokmakoff, A. A Phase-Sensitive Detection Method Using Diffractive Optics for Polarization-Selective Femtosecond Raman Spectroscopy. *The Journal of Physical Chemistry A* 2000, 104, 5711–5715.
- (145) Johnson, J. A.; Maznev, A. A.; Bulsara, M. T.; Fitzgerald, E. A.; Harman, T. C.; Calawa, S.; Vineis, C. J.; Turner, G.; Nelson, K. A. Phase-controlled, heterodyne laser-induced transient grating measurements of thermal transport properties in opaque material. *Journal of Applied Physics* 2012, *111* 023503, DOI: http://dx.doi.org/ 10.1063/1.3675467.
- (146) Chang, Y. J.; Cong, P.; Simon, J. D. Optical heterodyne detection of impulsive stimulated Raman scattering in liquids. *The Journal of Physical Chemistry* 1995, 99, 7857–7859.
- (147) Matsuo, S.; Tahara, T. Phase-stabilized optical heterodyne detection of impulsive stimulated Raman scattering. *Chemical Physics Letters* **1997**, *264*, 636–642.
- (148) Voehringer, P.; Scherer, N. F. Transient Grating Optical Heterodyne Detected Impulsive Stimulated Raman Scattering in Simple Liquids. *The Journal of Physical Chemistry* 1995, 99, 2684–2695.
- (149) Gedik, N.; Orenstein, J. Absolute Phase Measurement in Heterodyne Detection of Transient Gratings. Optics Letters 2004, 29, 2109–2111.

- (150) Gedik, N.; Orenstein, J.; Liang, R.; Bonn, D. A.; Hardy, W. N. Diffusion of Nonequilibrium Quasi-Particles in a Cuprate Superconductor. *Science* **2003**, *300*, 1410–1412.
- (151) Gedik, N. Recombination and Propagation of Quasiparticles in Cuprate Superconductors., Ph.D. Thesis, Lawrence Berkeley National Laboratory, May 2004.
- (152) Aleksiejunas, R.; Scăjev, P.; Nargelas, S.; Malinauskas, T.; Kadys, A.; Jarašiunas, K. Impact of Diffusivity to Carrier Recombination Rate in Nitride Semiconductors: From Bulk GaN to (In,Ga)N Quantum Wells. Jap. J. Appl. Phys. 2013, 52, 08JK01–5.
- (153) Chen, F.; Cartwright, A.; Lu, H.; Schaff, W. Hole Transport and Carrier Lifetime in InN Epilayers. Appl. Phys. Lett. 2005, 87, 212104–3.
- (154) Doan, H. Q. Surface Structure Probe of Transition Metal-Based Oxygen Evolving Systems with Spectroscopy., Ph.D. Thesis, University of California, Berkeley, May 2016.
- (155) Bartolini, P.; Taschin, A.; Eramo, R.; Torre, R. In *Time-Resolved Spectroscopy in Complex Liquids: An Experimental Perspective*, Torre, R., Ed.; Springer US: Boston, MA, 2008, pp 129–184.
- (156) Slayton, R. M.; Nelson, K. A. Picosecond acoustic transmission measurements. I. Transient grating generation and detection of acoustic responses in thin metal films. *The Journal of Chemical Physics* **2004**, *120*, 3908–3918.
- (157) Nakayama, T.; Tamura, S.; Yagi, T.; Rogers, J.; Nelson, K. A new photoacoustic/photothermal device for real-time materials evaluation: An automated means for performing transient grating experiments. *Physica B: Condensed Matter* **1996**, *219*, 562–564.
- (158) Maznev, A. A.; Nelson, K. A.; Rogers, J. A. Optical Heterodyne Detection of Laser-Induced Gratings. *Optics Letters* 1998, 23, 1319–1321.
- (159) Maznev, A. A.; Crimmins, T. F.; Nelson, K. A. How to make femtosecond pulses overlap. Opt. Lett. Sept. 1998, 23, 1378–1380.
- (160) Womick, J. M.; Miller, S. A.; Moran, A. M. Correlated Exciton Fluctuations in Cylindrical Molecular Aggregates. *The Journal of Physical Chemistry B* 2009, 113, PMID: 19382770, 6630–6639.
- (161) Goodno, G.; Dadusc, G.; Miller, R. Ultrafast Heterodyne-Detected Transient-Grating Spectroscopy using Diffractive Optics. J. Opt. Soc. Am. B **1998**, 15, 1791–1794.
- (162) Chen, Y.-W.; Kuo, J.-L. Density Functional Study of the First Wetting Layer on the GaN (0001) Surface. J. Phys. Chem. C 2013, 117, 8774–8783.
- (163) Chen, P.-T.; Sun, C.-L.; Hayashi, M. First-Principles Calculations of Hydrogen Generation Due to Water Splitting on Polar GaN Surfaces. J. Phys. Chem. C 2010, 114, 18228–18232.

- (164) Kibria, M.; Zhao, S.; Chowdhury, F.; Wang, Q.; Nguyen, H.; Trudeau, M.; Guo H.and Mi, Z. Tuning the Surface Fermi Level on p-Type Gallium Nitride Nanowires for Efficient Overall Water Splitting. *Nat. Commun.* **2014**, *5*, 3825–6.
- (165) Li, L.; Fan, S.; Mu, X.; Mi, Z.; Li, C.-J. Photoinduced Conversion of Methane into Benzene over GaN Nanowires. J. Am. Chem. Soc. 2014, 136, 7793–7796.
- (166) Scheuermann, A. G.; McIntyre, P. C. Atomic Layer Deposited Corrosion Protection: A Path to Stable and Efficient Photoelectrochemical Cells. *The Journal of Physical Chemistry Letters* 2016, 7, PMID: 27359352, 2867–2878.
- (167) Wu, J.; Walukiewicz, W.; Yu, K.; Ager III, J.; Haller, E.; Lu, H.; Schaff, W. Small Band Gap Bowing in  $In_{1-x}Ga_xN$  Alloys. *Appl. Phys. Lett.* **2002**, *80*, 921–923.
- (168) Fujii, K.; Ohkawa, K. Photoelectrochemical Properties of p-Type GaN in Comparison with n-Type GaN. Jap. J. Appl. Phys. 2005, 44, L909–L911.
- (169) Kim, S.; Ebaid, M.; Kang, J.-H.; Ryu, S.-W. Improve Efficiency and Stability of GaN Photoanode in Photoelectrochemical Water Splitting by NiO Cocatalyst. Appl. Surf. Sci. 2014, 305, 638–641.
- (170) Kibria, M.; Nguyen, H.; Cui, K.; Zhao, S.; Liu, D.; Guo, H.; Trudeau, M.; Paradis, S.; Hakima, A.-R.; Mi, Z. One-Step Overall Water Splitting under Visible Light Using Multiband InGaN/GaN Nanowire Heterostructures. ACS Nano 2013, 7, 7886–7893.
- (171) AlOtaibi, B.; Fan, S.; Vanka, S.; Kibria, M.; Mi, Z. A Metal-Nitride Nanowire Dual-Photoelectrode Device for Unassisted Solar-to-Hydrogen Conversion under Parallel Illumination. *Nano Lett.* **2015**, *15*, 6821–6828.
- (172) Wang, D.; Pierre, A.; Kibria, M.; Cui, K.; Han, X.; Bevan, K.; Guo, H.; Paradis, S.; Hakima, A.-R.; Mi, Z. Wafer-Level Photocatalytic Water Splitting on GaN Nanowire Arrays Grown by Molecular Beam Epitaxy. *Nano Lett.* **2011**, *11*, 2353–2357.
- (173) Fujii, K.; Ohkawa, K. Hydrogen Generation from Aqueous Water using n-GaN by Photoassisted Electrolysis. *Phys. Stat. Sol. C* **2006**, *3*, 2270–2273.
- (174) Ono M. Fujii, K.; Ito, T.; Iwaki, Y.; Hirako, A.; Yao, T.; Ohkawa, K. Photoelectrochemical Reaction and H<sub>2</sub> Generation at Zero Bias Optimized By Carrier Concentration of n-Type GaN. J. Chem. Phys. 2007, 126, 054708–6.
- (175) Waki, I.; Cohen, D.; Lal, R.; Mishra, U.; DenBaars, S.; Nakamura, S. Direct Water Photoelectrolysis with Patterned n-GaN. *Appl. Phys. Lett.* **2007**, *91*, 093519–3.
- (176) Zhuang, D.; Edgar, J. Wet etching of GaN, AlN, and SiC: a review. *Materials Science* and Engineering: R: Reports **2005**, 48, 1–46.
- (177) Huygens, I.; Strubbe, K.; Gomes, W. Electrochemistry and Photoetching of n-GaN. J. Electrochem. Soc. 2000, 147, 1797–1802.
- (178) Tseng, W.; van Dorp, D.; Lieten, R.; Vereecken, P.; Borghs, G. Anodic Etching of n-GaN Epilayer into Porous GaN and Its Photoelectrochemical Properties. J. Phys. Chem. C 2014, 118, 29492–29498.

- (179) Minsky, M. S.; White, M.; Hu, E. L. Room temperature photoenhanced wet etching of GaN. *Applied Physics Letters* **1996**, *68*, 1531–1533.
- (180) Youtsey, C.; Adesida, I.; Bulman, G. Highly anisotropic photoenhanced wet etching of n type GaN. *Applied physics letters* **1997**, *71*, 2151–2153.
- (181) Seo, J.; Oh, C.; Yang, J.; Yang, G.; Lim, K.; Yoon, C.; Lee, H. Allowable Substrate Bias for the Etching of n-GaN in Photoenhanced Electrochemical Etching. *physica status solidi (a)* **2001**, *188*, 403–406.
- (182) Luo, W.; Liu, B.; Li, Z.; Xie, Z.; Chen, D.; Zou, Z.; Zhang, R. Stable Response to Visible Light of InGaN Photoelectrodes. Appl. Phys. Lett. 2008, 92, 262110–3.
- (183) Huygens, I.; Theuwis, A.; Gomes, W.; Strubbe, K. Photoelectrochemical Reactions at the n-GaN Electrode in 1 M H<sub>2</sub>SO<sub>4</sub> and in Acidic Solutions Containing Cl<sup>-1</sup> Ions. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2301–2306.
- (184) Schäfer, S.; Koch, A.; Cavallini, A.; Stutzmann, M.; Sharp, I. Charge Transfer Across the n-Type GaN-Electrolyte Interface. J. Phys. Chem. C 2012, 116, 22281–22286.
- (185) Chakrapani, V.; Chandrashekhar, P.; Kash, K.; Anderson, A.; Sunkara, M.; Angus, J. Electrochemical Pinning of the Fermi Level: Mediation of Photoluminescence from Gallium Nitride and Zinc Oxide. J. Am. Chem. Soc. 2008, 130, 12944–12952.
- (186) Ye, H.; Chen, G.; Niu, H.; Zhu, Y.; Shao, L.; Qiao, Z. Structures and Mechanisms of Water Adsorption on ZnO(0001) and GaN(0001) Surface. J. Phys. Chem. C 2013, 117, 15976–15983.
- (187) Bermudez, V.; Long, J. Chemisorption of  $H_2O$  on GaN(0001). Surf. Sci. 2000, 450, 98–105.
- (188) Akimov, A.; Muckerman, J.; Prezhdo, O. Nonadiabatic Dynamics of Positive Charge During Photocatalytic Water Splitting on GaN(10-10) Surface: Charge Localization Governs Splitting Efficiency. J. Am. Chem. Soc. 2013, 135, 8682–8691.
- (189) De Gryse, R.; Gomes, W.; Cardon, F.; Vennik, J. On the Interpretation of Mott-Schottky Plots Determined at Semiconductor/Electrolyte Systems. J. Electrochem. Soc. 1975, 122, 711–712.
- (190) Reshchikov, M.; Morkoç, H.; Park, S.; Lee, K. Yellow and Green Luminescence in a Freestanding GaN Template. Appl. Phys. Lett. 2001, 78, 3041–3043.
- (191) Bandić, Z.; Bridger, P.; Piquette, E.; McGill, T. The Values of Minority Carrier Diffusion Lengths and Lifetimes in GaN and Their Implications for Bipolar Devices. *Solid State Electron.* 2000, 44, 221–228.
- (192) Chernyak, L.; Osinsky, A.; Temkin, H.; Yang, J.; Chen, Q.; Khan, M. Electron Beam Induced Current Measurements of Minority Carrier Diffusion Length in Gallium Nitride. Appl. Phys. Lett. 1996, 69, 2531–2533.
- (193) Chow, T. P.; Ghezzo, M. In Symposium E III-Nitride, SiC, and Diamond Materials for Electronic, 1996; Vol. 423.

- (194) Kumakura, K.; Makimoto, T.; Kobayashi, N.; Hashizume, T.; Fukui, T.; Hasegawa, H. Minority Carrier Diffusion Length in GaN: Dislocation Density and Doping Concentration Dependence. *Appl. Phys. Lett.* 2005, *86*, 052105–3.
- (195) Kozodoy, P.; Xing, H.; DenBaars, S.; Mishra, U.; Saxler, A.; Perrin, R.; Elhamri, S.; Mitchel, W. Heavy Doping Effects in Mg-Doped GaN. J. Appl. Phys. 2000, 87, 1832–1835.
- (196) Zhong, Z.; Qian, F.; Wang, D.; Lieber, C. Synthesis of p-Type Gallium Nitride Nanowires for Electronic and Photonic Nanodevices. *Nano Lett.* **2003**, *3*, 343–346.
- (197) Liaugaudas, G.; Dargis, D.; Kwasnicki, P.; Arvinte, R.; Zielinski, M.; Jarašiunas, K. Determination of Carrier Lifetime and Diffusion Length in Al-Doped 4H-SiC Epilayers by Time-Resolved Optical Techniques. J. Phys. D: Appl. Phys. 2015, 48, 025103–7.
- (198) Linnros, J.; Grivickas, V. Carrier-Diffusion Measurements in Silicon with a Fourier-Transient-Grating Method. *Phys. Rev. B* **1994**, *50*, 16943–16955.
- (199) Jarašiunas, K.; Šcăjev, P.; Nargelas, S.; Malinauskas, T.; Kato, M.; Ivakin, E.; Nesladek, M.; Haenen, K.; Özgür, Ü.; Morkoç, H. Recombination and Diffusion Processes in Polar and Nonpolar Bulk GaN Investigated by Time-Resolved Photoluminescence and Nonlinear Optical Techniques. *Mat. Sci. Forums* **2012**, *717-720*, 309–312.
- (200) Fujii, K.; Karasawa, T.; Ohkawa, K. Hydrogen Gas Generation by Splitting Aqueous Water Using n-Type GaN Photoelectrode with Anodic Oxidation. *Jap. J. Appl. Phys.* 2005, 44, L543–L545.
- (201) Valentin, C.; Selloni, A. Bulk and Surface Polarons in Photoexcited Anatase TiO<sub>2</sub>.
   J. Phys. Chem. Lett. 2011, 2, 2223–2228.
- (202) Paul, D.; Mitra, S. Evaluation of Mott's Parameters for Hopping Conduction in Amorphous Ge, Si, and Se-Si. *Phys. Rev. Lett.* **1973**, *31*, 1000–1003.
- (203) Ambegaokar, V.; Halperin, B.; Langer, J. Hopping Conductivity in Disordered Systems. *Phys. Rev. B* 1971, 4, 2612–2620.
- (204) Chen, R. Apparent stretched-exponential luminescence decay in crystalline solids. Journal of luminescence **2003**, 102, 510–518.
- (205) Kakalios, J.; Street, R.; Jackson, W. Stretched-exponential relaxation arising from dispersive diffusion of hydrogen in amorphous silicon. *Physical review letters* 1987, 59, 1037.
- (206) Pavesi, L.; Ceschini, M. Stretched-exponential decay of the luminescence in porous silicon. *Physical Review B* **1993**, *48*, 17625.
- (207) Chen, X.; Henderson, B.; O'Donnell, K. Luminescence decay in disordered lowdimensional semiconductors. *Applied physics letters* **1992**, *60*, 2672–2674.
- (208) Kanemitsu, Y. Photoluminescence spectrum and dynamics in oxidized silicon nanocrystals: A nanoscopic disorder system. *Phys. Rev. B* May 1996, *53*, 13515–13520.

- (209) Linnros, J.; Galeckas, A.; Lalic, N.; Grivickas, V. Time-resolved photoluminescence characterization of nm-sized silicon crystallites in SiO 2. *Thin Solid Films* **1997**, *297*, 167–170.
- (210) Linnros, J.; Lalic, N.; Galeckas, A.; Grivickas, V. Analysis of the stretched exponential photoluminescence decay from nanometer-sized silicon crystals in SiO2. *Journal of Applied Physics* **1999**, *86*, 6128–6134.
- (211) Scher, H.; Shlesinger, M.; Bendler, J. Time-Scale Invariance in Transport and Relaxation. *Physics Today* **1991**, *44*, 26–34.
- (212) Klafter, J.; Shlesinger, M. F. On the relationship among three theories of relaxation in disordered systems. *Proceedings of the National Academy of Sciences* 1986, 83, 848–851.
- (213) Johnston, D. C. Stretched exponential relaxation arising from a continuous sum of exponential decays. *Phys. Rev. B* Nov. 2006, 74, 184430.
- (214) Goodno, G. D.; Miller, R. J. D. Femtosecond Heterodyne-Detected Four-Wave-Mixing Studies of Deterministic Protein Motions. 1. Theory and Experimental Technique of Diffractive Optics-Based Spectroscopy. *The Journal of Physical Chemistry A* 1999, 103, 10619–10629.
- (215) Goodno, G. D.; Astinov, V.; Miller, R. J. D. Femtosecond Heterodyne-Detected Four-Wave-Mixing Studies of Deterministic Protein Motions. 2. Protein Response. *The Journal of Physical Chemistry A* 1999, 103, 10630–10643.
- (216) Miller, S. A.; Stuart, A. C.; Womick, J. M.; Zhou, H.; You, W.; Moran, A. M. Excited-State Photophysics in a Low Band Gap Polymer with High Photovoltaic Efficiency. *The Journal of Physical Chemistry C* 2011, 115, 2371–2380.
- (217) West, B. A.; Womick, J. M.; McNeil, L. E.; Tan, K. J.; Moran, A. M. Ultrafast Dynamics of Frenkel Excitons in Tetracene and Rubrene Single Crystals. *The Journal* of Physical Chemistry C 2010, 114, 10580–10591.
- (218) Dadusc, G.; Ogilvie, J. P.; Schulenberg, P.; Marvet, U.; Miller, R. J. D. Diffractive optics-based heterodyne-detected four-wave mixing signals of protein motion: From "protein quakes" to ligand escape for myoglobin. *Proceedings of the National Academy* of Sciences 2001, 98, 6110–6115.
- (219) Prokhorenko, V.; Halpin, A.; Miller, R. Coherently-controlled two-dimensional photon echo electronic spectroscopy. *Optics express* **2009**, *17*, 9764–9779.
- (220) Gallagher, S. M.; Albrecht, A. W.; Hybl, J. D.; Landin, B. L.; Rajaram, B.; Jonas, D. M. Heterodyne detection of the complete electric field of femtosecond four-wave mixing signals. JOSA B 1998, 15, 2338–2345.
- (221) Hybl, J. D.; Albrecht Ferro, A.; Jonas, D. M. Two-dimensional Fourier transform electronic spectroscopy. *The Journal of Chemical Physics* **2001**, *115*, 6606–6622.
## BIBLIOGRAPHY

(222) Pollock, K. L. TGS processing code., https://www.dropbox.com/sh/hqmzow375gmf5qx/ AADpBdMFgYZ8oYwqif0oWMg9a?dl=0, Accessed: 2016-09-22.