Ultrafast time-frequency spectroscopy based on few-cycle pump-probe transient reflectometry

Hemang Jani

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ULTRAFAST TIME-FREQUENCY SPECTROSCOPY
BASED ON FEW-CYCLE PUMP-PROBE TRANSIENT
REFLECTOMETRY

by

HEMANG JANI

A DISSERTATION

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in
The Optical Science & Engineering Program
to
The School of Graduate Studies
of
The University of Alabama in Huntsville

HUNTSVILLE, ALABAMA

2020
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03/28/2020

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Submitted by Hemang Jani in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Optical Science & Engineering (OSE) and accepted on behalf of the Faculty of the School of Graduate Studies by the dissertation committee.

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ABSTRACT

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Title Ultrafast Time-Frequency Spectroscopy Based On Few-Cycle Pump-Probe Transient Reflectometry

Over the last decade, advances in novel materials such as two-dimensional (2D) materials, metamaterials, plasmonics, and negative-electron-affinity (NEA) structures have triggered rapid growth in the development of ultrafast optoelectronic devices. This calls for simple yet effective approaches to characterize ultrafast dynamics in these materials and devices. An important aspect of this thesis research is to demonstrate one such approach by amalgamation of state-of-the-art in ultrashort light pulse source with a classical pump-probe methodology to develop a Few-Cycle Pump-Probe Reflectometer (PPR) system, which can offer both high temporal resolution and broad spectral coverage. As one of its applications, this work focuses on characterizing NEA semiconductor photocathode devices by offering a pre-photoemission investigation of photoelectron transport and relaxation in GaAs/AlGaAs based photocathodes. The results show the feasibility of using PPR in effectively characterizing photoemission performance not only based on the different doping architectures, but also based on different growth methods used for fabricating these photocathodes. A theoretical framework based on a carrier-diffusion model is presented to quantitatively verify the
physical understanding of the pump-probe reflectivity measurements on these photocathodes and to better explain the transient behavior of the reflectivity of these structures. This particular work is a new and original approach to the long-standing problem of time resolved photoemission from such photocathodes. Preliminary results of a time-frequency spectroscopic study of the transient dispersion of GaAs near its bandgap are also discussed, to further illustrate the capability of the reflectometer and disentangle fundamental ultrafast processes happening in optoelectronic devices.
Completing this Ph.D. thesis and achieving this feat was a long, but very edifying experience for me. Special thanks goes to my advisor Dr. Lingze Duan, who empowered me and gave me carte blanche, from day one, to handle state-of-the-art lab equipment and to design and build complex optics experiments. The hands-on experience I have gained thus far has given me a lot of confidence in the field of ultrafast optics, and has given me the tools to satisfy my fundamental curiosities.

I would like to acknowledge my doctoral committee members - Dr. Don Gregory, Dr. Patrick Reardon, Dr. Seyed Sadeghi and Dr. Yu Lei for their constant encouragement and support in helping me accomplish this research work. I am also thankful to Mr. Ted Rogers & Mr. Chris Underwood of Center for Applied Optics and former PULS group member (and my best buddy), Dr. Lin Yang for their immense help throughout my Ph.D. research.

This journey was also not possible without the support of my amazing friends. Many thanks to Emin and Sahar for sharing the graduate school journey with me. Special thanks to Rui, who not only contributed to the data collection, but also gave me amazing support during the last year of this thesis work.

Last, but definitely not least, I want to thank my entire family. I thank my parents Pankaj Jani, Hemlata Jani and my wife Amruta for their constant support and encouragement throughout this long journey to accomplish this milestone.
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You can’t Study the darkness by flooding it with light.

—Edward Abbey
This thesis is a journey of my candid efforts to counter this statement - in fact you can study the darkness by simply turning on the light !!

—Hemang Jani
CHAPTER 1

INTRODUCTION

The history of light-matter interaction and the subsequent science emerging out of this “energy” exchange mechanism weighs heavily in thousands of years of effort to describe the nature of light [1]. During the nineteenth century, these continuing efforts came to fruition and found a firm theoretical platform, thanks to the classic work of James Clerk Maxwell [2]. Ever since then, Maxwell’s equations and the constitutive relations have facilitated a foundational understanding of the relationships between the most experimentally accessible optical quantities of measure such as wavelength dependent reflectance \(R(\lambda)\) and transmittance \(T(\lambda)\), and quantities such as electrical permittivity \(\epsilon(\lambda)\) and magnetic permeability \(\mu(\lambda)\) which are most directly related to the electronic and magnetic structure of materials \([R,T] \iff [\epsilon, \mu]\) . The origin of these fundamental electronic and optical properties in a material is the complex dance between lattice, electronic and spin degrees of freedom and the time scale at which these fundamental interactions happen, measurements become increasingly important, which calls for time resolved methods capable of making these observations on an increasingly shorter time scale [3]. Quite intuitively, these techniques must be
capable of resolving these processes much like a strobe light is used to capture the stop-action motion of dancers on a dance floor.

The quest to resolve fast processes and the birth of time-resolved optical science began with the high-speed photography experiments performed by Eadweard Muybridge in 1878 [4]. Using multiple cameras equipped with fast shutters, allowing exposure times of the order of $10^{-3}$ s, Muybridge managed to capture different phases of the motion of a horse on the Palo Alto racetrack, shooting a slow-motion movie of the galloping phase and resolving the instant when all four hooves are lifted from the ground. Following this milestone result was the famous invention of stroboscopic photography credited to Harold Edgerton [5] pushing the time resolution down to the microsecond range. Somewhere between the timelines of these two important works lies the basal work by Abraham and Lemoine in 1899 [6], which employed two synchronized light pulses, the excitation or “pump” pulse which triggers a photoinduced phenomenon, and a delayed “probe” pulse that measured a time-dependent variation of an optical property of the sample, such as absorption or reflection. Perhaps it is not too great a leap to argue that this work can be credited as the coining work in the ensemble of experimental techniques known as Pump-Probe Methods. Following this basic methodology, some of the notable works, such as Norrish and Porter’s technique of flash photolysis [7] and the development of femtochemistry by Ahmed Zewail [8], both of which were awarded the Nobel Prize in 1967 and 1999 respectively, can be considered as bringing a paradigm shift in the family of time resolved techniques.

The continuation of the legacy of these past masters is to be found currently in the field of Ultrafast Optical Spectroscopy and has led to the development of a range
of time resolved techniques based upon specific applications [9]. This field of research has experienced an impetuous growth in the last decades, due to (i) the technological progress in the generation of ultrashort light pulses, in terms of their duration, frequency tunability, and stability/reliability, and (ii) the development of sophisticated spectroscopy techniques, going beyond the classical pump-probe, enabling to increase the amount of information on the processes under study. One important aspect of this thesis is the amalgamation of state of the art in an ultrashort light pulse source with a classical pump-probe methodology in order to develop a high-time-resolution pump-probe transient reflectometer (PPR) system with broadband detection. Most of the PPR experiments reported so far are designed either for narrow-band, time-domain measurement [10–13] or broadband, spectral-domain measurement [14–16].

In the case of time-domain PPR, the time evolution of the total reflected power is measured. This approach is schematically simple and often only requires a femtosecond oscillator as the light source [10]. Standard pulse width in time-domain PPR ranges between 30–100 fs and typical spectral width is 20–60 nm [12,13]. Because of the relatively narrow spectral range, the measured transient reflectivity only represents a portion of the overall dielectric function near the center wavelength. Such a drawback can be partially addressed by using a wavelength-tunable mode-locked laser, which provides an extra dimension to expand the spectral coverage [10]. However, from a practical point of view, tuning laser wavelength is often unreliable and cumbersome, and in some cases, even infeasible. Meanwhile, broadband, spectral-domain PPR can be achieved by broadening the probe pulses into “white light” and measuring the spectral response of transient reflectivity via a spectrometer. This al-
lows the full dielectric function to be characterized within a broad wavelength span (hundreds of nanometers) [17], which provides far more insight into the carrier dynamics than a simple time-domain measurement. The advent of nonlinear photonic crystal fiber in recent years has also significantly lowered the power requirement for generating such supercontinuum probes [18, 19]. This method, however, has two key weaknesses. First, its temporal resolution is often compromised during the nonlinear spectral broadening process [15, 16, 19]. Although temporal-resolution recovery with strongly chirped pulses is possible under certain circumstances [20], the required conditions (e.g., narrow-band sample absorption) are not always satisfied with photonic materials, and it is unclear if the technique can be applied under strong nonlinear spectral broadening. Moreover, spectral-domain PPR has a much higher demand on the pump pulse energy, which is typically required to create a reflectivity modulation strong enough to be detectable by a spectrometer. As a result, a multi-stage optical amplifier chain usually has to be used [15, 17], considerably increasing the cost, size, and complexity of the system.

Recently, the availability of broadly tunable few-optical-cycle light pulses has pushed the temporal resolution of pump-probe spectroscopy to the sub-10 fs domain, enabling the observation of extremely fast “primary” processes. The approach that remains central to this research is primarily based on such few-cycle femtosecond laser to develop a pump-probe system with both high temporal resolution and broad spectral coverage. Such capabilities have been demonstrated previously using chirped-pulse amplification (CPA) and nonlinear optical parametric amplifiers (NOPA) [21], which demand high baseline cost and high system complexity. However, the approach
taken in this research is based on a simple design featuring a few-cycle femtosecond laser and an ultra-broadband pump-probe system. The latter is the key innovation as it allows the pulse width and the spectrum of the laser to be preserved throughout the beam paths and eventually delivered onto the sample. The result is a low-cost (oscillator only), compact (small footprint) pump-probe reflectometer that can make time-domain and spectral-domain measurements simultaneously.

1.0.1 Outline of Research

The overarching theme of this dissertation is the development of a Few-Cycle Pump-Probe Reflectometer system with both high temporal resolution and broad spectral coverage. As one of its applications, this work also focuses on characterizing NEA semiconductor photocathodes devices by offering a pre-photoemission investigation of photoelectron transport and relaxation in a GaAs/AlGaAs based photocathodes. This particular work is a new and original approach to the long standing problem of time resolved photoemission from such photocathodes. Also, a time-frequency spectroscopic study of the transient dispersion of GaAs near its bandgap is discussed at the end of this thesis, to further showcase the capability of the reflectometer in offering a comprehensive way to disentangle fundamental ultrafast processes happening in optoelectronic devices. In this essence, the rest of the thesis is detailed primarily in six more chapters, as presented below.

Chapter 2 and Chapter 3 are dedicated mostly for the background information. This knowledge will be critical in understanding the experimental/theoretical techniques and results described later in the thesis. Chapter 2 is primarily devoted
to Ultrafast Spectroscopic Techniques. Although, there is plethora of time resolved techniques available in literature, the effort here is to hone in on a couple of these techniques, narrow down on couple of them and to discuss them in little detail with an ultimate aim to recognize the superiority of the pump-probe method – which stays central to the thesis research. A brief discussion about fundamental optical sampling technique is also laid down as it remains the backbone behind any pump-probe methodology. In order to have a general understanding of various parameters involved in designing a pump-probe experiment, a universal pump-probe scheme (both transmission and reflection geometry) is outlined. Moving further, some of the governing principle pertaining to a few cycle PPR, such as few cycle pulse generation, few cycle pulse management and detection are included at the end of this chapter. Chapter 3 is entirely devoted to Negative Electron Affinity (NEA) photocathodes and the fundamental concepts necessary to understand this unique III-V semiconductors devices. Transient processes, such as carrier relaxation and carrier transportation near device surfaces of NEA photocathodes, remains central to their optimal operation. An important arm of this thesis research is to portray PPR technique as a distinctive method, which allows the studies of these materials with high reproducibility and throughput. In this essence, a carrier diffusion model is detailed at the end of this chapter in order to support the experimental approach taken to understand the dynamic response of this NEA photocathodes.

The primary goal of chapter 4 is to lay down various steps involved in building a few-cycle pump-probe reflectometer. The primary light source for the research is a Mode-locked Ti:sapphire laser. To understand how such lasers works, the basic
design of this oscillator is explained. Of particular importance to PPR design, is to maintain the temporal and spectral profile of the pulse through out the experiment. In this essence, how the vChirp software was used to decide the total footprint of the reflectometer and how specific ultrafast optics, viz. double chirped mirrors, broad band beam splitter etc. plays critical role in this design is explained. To conclude this chapter, final design of the few cycle PPR along with its CAD model is included.

Chapter 5 and Chapter 6 are focused around experimental and theoretical investigations of NEA Photocathodes. Chapter 5 lays the foundation of using PPR in effectively characterizing photoemission performance based on the different doping structure and different growth method used for these photocathodes. By comparing the experimental results with the theoretical model of Chapter 3, these results also validate the feasibility of using diffusion only model to characterize gradient doped devices. Chapter 6 adds one step further in the investigation of NEA photocathode devices using PPR by adding wavelength-resolved measurement capability to the system. As a proof of concept, a uniformly doped NEA photocathode is investigated in this chapter. Excellent theory and experiment comparison at different detection wavelengths portrays the robustness of PPR technique and the applicability of carrier diffusion model, for a comprehensive characterization of NEA devices.

Chapter 7 is the final leg of this thesis. In this chapter, the primary goal is to highlight both the broad spectral range (300 nm) and the fine temporal resolution (10 fs) capability of the few cycle PPR. The results of this chapter offers a comprehensive picture about important carrier dynamics processes such as carrier cooling, carrier
decay, band filling, and bandgap renormalization in GaAs whereby revealing new
details unattainable with conventional pump-probe methods.
CHAPTER 2

ULTRAFAST SPECTROSCOPY

2.1 Overview of Ultrafast Spectroscopic Techniques

The primary goal of this chapter is to accentuate one particular time resolved technique known as the Pump-probe method, which can deliver the means to access the timescales of carrier processes in materials (typically in femtoseconds and picoseconds). As introduced briefly in Chapter 1, in this technique, an ultrashort laser pulse is split into two portions; a stronger beam (pump) is used to excite the sample, generating a non-equilibrium state, and a weaker beam (probe) is used to monitor the pump-induced changes in the optical constants (such as reflectivity or transmission) of the sample. Measuring the changes in the optical constants as a function of the time delay between the arrival of pump and probe pulses yields information about the relaxation of electronic states in the sample. Nevertheless, in order to appreciate the superiority of this method, the wide and diverse literature of time resolved methods decrees a brief introduction to some of these methods. Next few subsections will be devoted to some of these methods and efforts will be to draw some comparisons between these methods and the few-cycle pump-probe spectrometer used in this thesis in terms of time resolution, complexity and other relevant metrics.
2.1.1 Ultrafast Luminescence spectroscopy/ Time-resolved photoluminescence Spectroscopy (TRPL)

The overarching aim of all TRPL techniques stems from the same concept as applied in pump-probe methods. The Fluorescent material under investigation is excited using a pulsed laser source or by an on/off modulated light source and subsequently, the emission is recorded while the excitation source is turned off.

2.1.1.1 TCSPC: Time Resolution 30 ps

Time-Correlated Single Photon Counting is one of the most widely used variant of TRPL family of time resolved methods. The method is based on the repetitive, precisely timed registration of single photons of, e.g., a fluorescence signal. TCSPC modules are commercially available and come either as a computer card or a stand alone unit with a USB computer connection. These modules are primarily used for emission lifetime measurements, however they can also be used for fluorescence correlation spectroscopy. In a typical TCSPC measurements [22], the fluorphores are excited with a periodic light source. The pulsed laser (represented by the laser diode driver and laser head as shown in Fig. 2.1(a)) sends a laser pulse towards the sample under study. Simultaneously, an electronic SYNC signal is sent to the TCSPC timing electronics. The timing electronics records this time when the SYNC signal was sent, which is used later in creating the lifetime decay curve. The laser pulse is sent through a neutral density (ND) filter, which reduces the intensity of the laser pulse. The ND filter is needed because if the laser power is too high, the overloading of the
detector can cause damage. Furthermore, too many counts per second at the detector can lead to errors in the lifetime decay measurement. The laser pulse excites the fluorophores on the sample, which decay and emit photons which are collected via the experiment optics and sent to the fast and sensitive photodetector. The detector can either be a photo multiplier tube (PMT) or a single photon avalanche photodiode (SPAD). Both PMT and SPAD are available with a broad range of specifications: therefore the choice for a specific detector strongly depends on the application and its requirements. A cut-off filter is placed in front of the detector to eliminate the possibility of stray photons from ambient light near the wavelength of interest into the detector. When the detector registers an event (a photon striking the detector sensor), an electronic signal is sent to the timing electronics. At this point, the timing electronics have recorded both, the SYNC signal (excitation time) and the detector signal (detected photon time). Extracting the lifetime decay from this process makes use of a timebinning concept and this procedure rests on the timing electronics. The main role of this unit is to quantify the time delay between the SYNC signal and the detection signal caused by a photon. This time delay represents how long the sample was in an excited state before returning to the ground state and releasing a photon. The timing electronics quantifies the time delay of thousands to millions of the emissive events per second, and creates a histogram by binning the time delay Fig. 2.1(b). The resulting histogram is a plot of counts per second as a function of time delay. The base resolution (minimum decay lifetime that the timing electronics can accurately measure) can be in tens of picoseconds.
Figure 2.1: (a) Simple experimental set-up for fluorescence decay measurements with TCSPC. (b) A classic TCSPC histogram, which displays measured time differences from which the fluorescence lifetime is extracted by mathematical means. Figure adapted from [22]

2.1.1.2 Streak Camera: Time Resolution 1 ps

Another subcategory of TRPL methods is using streak cameras. The streak camera is an ultra-high-speed detector which captures light emission phenomena occurring in extremely short time periods and delivers intensity vs. time vs. position (or wavelength) information. It's name "streak camera" dates back to the early days of the high speed rotating drum cameras. These cameras would "streak" reflected light onto film. No other instruments which can directly detect ultra-fast light phenomena have better temporal resolution than the streak camera. The general purpose of a streak camera is to convert the temporal dependence of an optical signal into a spatial profile that is recorded with an optical camera. The operating principle of a streak camera [9] used for time resolved measurements is schematically shown in Fig. 2.2.

The light pulse to be measured is projected onto the slit and is focused by a lens into an optical image on the photocathode (PC) which produces electrons through the photoelectric effect. Here, the photons are converted into a stream of electrons
Figure 2.2: The operating principle of a streak camera. Figure adapted from [9]

proportional to the intensity of the incident light. The electrons are accelerated in a cathode ray tube toward a microchannel plate (MCP). On their trajectories, they pass through a pair of sweep electrodes (SEs) that generate an electric field perpendicular to the main propagation direction of the photoelectrons. The applied sweep voltage is synchronized to the excitation pulse and ramped up at high speed (as fast as a few hundred ps), resulting in a photoelectron deflection that depends on the moment when they pass through the SEs. This means that the early part of the pulse is deflected less than the later part of the pulse, so that different parts of the pulse strike the microchannel plate (MCP) at different positions. Thus, the temporal structure of the pulse is converted into a spatial distribution, or streak, pattern. As the electrons pass through the MCP, they are multiplied several thousands of times and are then bombarded against the phosphor screen, where they are converted back into visible light. The fluorescence image corresponding to the early part of the incident light pulse is positioned at the top of the phosphor screen, with later parts positioned in descending order; in other words, the axis in the perpendicular direction
on the phosphor screen serves as the temporal axis. The brightness of the fluorescence image is proportional to the intensity of the corresponding incident light pulses and the position in the horizontal direction on the phosphor screen corresponds to the wavelength of the incident light.

Figure 2.3: (a) Principle of the measurement in a radio-frequency streak method. Figure adapted from [23]. (b) In order to measure the temporal profile of the electron bunch, a dipole mode RF deflection cavity — which projects the longitudinal bunch in a transverse direction. Figure adapted from [24]

It will be seen in the later chapters of this thesis, one important aspect of this research is understanding the transient behaviors of photoelectrons in GaAs photocathode. One example of these transient behaviors, such as their transport and relaxation upon the excitation of ultrafast laser pulses, whereby seeking a simple alternative to characterize these photocathodes. Several groups in the past have studied photoelectron diffusion in GaAs photocathodes by characterizing time-resolved profiles of the emitted electron bunches. As shown in Fig. 2.3 (a), Hartmann et al. [23] uses a method similar to the streak camera for the electron bunch analysis. The basic concept reported in their paper is a radiofrequency streak method. This method trans-
forms the phase (time) dependent intensity of the electron bunch into a transverse spatial profile and report a time resolution of about 1.1 ps. More recently, Honda et al. [24] has also used a similar concept based on radiofrequency streak method which projects the longitudinal bunch in a transverse direction and subsequently extract their temporal profile with a time resolution of their system to be approximately 3.5 ps. Details about their method in order to extract the temporal profile of emitted electron bunches can be found in these references [24, 25].

While these aforementioned efforts have resulted in considerable insight into the ultrafast carrier dynamics in GaAs photocathodes, their results are all based on post-photoemission measurement, which can only offer an indirect picture of photoelectron transport inside the devices. On other hand, approach taken in this thesis is based on the pump-probe method, which can directly probe photo electron accumulation on the surface of a GaAs photocathode with a *ultrafast* time resolution, hence offering a pre-photo emission scheme for the study of ultrafast photoelectron dynamics inside the device.

2.1.1.3 Photoluminescence Upconversion (PLU): Time Resolution 100 fs.

Ultrafast luminescence spectroscopy [3] using sum frequency generation or Photoluminescence up-conversion is a technique that provides a means for measuring low-level luminescence signal and has been applied for wide variety of investigations in semiconductors [26]. While TCSPC and streak camera systems are commercially available, the PLU technique [27] relies on a home-built setup. The basic concept of PLU is explained here in conjunction with Fig. 2.4. The output of an ultrafast laser is divided
into two beams and the sample is excited by one of these two beams. The resulting luminescence signal from the sample is collected and refocused on a non-linear crystal, preferably by reflective, aberration-free optics to avoid pulse spreading through dispersion. The second laser beam is suitably delayed via a mechanical delay stage and also focused and spatially overlapped with a photoluminescence (PL) signal on the non-linear optical crystal. The resulting PL signal from the sample is frequency mixed (gated) with a second synchronous laser pulse. The angle between the two beams and the angle of the non-linear crystal are adjusted for phasematched sum-frequency generation at a given luminescence photon energy [27]. The sum-frequency signal is generated only during the gating laser pulse as shown in the lower half of Fig. 2.4. Furthermore, Fig. 2.4, which basically shows that fraction of the PL, PL(t), that temporally overlaps with the gating pulse mixes with it and produces an optical signal at the sum or difference frequency. The gated PLU(t) (PL upconverted) signal is proportional to the peak intensity of the gating pulse. The frequency mixed signal is then spatially and spectrally filtered to reduce the background signal from the upconverted PL and gating pulse and detected by a PMT. Since PMTs are available with excellent performance in the blue and UV spectral range, sum-frequency rather than difference-frequency generation is used and hence the term "PL Upconversion". Time evolution of luminescence at a given photon energy can be obtained by scanning the relative delay between the two laser beams. Time-resolved luminescence spectra can be obtained by keeping the delay fixed and scanning both the angle of the non-linear crystal and the spectrometer in a synchronised manner.
Since this technique is in the optical range, a time resolution of around 100 fs is achievable which is mainly limited by the temporal widths of the excitation and gating laser pulses and the spectral bandwidth of the frequency mixing process that happens in the non-linear optical crystals. The up-converted signal, and hence the sensitivity of PLU, can be significantly enhanced by increasing the thickness of the non-linear crystal. However, the increase of the PLU sensitivity comes at the expense of temporal resolution. Increasing crystal thickness induces second-order dispersion effects which causes a temporal broadening of the gating pulse and a temporal walk-off between PL and gating pulses. Both effects reduce the up-conversion efficiency and the time resolution. Moreover, this method also requires the use of OPO or OPA since the governing parameter to produce an up-converted signal in the non-linear crystal is the intensity of ultrashort pulses. Hence, a multi-stage optical amplifier chain is usually used which considerably increases the cost, size, and complexity of the system.

2.1.2 Pump-Probe Spectroscopy: Time Resolution 10 fs.

Ultrafast pump-probe spectroscopic techniques are one of the most widely used forms of time-resolved methods which facilitates the achievement of femtosecond time resolution and as a result, provides the means to anatomize some of the fastest processes happening in semiconductors. There are two broad schemes of this technique, viz. degenerate and non-degenerate pump-probe spectroscopy. In the case of former, the output pulse train from a single ultrafast laser is divided into two separate pulse trains. While in the latter case, one can use two synchronized lasers at different wavelengths
Figure 2.4: (a) Schematic of the luminiscence upconversion setup using either an ultrafast single laser for both exciting the sample and gating the luminescence in the non-linear crystal, or one laser for exciting the semiconductor (resonantly or non-resonantly) and a synchronized ultrafast laser at different wavelength for gating the luminescence in the non-linear crystal. (b) Schematic showing how sum frequency generation acts as a gate. Figure adapted from [3]

or a laser and white light source. In both cases, the sample under investigation is excited by one pulse train (pump) and the changes it induces therein are probed by the second pulse train (probe), whose arrival at the sample is time-delayed by introducing an optical delay in its path. Various material properties can be probed by this method by monitoring some property related to the probe such as reflectivity, absorption, luminescence or Raman scattering. In an ultrafast pump-probe spectrometer, the fundamental limit of the time resolution is primarily dictated by the pump and probe pulse duration and the interval between the measured time delays. The variable stage, which is responsible for introducing an optical delay and hence time-delayed arrival or probe pulses at the sample, usually consists of a retro-reflector mounted on a motorized stepper stage. The trick in achieving femtosecond time resolution, in part, lies in the ability of the smallest step size of the motorized stepper stage. For example, for each micrometer of path length difference, the relative time delay
between the pump and probe is changed by 3.33564 fs. However, for the case of a retro-reflector, this value doubles since for each micrometer of stage movement a path delay of 2 µm is generated. Most of the commercially available motion controllers can have accuracies of 0.1 µm, which translates to a precision of a single femtosecond for the time delay between the pump and probe pulses. Hence, with the advent of few-cycle ultrafast lasers and state-of-the-art ultrafast optics, pump-probe methods are one of the most sophisticated techniques that can allow us to take a tour at sub 10 fs time resolution.

### 2.2 Optical Sampling: A Prelude to Pump-Probe technique

A typical laboratory setup to characterize an optical signal is to use a photodetector for detection and an oscilloscope to display the measured temporal variation of the generated photocurrent versus the time. However, in this conventional setup, with “electrical” sampling oscilloscopes and the “fastest” photodetectors available today, the overall bandwidth of the measurement system is limited, compromising the time resolution required to characterize the full ultrafast optical signal. This bandwidth limitation can be extended by shifting the sampling process from the electrical to the optical domain and this general technique is called optical sampling.

The basic idea behind an optical sampling technique is shown in Fig. 2.5 [28]. Here the signal to be sampled and reconstructed is shown in the form of a black Gaussian profile of optical data bits, each with a duration of 6.25 ps corresponding to a bit rate of 160 Gbit/s. These signals are passed through optical gates with the time between two sampling instants (gates) to be 3.2 ns, which corresponds to a sampling
frequency of roughly 310 MHz. The gating window, or in other words the period of time for which the gate transmits the data signal, creates several slices of optical data bits (black Gaussian profile). These slices are called optical samples, which are nothing but the instantaneous power of the signal at the moment when the gate is open/transmits. Hence by exploiting a significantly slower sampling frequency, one can circumvent the need for high-speed electronic signal processing to detect and reconstruct optical signals with a low bandwidth detector.

This basic principle of optical sampling also serves as the backbone of any pump-probe spectroscopic technique. As shown in the above Fig. 2.6, a pulsed laser is used to generate two high-speed pulse trains using a beam splitter. The top stream of pulses (pump beam) is used to excite the sample and to generate a sample response, depicted by the black stream of curves on the right side of the sample. To gate the measurement of this optical signal, another stream of pulses (probe beam) is used as
Figure 2.6: The operating principle of optical sampling in a pump-probe scheme.

A gating window, which only allows the detector to “see” the signal within very brief periods of time. The detected power, therefore, reflects the instantaneous power of the signal at the gating moment. Despite the fact that the response of the detector can be much slower than the signal pulse or the gate, the gating period is adjusted in such a way that the timings of consecutive gates and signal pulses gradually “walk-off” from each other. This is usually done by introducing a delay line in either the pump or probe arm to generate a relative time lag between the arrival of these pulse trains on the sample. This will create several optical samples by making several slices of the full ultrafast signal. Hence, the full ultrafast time-domain signal
is not measured at once but is reconstructed by probing the pump-induced change in
the system reflectivity or transmission at a given time delay using a second ultrafast
pulse and repeating the measurement multiple times for multiple time delays. Each
individual data sample is the average signal over many reflected or transmitted pulses
at a given time delay, thus eliminating the detector response time as a limitation of
the temporal resolution. In an ultrafast pump-probe spectrometer, the minimum
time resolution is limited by the pump and probe pulse durations and the interval
between the measured time delays. In this way, the temporal resolution of a few tens
of femtoseconds can be achieved (depending on the laser source and the stage that is
chosen) while using a detector with a response time of several nanoseconds.

2.2.1 General Pump-Probe scheme (transmission and reflection)

The purpose of this section is to layout a brief overview of the various steps involved in
designing a pump-probe system. More specific details about the system designed for
this research will be covered in Ch. 4. Shown in Fig. 2.7 is a description of a standard
pump-probe scheme, which can either be configured as a differential transmission
spectrometer or a differential reflection spectrometer. As mentioned in Section 2.1.1,
there are two broad arrangements of a pump-probe experimental design, one being a
degenerate pump–probe spectrometer that uses pump and probe pulses of the same
wavelength. The other arrangement is a non-degenerate pump–probe spectrometer
that uses different pump and probe wavelengths. Non-collinear refers to the angle
between pump and probe pulses and is generally a preferred geometry for a good
signal-to-noise ratio because, in this configuration, the pump power is prevented to
Figure 2.7: Time-resolved differential reflection spectrometer using degenerate pump–probe spectroscopy. The system can be similarly configured for time-resolved differential transmission, with the collection optics and detection relocated behind the sample. Figure adapted from [9].

fall on the detector. We will mostly confine ourselves to non-collinear degenerate pump-probe system geometries.

As shown in Fig. 2.7, the output of the laser is first fed into a dispersion compensating unit, which is generally comprised of prism pair [29] sequence or specially designed double chirped mirrors [30]. This part is necessary for any pump-probe scheme to preserve the minimum temporal widths of the laser pulses, which eventually contributes to the system temporal resolution. After this unit, the main laser beam advances towards the actual interferometer, where the laser beam is split into two components using a beam splitter, which are the pump and probe beams. The transmitted pump beam receives the majority of the optical power and is used to optically perturb the sample from equilibrium. The reflected beam becomes the probe
beam and is used to sample the electronic configuration of the sample at a fixed time delay determined by the difference between the pump and probe path lengths.

The pump beam passes through a broadband half-wave plate to rotate its polarization ($\hat{\sigma}$ after the half-wave plate) so that it is perpendicular to the probe beam polarization ($\hat{p}$). An optical chopper modulates the pump beam frequency using a mechanical chopper that is used as the reference input to a lock-in amplifier. A lens or off-axis parabolic mirror (to minimize dispersion or nonlinear effects) focuses this pump beam onto the surface of the sample to be studied. This lens usually has a shorter focal length than the lens used to focus the probe beam to ensure that the diameter of the focused pump spot is larger than that of the probe spot. The relative power of the probe beam is usually much less than the pump beam (ideally a pump/probe power ratio $>10:1$) so that the probe merely samples the material properties ($\Delta R/R$ or $\Delta T/T$) at each time delay without significantly altering them.

After the beam splitter, the probe beam travels through a variable-length delay stage to control the optical path length and, therefore, the relative timing of the pump and probe pulse incidence on the sample. This stage is the origin of the temporal delay and the ultrafast resolution of this system; its minimum step size, along with the laser pulse width, restricts the temporal resolution of the system. This probe beam is then focused onto the sample position so that it is spatially overlapped with the focused pump beam spot. The focused spot size of the probe beam should be smaller than that of the pump (typically a pump/probe ratio $>2:1$) so that the probe measures an area of the photoexcited sample that is approximately uniformly excited. The chopped pump beam modulates the reflectivity of the sample at the
chopper frequency $f_c$, which then modulates the transmitted or reflected probe beam power at that chopper frequency. As a result, both the pump and probe beams have a component at the chopper frequency, but only the modulated probe beam is dependent on the pump-induced change in the material properties.

In a degenerate experiment, both the scattered pump beam and the transmitted or reflected probe beam are incident on the detector and the lock-in amplifier is unable to distinguish between them. It is at this point, the role of polarization optics (half-wave plate and polarizing beam splitter) is realized as a critical component in this experiment, which is needed to separate the pump and probe beams, as the scattered pump beam will otherwise saturate the lock-in amplifier if it is incident on the detector. The pump beam polarization is rotated by 90° by the half-wave plate ($\hat{p} \rightarrow \hat{s}$) before incidence on the sample. After either reflection (as shown in Fig. 2.7) or transmission through the sample, a polarizing cube beam splitter or broadband polarizer splits the pump polarization ($\hat{s}$) from the perpendicularly polarized probe beam ($\hat{p}$). The probe beam is then focused onto the detector while the pump beam travels a different physical path towards the beam dump.

After the polarizing beam splitter, the probe beam is focused onto a detector and converted to an electrical signal. As discussed earlier, the detector does not need to have the time resolution to measure the full ultrafast signal (i.e., a detector with tera- or petahertz bandwidth). This detector must, instead, be capable of resolving the signal at the chopper frequency. The electrical signal at the chopper frequency is then measured using a lock-in amplifier to isolate the changes in the probe beam transmission or reflection at each value of the pump-probe delay. The temporal
resolution instead comes from the relative optical path length difference between the pump and the probe pulses. The full ultrafast signal results from averaging repeated measurements of the photoinduced change to the probe signal over the full range of pump-probe delays.

2.2.2 Pump-Probe Reflectometry Spectroscopy

Over the last decade, the advance in novel materials such as two-dimensional (2D) materials, metamaterials, plasmonics, and negative-electron-affinity (NEA) structures has triggered rapid growth in the development of ultrafast optoelectronic devices [31–34]. This sparks an urgent demand for techniques capable of characterizing ultrafast carrier dynamics in such devices [35–38]. Transient processes such as carrier relaxation and carrier transportation near device surfaces are especially important to the operation of many ultrafast devices including NEA photocathodes [37], fast photoconductive switches [38], and photodetectors based on 2D materials [39]. A comprehensive study of these processes requires time-resolved, broadband reflective spectroscopy with femtosecond-scale temporal resolutions.

Optical reflectometry is a versatile diagnostic technique that is often used to characterize optical constants such as the index of refraction and the group index [40, 41]. Combining the concept of optical reflectometry with the femtosecond pump-probe method leads to pump-probe reflectometry (PPR), a technique especially capable of characterizing ultrafast optical properties [17]. In a typical PPR scheme, the surface reflectivity of a device sample is measured at various time delays after the material is optically excited by energetic “pump” pulses [10–13, 17]. Since
the transient variation of reflectivity is determined by the transient variation of dielectric constant, which in turn is strongly influenced by the evolution of free-carrier population upon excitation, PPR is able to provide a direct picture of ultrafast carrier dynamics inside the material [10,11,13]. Compared to other time-resolved techniques such as ultrafast luminescence spectroscopy [26] and time-resolved photoelectron spectroscopy [42], PPR is easier to realize experimentally and better suited for studying semiconductor devices [43].

2.3 Few-cycle Pump-Probe Reflectometry

2.3.1 Few-cycle Pulse generation

Ultrashort pulses are key to numerous fields of science and technology. One particular technology that remains central to the ultrafast revolution is the Ti:sapphire laser. Ever since its invention in 1982 by Peter Moulton [44], Ti:Sapph has been the working horse of mode-locking, offering its services to a wide spectrum of applications ranging from semiconductor physics to biological imaging [45]. Their unique temporal and spectral properties make them an extremely valuable tool in many fields. The femtosecond laser of the scientific line used for this research is a passively mode-locked solid-state laser. The key mechanism at the core of ultrashort (few-cycle) pulse formation in our Ti:sapphire laser is the nonlinear optical Kerr effect. The optical Kerr effect is a third-order nonlinear process, where the refractive index of the material is intensity dependent: \( n(I) = n_0 + n_2 I \); where \( n_0 \) and \( n_2 \) are the linear and nonlinear refractive indices, respectively and \( I \) is the light intensity. Because of this non-linear
effect, there is a lensing effect in the gain medium (Ti:Al₂O₃) which establishes preference for generation of intense ultrashort laser pulses as shown in Fig. 2.8(a) [46].

![Figure 2.8](image)

**Figure 2.8**: (a) Kerr lens mode locking obtained through a Kerr lensing effect at an intracavity focus in the gain medium (b) A typical few-cycle laser pulse emitted from KLM Ti:sapphire laser. Figure adapted from [46]

A typical laser pulse that is emitted by the Ti:sapphire is shown in Fig. 2.8(b). This extremely short pulse is referred to as a “few-cycle” laser pulse, because the pulse duration is only a small multiple of an optical cycle. Mathematically, it is represented as $E(t) = A(t)(\epsilon^{i(\omega_0 t)})$ with the electric field travelling with phase velocity ($\nu_p$) and the pulse envelope travelling with the group velocity ($\nu_g$). In practice, the pulse duration of KLM Ti:Saphh is limited by the dispersion management in the cavity, the gain bandwidth of the active medium and the optical period of the carrier wave. In order to consider the practical aspects of our experiments and to preserve the few-cycle (< 8 fs) nature of laser pulse at the target sample, external cavity dispersion compensation plays a critical role and it will be explained in detail in Chapter 4.
2.3.2 Few-cycle pulse management (dispersion reduction and compensation)

Dispersion is the phenomenon where the phase velocity of a wave depends on its frequency. For a laser to develop a short pulse, all the allowed lasing frequencies must coherently add to form a circulating pulse in the cavity. This requires that all the modes experience the same round-trip cavity time, or, equivalently, that the optical length of the cavity be independent of frequency. This is usually not the case due to the dispersive nature of most materials. Due to dispersion, different frequency components of the pulse travel at different velocities. Quite intuitively, one can think of a short pulse being made up of a set of much longer wave packets of a narrow spectrum, all added together coherently. In a dispersive system, these wave packets all travel at different velocities and consequently the initial short pulse may broaden. Since the Ti:sapphire crystal and other optical elements in the cavity are dispersive, the pulse is deformed as it passes through optical elements due to the wavelength dependence of the refractive index. To take a deeper look in this phenomenon, we submit to a function that plays a central role in ultrafast optics, the spectral phase $\varphi(\omega)$, which is the phase accumulated by the spectral component of the pulse at frequency $\omega$ upon propagation between the input and output reference planes that defines the optical system. When a pulse propagates through a dispersive material, its spectral phase $\varphi(\omega)$ is affected. By expanding it in a Taylor series around the central frequency $\omega_0$, $\varphi(\omega) = \sum_n \frac{1}{n!} \varphi^{(n)}(\omega_0)(\omega - \omega_0)^n$, we can identify three major effects, corresponding to the first three terms in this series: (a) $\varphi^{(0)}(\omega_0)$, overall phase
accumulation – the propagation phase added to all frequencies, (b) $\varphi^{(1)}(\omega_0)$, group delay – the entire pulse is delayed compared to a pulse propagating in free space, and (c) $\varphi^{(2)}(\omega_0)$, group delay dispersion (GDD or chirp) – a frequency-dependent group delay of the different spectral components of the pulse. GDD is very important since this term causes a temporal broadening of the pulse in every round trip through the cavity. This effect limits the generation of ultrashort pulses, or even, will disable the mode-locking, and therefore needs to be compensated for. For Ti:sapphire crystal, it exhibits positive GDD in the visible and near IR and leads to a temporal broadening of the pulse. Therefore, a way of generating negative GDD is needed to compensate for the positive dispersion inherent to optical materials and nonlinear effects.

There are three common methods for generating anomalous (negative) dispersion in the ultrafast community, viz. prism pair compressor, dispersion compensating mirrors (based on chirped mirror technology) and grating compression. Prism pair compressors are the most common technique to introduce negative dispersion and they were first introduced by Fork et al. [29]. In this Section, we will briefly go over prism pair compressors and explain chirped mirror technology in Chapter 4, which is used for dispersion compensation in this research. Prism compressors, because of their low cost and flexibility, are the most common technique to introduce negative dispersion. While they can be used for intracavity usage, they are more commonly used in extracavity to compensate for dispersion that results from optical elements in an experimental setup. A schematic representation of prisms configured to introduce tunable dispersion is shown in Fig. 2.9 (a) [9]. This symmetric configuration of prisms allows for the beam to be spatially dispersed, compressed, and recombined in
a single pass. A more simple design, with the second pair of prisms replaced by a retro-reflecting mirror, is now the standard configuration.

**Figure 2.9:** (a) Schematic representation of a four-prism compressor that is capable of introducing negative GDD. Often, a mirror is placed after a two-prism sequence to retroreflect the beam and simplify alignment. (b) Schematic representation of the beam path through a two-prism compressor. Figure adapted from [9]

The prisms in the compressor are rotated 180° with respect to each other so that their bases remain parallel. Properly aligned prisms allow the beam to propagate parallel to their bases. The prism compressor generates negative dispersion by introducing a wavelength-dependent path length. To finely tune the dispersion, one or both of the prisms are mounted on translation stages that allow them to be inserted into the beam (introducing positive material dispersion). In Fig. 2.9 (b) L is the apex-to-apex distance and H is the sum of the length of insertion of both prisms into the beam. A very nice summary of SOD and higher-order dispersion effects of grating pairs, prism pairs, and materials is given in Ref. [47]
2.3.3 Detection:

After one has designed a pump-probe scheme, the last part of the system is the type of detector to be used for our experiments. There are a couple of parameters that dictate the choice of the detector for any pump-probe scheme. First is the response time of the detector chosen. In Section 2.1.1, we have already outlined how to circumvent the need for high-speed electronics and detectors by employing an optical sampling approach. The femtosecond temporal resolution of the system is a courtesy of the path length difference between pump and probe pulses, whereby depending on the quality of the delay stage, and not on the response time of the detector itself. For a chopping frequency (while using a lock-in amplifier) of a couple of hundreds of Hz, it would require a detector response time of a few ms. This is easily achieved with most of the commercial semiconductor photodiodes. The next parameter is the wavelength sensitivity of the detector. For the choice of semiconductor photodiode to generate a measurable signal, the probe photon energy should be higher than the bandgap of the semiconductor material.

2.3.3.1 Lock-in detection

A key aspect of any pump-probe measurement scheme is the fact that the time resolution is governed by the duration of the laser(probe) pulses and not the bandwidth of the photodetectors or the signal recording electronics. The Ultrafast time resolution of a pump-probe scheme is the result of repeated measurements of the change to the probe pulse reflectivity (or transmission) over a range of pump-probe delays, $\tau$. As
the pulse repetition rates of the lasers used in these experiments are typically between a few kHz to hundreds of MHz, the signal-to-noise ratio (SNR) of the individual pulses is often very small and hence sensitive detection electronics and heavy averaging is needed to create the highest SNR and recover the full ultrafast response signal. A lock-in detection scheme with a low-noise detector is one of the most commonly employed detection techniques to reduce system noise. In a lock-in based pump-probe experiment, the power of the pump beam is modulated “on” and “off” at a known frequency, say \( f_c \) as shown in Fig. 2.10 (a) [9]. Let us denote the pump laser repetition rate by \( f_{\text{laser}} \) and for sake of simplicity choose the chopping frequency to be \( f_c = f_{\text{laser}}/2 \). If the experiment is employing a 1 kHz repetition rate laser, then \( f_c \) will be 0.500 kHz, which means that “on” represents the case when only one pulse is transmitted by the chopper and the “off” state represents one pulse that will be blocked by the chopper. In general, pump-probe experiments employ high-repetition-rate lasers and the chopper is not synchronized to the laser repetition rate. Hence, for most of the cases, the “on” state means many optical pulses will be transmitted and “off” will block many optical pulses. In both cases, the probe beam is not chopped. However, in order to remove the additional background scattered pump light, which cannot be removed efficiently by cross polarizing the pump and probe beam or by wavelength filter technique as mentioned in Section 2.2.2, one can modulate both the pump and the probe at different frequencies, \( f_{c1} \) and \( f_{c2} \). The lock-in reference is then set to the sum of these two frequencies.

Because of the modulation of the pump beam, there will be twice as many probe pulses as pump pulses for a 50:50 chopper duty cycle (50% “on” and 50% “off”).
Figure 2.10: A simulation of a time-resolved differential transmission (or reflection) experiment at one value of the pump–probe delay $\tau$ using lock-in detection. Figure adapted from [9].

One-half of the probe pulses will be incident on the sample without a pump pulse to perturb their optical properties and the other half will be incident on the photoexcited sample. The modulated probe signal at the chopper frequency $f_c$ will, therefore, be proportional to the change to the material properties due to the photoexcitation as shown on the bottom of Fig. 2.10. To correctly measure the sign of the differential transmission or reflection, the phase of the lock-in should be set by the Auto-phase option on the front panel of the lock-in display. Once this is done, a positive lock-in
voltage $\Delta V$ corresponds to an increase in the sample transmission (reflection) and a negative signal to a decrease in transmission (reflection).

The lock-in time constant $\tau_{\text{lock-in}}$ should be $2 \times$ to $3 \times$ the acquisition time to allow the lock-in sufficient time to stabilize; for example, a $\tau_{\text{lock-in}} = 300$ ms time constant would permit an $\sim 1$ s acquisition time per point. The change in voltage at the chopper frequency is $\Delta V = -0.5$ mV in the previous example. To determine the differential change of the sample property, the measured $\Delta V$ should be divided by the full voltage of the detector absent the pump beam $V$; this is $V = 3$ mV in the previous example. The ratio ($\Delta V/V = -16.7\%$ in this example) at this delay $\tau$ is either $\Delta T/T(\tau)$ or $\Delta R/R(\tau)$ depending on the experiment configuration; typical values are often much smaller than this example (i.e., $\Delta R/R \sim 10^{-4} - 10^{-6}$). The full ultrafast temporal dynamics, $\Delta T/T(\tau)$ or $\Delta R/R(\tau)$, results from repeating this measurement for multiple values of the pump–probe delay $\tau$. 
CHAPTER 3

NEGATIVE ELECTRON AFFINITY PHOTOCATHODES

3.1 Introduction

The term “Negative Electron Affinity” (NEA) is used to describe a class of III-V semiconductor photocathodes in which the vacuum potential energy is lower than the conduction band minimum in the bulk flat region. Facilitating such conditions is usually the courtesy of a “work-function lowering” material, which is applied on the surface of photocathodes. Ensuing this surface activation process, the photo-excited electrons which are generated deep in the bulk region, and are thermalized to the conduction-band minimum, diffuse towards the surface and escape easily into the vacuum due primarily to the NEA condition, and hence significantly improving the efficiency of such devices. Owing to its tremendous applications for night vision and other low-light applications, these families of photocathodes have attracted a lot of interest over the last two decades due to their high quantum efficiency and low dark emission. Although there has been a lot of work dedicated to the improvement of the design and the performance of III-V photocathodes [48–51], the majority of these prior efforts have focused on the steady-state parameters such as spectral response and quantum efficiency of GaAs-based photocathodes [52–56]. The dynamic proper-
ties of these photocathodes have received relatively less attention [57–59]. However, growing demand for time-resolved electron beams in recent years has prompted a surge of interest in carrier dynamics inside GaAs photocathodes [23,24,57,58,60–63]. Understanding the transient behaviors of photoelectrons, such as their transport and population decay upon the excitation of ultrafast laser pulses, proves to be an important step toward high-quality electron sources [24].

One important aspect of this research is to demonstrate a simple yet effective approach to study photoelectron dynamics in GaAs photocathodes. The method is based on an optical technique called pump-probe reflectometry (PPR), which will be described in detail in the next chapter. This technique measures the ultrafast variations of reflectivity from a semiconductor sample upon the injection of a femtosecond excitation (or “pump”) pulse [17]. Since the transient behavior of reflectivity is determined by the transient property of the refractive index, which is closely related to carrier concentrations [64,65], PPR is able to directly probe the accumulation of free carriers near the device surface. This provides a pre-photoemission scheme for the study of ultrafast photoelectron dynamics in GaAs photocathodes with ultrafast time resolutions [66].

In this chapter, a theoretical framework based on a carrier-diffusion model is presented to quantitatively verify the physical understanding of the pump-probe differential reflectivity measurements on these photocathodes and to better explain the transient behaviors of reflectivity of these structures.
3.1.1 What is NEA Photocathode

Ever since their discovery by Scheer and van Laar (1965) [67], semiconductor photocathodes have shown promising results for generating high average currents by the virtue of their high quantum efficiency in the UV or VIS spectral ranges. Their efficiency, which primarily depends on the emission of electrons from the surface of solid into the vacuum, has been dramatically improved with the advent of negative electron affinity (NEA) materials. The literature in this area is enormous and today a complete bibliography would run into many thousands of references. Instead of providing such a list, in this and few subsequent sections, a brief introduction of the NEA concept is presented based on the excellent review paper of early work [49].

Fig. 3.1(a) is the energy band diagram for a typical p-type semiconductor/vacuum interface, showing the valence band maximum $E_v$, the conduction band minimum $E_c$, the Fermi level $E_f$, and the band-gap energy $E_g$. It is assumed that the semiconductor surface is essentially clean-free of oxides and impurities. In general, the energy bands are bent near the surface owing to the presence of the surface states [68] and will be described in detail in later sections. The distance in energy from the conduction band minimum to the vacuum level $E_o$ at the surface is the electron affinity $\chi$. The difference between $E_o$ and $E_f$ is the work function $\phi$ of the material. To escape into the vacuum, electrons in the conduction band minimum of the semiconductor must be given the energy to surmount the positive barrier at the surface $\chi$. Typically, $\chi$ is 3 to 4 eV.
A positive electron affinity (PEA) surface is one for which the vacuum level lies above the bulk conduction band minimum as in Fig. 3.1(a). Through specific treatments of certain semiconductor surfaces, the vacuum level can be lowered to a point beneath the bulk conduction band minimum as shown in Fig. 3.1(b). Since the bent band region of the surface of NEA materials is, at most, a few hundred angstroms wide, it does not significantly affect the internal excitation and electron transport processes in the bulk of the material. The term negative electron affinity more precisely means negative effective electron affinity \( \chi_{\text{eff}} < 0 \), and it refers to the condition for which the vacuum level lies below the conduction band minimum \textit{in the bulk} [to the left of the bent band region in Fig. 3.1(b)]. Thus one can have NEA and still have a positive actual electron affinity \( \chi \) as shown in Fig. 3.1(b).

The definition of the NEA condition can be better understood through the energy band diagram of Fig. 3.1(b). To obtain NEA, the difference between the bulk conduction band minimum and the Fermi level must be greater than \( \phi \); that is,

\[
(E_c - E_f) > \phi. \tag{3.1}
\]

To maximize the quantity \( (E_c - E_f) \), heavily doped p-type semiconductors are used which have a Fermi level close to the valence band maximum. In this case, \( (E_c - E_f) \approx (E_c - E_v) \equiv E_g \), and the condition for NEA becomes

\[
E_g > \phi. \tag{3.2}
\]

The quantity \( (E_g - \phi) \) is termed the degree of NEA, and its value influences the fraction of electrons emitted into vacuum. Given the NEA condition, an electron with energy greater than or equal to \( E_c \) encounters no work function barrier at the surface of the
Figure 3.1: Band diagrams showing (a) positive electron affinity and (b) negative electron affinity conditions in relation to band-gap energy $E_g$ and work function $\phi$.

semiconductor, and, therefore, it can escape into vacuum. This fact distinguishes the NEA surface from the conventional (PEA) electron emitter surface, leading to the development of a class of electron emission devices with improved performance.

3.1.2 Advantages Compared to Other Photocathodes

The fundamental difference between a Conventional Emitter (Photocathode) and a NEA Emitter (Photocathode) stems from the basic idea of the efficiency of electron emission from its surface, which can be quantified by the Quantum Yield of the Photocathode. The band diagram description as detailed in Section 3.1.1 serves as a first glance for a qualitative demarcation between these two classes of photocathodes. This difference is further exemplified mainly through a comparison of the photoemission process for each case. The photoemission process entails three steps, which are i) optical absorption leading to photoexcitation, ii) transport to the surface and iii) escape to the vacuum. Commonly used photocathode materials include metals like Cu, Mg, Pb and Nb and semiconductors like CsTe, alkali-antimonides [69] and III-
V semiconductors activated to a negative electron affinity (NEA). The supremacy of NEA emitters lies primarily in the intricacies involved in steps (ii) and (iii). Although photoexcitation is more or less the same for both classes of emitters, the optical absorption length also plays a key role in how many electrons can be excited to the conduction band for a specific intensity of the light. A high optical absorption length would mean that electrons deep in the material can be excited to the conduction band. Amongst direct bandgap semiconductors, GaAs has a high optical absorption coefficients [70] and therefore is a good candidate to be used as a photoemitter.

During the second step, the excited electrons in the conduction band approach the surface from the bulk of the material. While approaching the surface, the electrons go through different scattering processes and thermalize to the bottom of the conduction band. Depending on what the dominant scattering mechanism is, the electrons will either have enough energy to stay at the conduction band while they reach the surface or will lose enough energy in scattering processes while approaching the surface to drop down to the valence band and not be able to leave the surface. For example, if electron-electron scattering is the dominant mechanism, the excited electrons will lose their energy shortly after being excited to the conduction band and get back to the valence band. This process is dominant in metals and solely responsible for the low quantum efficiency for metal photocathodes compared to semiconductor photocathodes. The escape depth depends on the excitation energy of the radiation, the details of the absorption process, and the energy dependence of the transport process. Empirically, it is found that the escape depth for conventional cathodes is a few hundred angstroms [49]. On the other hand in semiconductors, electron-phonon scat-
tering is the dominant mechanism that is not as lossy compared to electron-electron scattering. Scattering lengths in semiconductors are much higher and the excited electrons in the bulk have a high probability to reach the surface for emission. This is because the thermalized minority electrons survive for relatively long times before they recombine across the bandgap. During this time, known as the minority electron lifetime, the electron diffuses over distances as long as several micrometers. These diffusion lengths are several orders of magnitude longer than the escape depths for conventional emitters, and herein lies one of the great advantages of NEA emitters. Electrons diffuse to the NEA surface from relatively deep in the material and escape into the vacuum, thus increasing the emission efficiency in regions of the spectrum where optical absorption is weak [49].

The third and final step of photoemission is the emission of electrons from the surface of the material to vacuum. The probability of emission of an electron from the surface to vacuum is dependent on the surface characteristics of the material. For GaAs, the surface can be treated such that the potential difference between the vacuum level and conduction band minimum is negative. This condition is called Negative Electron Affinity and will be discussed briefly in the next few sections.

### 3.1.3 Applications

III-V semiconductor photocathodes with negative electron affinity (NEA) have attracted a lot of research interest over the last two decades owing to their high quantum efficiency and low dark emission, which are crucial parameters for low-light applications such as photomultipliers, low-energy electron microscopes, and night-vision im-
age intensifiers [71–76]. The development of the next-generation free-electron lasers and coherent X-ray sources also puts such photocathodes in high demand as the ideal electron-beam injector with low thermal emittance, high average current, and good polarization purity [57,61,77–80]. More recently, the emerging concept of space X-ray communication (XCOM) prompts new interest in transmission-mode semiconductor photocathodes [81] and similar structures are also gaining interest as efficient solar energy converters [82,83].

3.2 Basic Characteristics

3.2.1 Band Bending and Cs/O Activation

The advantage of NEA photocathodes stems primarily from the relationship between the potential barrier at the surface and the bottom of the conduction band in the bulk of the material. Generally, surface activation of such devices creates a favorable condition, which can be qualitatively defined as lowering of the potential barrier at the surface below the bottom of the conduction band and as a result, the device is said to have achieved a negative electron affinity. So, the understanding of the structure of any NEA Photocathode and hence the ability to achieve high Quantum efficiency depends primarily on two concepts: The formation of Band Bending Region (BBR) near the device surface, and the lowering of potential barrier at the semiconductor surface by treatment. In practice, this condition is obtained by heavy p-doping of the semiconductor (to encourage downward band bending at the surface) and by adding...
a thin film (several atomic layers) of cesium oxide (Cs,O) on the clean semiconductor surface. In this section, these two concepts will be briefly introduced.

**Reason for Band Bending Region Formation (Surface states and Fermi-Level Pinning):** Surface by definition is a defect since the surface of any semiconductor is the place where the periodicity of the crystal structure stops/is broken and hence the chemical nature of the surface is that some atoms are sitting on the surface that do not have the sufficient numbers of neighboring atoms that it can bond to. So the surface states contain a lot of incomplete chemical bonds, which are sometimes called the dangling bonds. These incomplete bonds produce energy levels that are located within the bandgap, just as the bulk defects and impurities produce energy levels that are located within the bandgap. The nature of these defect states/surface states are not well known in general and there are many varieties of defect states possible depending on the exact termination of the surface. Usually, the density of surface states is large ($\sim 10^{15} \text{ cm}^{-2}$) in comparison with the bulk dopant states in regions of the bulk semiconductor parallel to the surface ($\sim 10^8 - 10^{12} \text{ cm}^{-2}$). Therefore, the Fermi level of the semiconductor is almost independent of the bulk dopant concentration and is pinned by the surface states, which is referred to as the Fermi level pinning effect.

Fig. 3.2 shows the alignments (and bending) of the energy bands at the semiconductor/surface interface for the case of both n-doped and p-doped semiconductors [68]. It qualitatively portrays how the band bending depends on the type of doping. In Fig. 3.2(a), one starts with an assumption that the surface state is half-filled and centered at the midgap. When the semiconductor is undoped (intrinsic
Figure 3.2: Schematic electron energy levels near the surface of a clean semiconductor: (a) undoped (intrinsic) semiconductor; (b) disequilibrium and (c) equilibrium between n-type bulk and its surface; (d) disequilibrium and (e) equilibrium between p-type bulk and its surface. Figure adapted from [68].

For a p-type semiconductor, $E_F^{(bulk)}$ is closer to the valence band, which is lower than $E_F^{(surf)}$ under disequilibrium (Fig. 3.2d). The electrons will transfer from the surface to the bulk, causing downward band bending.
As mentioned previously, the overall quantum yield of a photocathode can be analyzed in terms of the three-step model of photoemission developed by Spicer [84], and the final step in such analysis involves the surface potential barrier which is, in part, determined by the nature of the (Cs,O) activating layer. Fundamental understanding of the lowering of the potential barrier at the semiconductor surface by (Cs,O) treatment has been analyzed in detail previous works [85]. However, the method of (Cs,O) treatment, the so-called “yo-yo” technique, has so far remained empirical [86] and the standard experimental process it involves is as follows: The yo-yo method begins by initially depositing cesium on the surface of the cathode, which increases the photocurrent and thus the QE of the cathode to a peak when there is approximately a monolayer of cesium on the surface of the cathode. Once the monolayer of cesium is surpassed the surface of the cathode is overdosed with cesium, consequently reducing the photocurrent. Once the photocurrent reaches one half of the original peak due to cesium, the cesium is turned off and the cathode is exposed to the oxidizing gas via the leak valve connected to the oxidizing channel on the QE chamber. The photocurrent recovers once the overdosing of cesium is finished and continues to climb due to exposure to the oxidizing gas. However, eventually, this gain also peaks, at which point the leak valve is closed and the cesiator is once again turned on. This causes another overdose of cesium on the surface of the cathode from which the photocurrent sharply declines, but once the photocurrent has reached half of the previous peak, once again the Cesium is turned off and the leak valve of the oxidizing agent is opened. The peak in photocurrent rises with each exposure to the oxidizing gas yet this gain in QE plateaus after a number of alternating depositions of cesium.
and the oxidizing gas, called yo-yo’s. Once the QE of the cathode has plateaued by as few as 7-10 yo-yo’s or as many as 12-17 yo-yo’s the activation process is complete and the leak valve is closed and the cesiator is retracted. A typical yo-yo activation is displayed in Fig. 3.3 (a). An important part of understanding an activated surface is obtaining the potential barrier profile for electron escape into vacuum. Such a profile is proposed in Fig. 3.3 (b) based on the structural information obtained in [85,87]. The most important feature of this potential profile is the separation of the dipole potential drop at the surface into two parts, dipole I across the O-GaAs layer and dipole II across the Cs\(^+\)-O\(^{-2}\)-Cs\(^+\) layer. These two layers are formed as a result of the successive deposition of Cs and O following the empirical yo-yo method as described before and their effect in lowering of the potential barrier and its exact structure has been analyzed in detail using photoelectron spectroscopy [87]. Based on this work, O-GaAs-[Cs] dipole lowers the vacuum level to $\leq 1.4$ eV, the cesiated work function of p-GaAs [87] above the Fermi level. The final work function of a typical (Cs,O) activated surface is -0.9 eV [85,87]. These two potential drops are qualitatively shown in Fig. 3.3 (b).

### 3.2.2 Static: Spectral Response and Quantum Efficiency

The most relevant properties for a photocathode which qualify as its Figure of Merit are its quantum efficiency and its spectral response, the photoemission response time, the thermal emittance (or intrinsic emittance), mean transverse energy, and the lifetime of the photocathode. Here, we summarize the main definitions used in this chapter to understand the static properties of these photocathodes.
Quantum efficiency (QE) is defined as the number of electrons per incident photon and is given by the formula

\[
QE = \frac{I/e}{P/h\nu},
\]

or, in practical units

\[
QE[\%] = 124 \frac{I[A]}{P[W] \lambda[\mu m]},
\]

where \( I \) is the current emitted by the cathode, \( P \) is the laser power incident on the cathode, the electron charge \( e = 1.602 \times 10^{-19} \text{C} \), the Planck constant \( h = 6.626 \times 10^{-34} \text{Js} \), and \( \nu \) and \( \lambda \) are the frequency and wavelength of light, respectively. Other related definitions commonly used are spectral responsivity \( R \) (measured in units of ampere per Watt) and quantum yield \( (Y) \), defined as the number of electrons emitted per absorbed photon. Furthermore, the quantum yield formula for reflection-mode (r-mode) photocathodes, in which the light is incident on the cathode vacuum surface,
can be solved from the diffusion model based on the three-step process, and the quantum yield \( Y(\hbar \nu) \) is expressed as follows: \[88\]

\[
Y(\hbar \nu) = \frac{\xi(1 - R_{\hbar \nu})}{1 + \frac{1}{\alpha_{\hbar \nu} L_D}},
\]

(3.5)

where \( \xi \) is the surface electron escape probability, \( R_{\hbar \nu} \) is the reflectivity of photocathode surface, \( \alpha_{\hbar \nu} \) is the absorption coefficient of the photocathode material, and \( L_D \) is the electron diffusion length. From Eq. 3.5, it can be seen that, for the given optical properties of the cathode, the \( Y(\hbar \nu) \) is mainly influenced by \( L_D \) and \( \xi \) simultaneously, which are related to the material growth and activation craft. How the photocathode properties change based on the active layer doping activation craft and particular growth method used will be discussed in subsequent chapters.

Spectral response, not to be confused with spectral responsivity, is a measure of \( QE \) as a function of the incident photon's wavelength. From the point of the laser system, the preferred photocathodes have a good spectral response in the visible range. GaAs photocathodes are broadband devices typically operating between 500–900 nm, where they reach peak quantum yields \[50,52\]. When studying such devices, it is ideal to use broadband ultrafast light sources with as much spectral overlap as possible to the device operating wavelength range.

### 3.2.3 Dynamic: 3-Step Model

In 1958, Spicer \[89\] developed a model or theory in an effort to gain a comprehensive understanding of the photoemission process, often referred to as Three Step Model. By treating photoemission as bulk rather than a surface effect, the theory divided photoemission in terms of three successive steps viz. a) optical excitation of electrons
from the valence band to the conduction band, b) transport of excited electrons to the surface, c) emission of electrons from the surface. This adaptation has allowed photoemission to be related to parameters of the emitter, such as optical absorption coefficient, electron scattering mechanisms, and the height of the potential barrier at the surface. Using simple equations and established parameters, this theory has found to be very useful in predicting the performance of photocathodes and in understanding the details of the unexpected phenomena appearing when photocathodes are pushed into new practical domains. Over the past several years, this theory has provided a practical means of understanding the photoemitter in a better way and has been a reasonable starting point for almost all the research pertaining to photocathodes, be it related to characterising its static or dynamic properties.

Similar to several studies conducted on semiconductor NEA photocathodes, the carrier diffusion model presented in this research will also submit to Spicer’s 3-step photoemission model to lay the foundation for the theory, and for the sake of clarity, each step involved in this Three Step Model is as shown in Fig. 3.4. The transport stage in this model is, however, the most complex one among the three, with critical implications to the time response and quantum yield of devices [90,91]. It involves not only electrons migrating toward device surfaces but also their cooling and recombination along the process. Measurements made with both bulk and thin-film GaAs samples have shown that electrons excited into the conduction band thermalize very quickly to the bottom of the conduction band and the transport process can be very well described by the thermal diffusion model [23,62,84]. Several groups have studied photo-electron diffusion in GaAs photocathodes by characterizing time-resolved
profiles of the emitted electron bunches [23, 24, 62, 63]. Notably, Hartmann et al. reported the first high-precision measurement of temporal profiles of picosecond electron bunches from an NEA GaAs photocathode using a synchronized spatial pulse imaging system [23]. They also developed an electron diffusion model that has been widely adopted in subsequent research. The same group later reported characterization of response time and spin relaxation time of thin III-V photocathodes [62]. More recently, Honda et al. studied the effects of active layer thickness, boundary conditions and excitation wavelength on the temporal response of GaAs photocathodes [24], and Jin et al. investigated electron transportation in GaAs/GaAsP strained superlattice photocathodes [63]. Both works appear to validate the effectiveness of the diffusion model.

![Figure 3.4](image)

**Figure 3.4:** Depiction of Spicer’s Three Step Model for photoemission.

While these aforementioned efforts have resulted in considerable insight into the ultrafast carrier dynamics in GaAs photocathodes, their results are all based on post-photoemission measurements, which can only offer an indirect picture of pho-
to electron transport inside the devices. This is because emissions of photoelectrons strongly depend on surface conditions of the devices such as chemical compositions and scattering in the Cs/O activation layer [92, 93]. Since the activation layer is not involved in electron transport, a post-emission characterization may be heavily skewed by the emission conditions and hence fails to reflect the true properties of the diffusion process. Moreover, post-emission characterization of photoelectron dynamics requires ultra-high vacuum environment and high bias voltages (> 100 kV) [24,57]. Such demanding conditions prevent the method from being widely applied.

The approach taken in this research is based on the Pump-Probe Reflectivity method as outlined in Section 2.2.2. This method has long been used in solid-state physics to study material properties [11,13,14,94,95]. However, it has not been directly applied to photocathodes, which typically features layered doping structures to enhance carrier transport toward device surfaces. The potential of the method also rests upon its simplicity compared to the post-emission schemes. The measurements are performed in the atmosphere with completely passive samples (no need to apply voltage) and will be presented in subsequent chapters. It is hoped that this novel experimental approach, along with the theoretical model presented in this chapter, is able to outline a new pathway towards understanding the dynamics of III-V photocathodes, which can ultimately lead to better device architectures and performances.

3.2.4 Uniform Doping vs. Exponential doping

The key goal of any NEA photocathode is to achieve high Quantum efficiency, which mainly depends on the formation of Band Bending Region (BBR) near the device sur-
face and the lowering of potential barrier at the semiconductor surface by treatment. As asserted before, these conditions are obtained primarily by heavy p-doping of the semiconductor (to encourage downward band bending at the surface) and by adding a thin film (several atomic layers) of cesium oxide (Cs,O) on the clean semiconductor surface, respectively. However, the improvement of GaAs photocathode quantum efficiency also depends on electron diffusion length and surface electron escape probability. Surface escape probability can partly be addressed by lowering the surface potential barrier and also by making the band-bending region (BBR) smaller to decrease the possibility of scattering and recombination. The width of the band-bending region (in cm) is given by [96]

\[ W = \sqrt{\frac{2\epsilon V_{BB}}{qN_A}}, \]  

(3.6)

where \( q \) is the electron charge (in C), \( \epsilon \) is the dielectric constant (in F/cm), \( V_{BB} \) is the amount of band bending (in V), and \( N_A \) is the acceptor doping concentration (in cm\(^{-3}\)). \( W \) can be made small by using a high doping density, \( N_A \). Unfortunately, high doping density also causes a short diffusion length, which reduces the photocathode quantum yield. To obtain a long electron diffusion length, low p-type doping concentration for GaAs material is required, but high p-type doping concentration is also necessary to obtain a narrow surface band bending region. These requirements for p-type doping concentration of GaAs material are contradictory.

To address this problem, many experimental and theoretical investigations [97–99] have shown that by optimizing the p-type doping concentration of the GaAs material, highest quantum efficiency can be obtained between \( 8 \times 10^{18} \) and \( 1 \times 10^{19} \) of p-
type doping concentration. It should, however, be pointed out while this optimization can improve integral sensitivity, this method is only a compromise between electron diffusion length and surface electron escape probability. One important development in this direction is the introduction of a gradient (or exponential) doping structure in the active layer of such devices. This method balances the requirements for long electron diffusion lengths and narrow surface band bending regions [100–102] and has shown promising results for enhancing the quantum efficiencies and spectral response in both transmission mode (t-mode) photocathodes [103] and reflection mode (r-mode) photocathodes [104].

\[ L_D = \sqrt{D\tau}, \]

where \( \tau \) is the mean lifetime of electron, \( D \) is the

**Figure 3.5:** Doping architecture of NEA GaAs photocathodes: (a) uniform-doping NEA GaAs and (b) gradient doping NEA GaAs.

Fig. 3.5 shows the classic example of NEA GaAs photocathode with a different doping architecture in their active layers. Fig. 3.5(a) shows a 2 \( \mu \)m thick uniformly doped GaAs active layer and Fig. 3.5(b) shows similar photocathode, however the 2 \( \mu \)m active layer is divided into 4 different doping level sections. Now the diffusion length is given by \( L_D = \sqrt{D\tau} \), where \( \tau \) is the mean lifetime of electron, \( D \) is the
diffusion coefficient of GaAs, and $\tau$ is mainly determined by the doping concentration. The greater the doping concentration, the more scattering, and the smaller the $\tau$. It could be known from Fig. 3.5 that the average doping concentration of Fig. 3.5(b) is smaller than that of Fig. 3.5(a), so the $\tau$ of gradient doped sample is higher.

Furthermore, based on the arguments of Zhi Yang et al. [101], it can be inferred that electron diffusion lengths of gradient doped structure will be higher as compared to their uniform doped counterpart, because the diffusion coefficient of the former will be higher.

Because of the unique doping architecture of gradient doped photocathodes, these modifications will also improve the electron escape probability from these devices. When the electrons reach the surface with energy higher than the vacuum level energy, they can be either transmitted or reflected by the surface potential barrier. The band structure and surface potential barrier of uniform-doping NEA GaAs and gradient doping NEA GaAs are shown in Fig. 3.6. According to the widely accepted double-dipole model [85], there are two surface potential barriers, which are called potential barrier I and potential barrier II. The electrons escape to the vacuum through the barriers by the tunnel effect. It is shown in Fig. 3.6 that potential barrier I is high but thin, while potential barrier II is low but thick, so if the electrons can escape to the vacuum through potential barrier I, the escape probability $\xi$ could be higher because it is thinner than potential barrier II. On one hand, almost all the electrons in uniform doping GaAs do not have enough energy to escape to the vacuum through potential barrier II. They have no choice but to escape to the vacuum through potential barrier II, which is thick. On the other hand, there are interfacial and surface
electric fields in the bulk of gradient-doping GaAs. There is a band-bending region at each interfacial layer between two different doping concentration sections. Each band-bending region has an electric field. Electrons will be accelerated in each band bending region. This mechanism will add additional drift apart from diffusion in the active layer of the photocathode. Zhi Yang et. al. [101] has shown that the energy of the electrons that reach the surface of gradient doped device is about 0.059 eV higher than that of a uniformly doped sample, and more electrons could escape to the vacuum through potential barrier I, so escape probability of a gradient doped device is higher than uniform doped sample. The introduction of a gradient doping architecture in the active layers of NEA photcathodes is considered an important step towards the improvement of the performance of these devices. The detailed theoretical and experimental analysis will further attest to this fact with the results presented in Chapter 5.

**Figure 3.6:** Band structure and surface potential barrier of NEA GaAs photocathodes: (a) uniform-doping NEA GaAs and (b) gradientdoping NEA GaAs.
3.3 Photoelectron Transportation - A Diffusion Model

The photocathode used as a reference for the development of the theoretical model is a GaAs/AlGaAs device fabricated with metal-organic chemical vapor deposition (MOCVD) [105]. Its doping structure is as shown in Fig. 3.7 and its corresponding band structure is as shown in Fig. 3.8. This kind of schematic view of device structures is universally used in the field of semiconductor photocathodes, as is evident from all the cited references on this topic. It uses Si-doped GaAs (370 µm) as the substrate. A 0.7-µm layer of p-Al$_{0.57}$Ga$_{0.43}$ with a doping concentration of $3 \times 10^{18} \text{cm}^{-3}$ is directly grown on the substrate to serve as the buffer layer. Grown on top of the buffer layer is the active layer, which is 1.7 µm of p-GaAs uniform-doped at $1 \times 10^{19} \text{cm}^{-3}$. The surface of the device is activated with Cs/O.
3.3.1 A Two-Layer Assumption

In order to understand in detail the dynamics of photoelectrons in GaAs photocathodes, a theoretical framework has been developed based on a two-layer model. Specifically, the heavily $p$-doped GaAs layer is divided into two distinctive sub-layers: a wide active layer (AL) where most of the photoelectron generation and transport take place, and a very thin band-bending region (BBR) near the surface where photoelectrons accumulate after diffusion and become trapped. The two layers are conceptually illustrated in Fig. 3.8.

Fig. 3.8 also exemplifies each step involved in the photoemission process as described by Spicer’s 3-step model [106]. The first step is the excitation of electrons from the valence band to the conduction band following the absorption of an optical pulse. The second step is the transport of excited electrons to the surface, during which the excited electrons scatter with phonons and other electrons, losing energy and thermalizing towards the conduction band minima. The active layer ($p$-doped GaAs bulk layer) is uniformly doped and hence there is no built-in electric field. As a result, the main mechanism by which the electrons move towards the surface is diffusion. Due to the presence of surface states, the energy bands of heavily $p$-doped GaAs bend downward near the surface [49]. This so-called band bending region effectively serves as a potential well for electrons, trapping the photoelectrons that have diffused into the vicinity of the surface. This diffusion-accumulation picture underlies the theoretical model, which will be discussed in detail in subsequent sections. The third and final step is the emission of electrons. With the Cs/O surface-activation
layer, the vacuum level falls below the bulk conduction band minima, allowing some of the photoelectrons trapped in the band bending region to escape into the vacuum. Some electrons that are excited close to the surface can also reach the vacuum without complete thermalization.

Figure 3.8: The band scheme of typical GaAs NEA photocathodes, with the definitions of active layer and band bending region.

In both layers, a general continuity equation can be written as

\[
\frac{\partial n(r, t)}{\partial t} + \nabla \cdot J(r, t) = G(r, t) - \Gamma n(r, t),
\]

(3.7)

where \(n(r,t)\) is electron concentration as a function of space and time, \(J(r,t)\) is electron flux, \(G(r,t)\) describes electron generation by photo-excitation, and \(\Gamma\) is electron decay rate, which combines all the effects that lead to the reduction of photoelectron population.
3.3.1.1 Active Layer

Between the two layers, the BBR is treated in our model as an infinitely thin layer of electron “sink”. All the electrons diffusing into the BBR are trapped in the electron sink without any returning back to the AL. This assumption is justified because i) the BBR has been shown to be about 10-70 nm wide for typical doping levels [90] (compared to 1-2 µm for the AL) so its impact on photoelectron generation is very small and ii) the potential well formed within the BBR can effectively trap electrons, making electrons less likely to diffuse back into the AL. With this assumption, the analysis of photoelectron generation and diffusion is contained only within the AL, while the BBR contributes a Dirichlet boundary condition near the device surface [23].

The inner boundary of the AL interfaces with the AlGaAs buffer layer, which forms a potential barrier for photoelectrons, as shown in Fig. 3.8, and hence results in a Neumann boundary condition. It is further argued that photoelectron generation by femtosecond pulses can be treated as an instantaneous process, which sets up an initial distribution of electron population. The ensuing photoelectron transport is a diffusion process based on this initial condition and the boundary conditions. In addition, since surface recombination and photoemission are the dominant decay process, it is reasonable to lump all the electron relaxation processes into the BBR and assume the diffusion in the AL decay-free. Neglecting any transverse inhomogeneity of the electron population, the only change to the electron flux occurs along the longitudinal direction $x$ (i.e. depth from the device surface, as indicated in Fig. 3.8. Thus, $J(r,t)$
can be replaced by $J(x, t) = -D[\partial n(x, t)/\partial x]x$, where $D$ is diffusion coefficient. The continuity Eq. (3.7) is then reduced to a one-dimensional (1D) diffusion equation

$$\frac{\partial n(x, t)}{\partial t} = D\frac{\partial^2 n(x, t)}{\partial x^2}, \quad (3.8)$$

with an initial condition $n(x, t = 0) = n_0 e^{-a_0 x}$ and boundary conditions $n(x = 0, t) = 0$ and $\partial n(x = d, t)/\partial x = 0$. Here, $d$ is the thickness AL and $\alpha$ is the absorption coefficient of AL.

The general solution to this equation is

$$n(x, t) = 2n_0 \sum_{i=1}^{\infty} b_i \sin (a_i x) e^{-a_i^2 Dt} \quad (t > 0), \quad (3.9)$$

where the expansion coefficients $a_i$ and $b_i$ can be derived from the initial condition as

$$a_i = \frac{(2i - 1)\pi}{2d} \quad \text{and} \quad b_i = \frac{a_i + (-1)^i \alpha e^{-\alpha d}}{d(\alpha^2 + a_i^2)}. \quad (3.10)$$

Now, in order for the computation result to best simulate the experimental results, the photoelectron distribution was computed with the consideration of the
broadband nature of femtosecond pulses. Shown in Fig. 3.9 (a) is the broadband spectrum of the incoming pump pulse which impinges on the sample. The whole spectrum is divided from 700 nm to 920 nm into slots of 5 nm width on either side of center wavelength, which increases in steps of 10 nm. The area under each slot is computed and is defined by $A_i$, which will eventually be used as a weight factor for $\alpha$ calculations. In this way, the relative optical excitation power at different wavelengths have been derived from the actual pump pulse spectrum and the wavelength-dependent absorption coefficient $\alpha(\lambda)$ for GaAs has been taken into account. Fig. 3.9 (b) shows the initial distribution of the carriers, $n(x,t = 0, \alpha)$, for different $\alpha$ values corresponding to its respective wavelength [90]. Hence, for all the subsequent simulations, the value of alpha was derived by using $\alpha = A_1\alpha_1 + ... + A_n\alpha_n$. The dark blue curve in Fig. 3.9 (b) is the initial distribution of carriers by considering the derived $\alpha$ value as mentioned above.

Fig. 3.10(a) shows the initial distribution of the electron concentration $n(x, t = 0)$ and several subsequent distribution curves at various time delays. An AL thickness of 1.7 $\mu$m has been used in these calculations to reflect the actual dimension of the tested device. All curves have been normalised to $n_0$. The traces demonstrate the time-evolution of electron concentration in the AL as electrons gradually migrate from the AL into the BBR. The total electron population inside the AL, $N(t)$, which corresponds to the integral of $n(x,t)$ across the entire AL, exhibits a monotonic decrease over time as shown in Fig. 3.10(b) (Trace (i)). The total number of electrons injected into the BBR, on the other hand, monotonically increases as illustrated by Trace (ii) in Fig. 3.10(b). The AL-to-BBR injection flux at any given time can be
defined as $J(t) = -dN(t)/dt$ and is shown in Fig. 3.10(b) as Trace (iii). The photo-electron injection from the AL to the BBR is very strong immediately following the excitation but quickly tapers off after just a few picoseconds.

**Figure 3.10**: Diffusion of photoelectrons inside the active layer: (a) time evolution of the electron concentration distribution in the AL; (b) total electron population and flux: (i) total electron population inside the AL as a function of time, (ii) total electron population injected from the AL into the BBR, and (iii) total electron flux injecting into the BBR as a function of time.

### 3.3.1.2 BBR

Moving on to the BBR, one can again begin with the continuity Eq. (3.7). Taking the integral $\int dx$ from $x = 0^-$ to $x = 0^+$ (i.e., across the thickness of the BBR) on both sides of Eq. (3.7) and neglecting the generation term $G(r,t)$ as discussed earlier yield a modified continuity equation for the BBR

$$\frac{\partial S(t)}{\partial t} = J(t) - \Gamma S(t), \quad (3.11)$$

where $S(t)$ is the total free-electron population in the BBR (averaged over surface area). The general solution of Eq. (3.11) is given by
\[ S(t) = \int_0^t J(\tau) e^{-\Gamma(t-\tau)} d\tau, \] (3.12)

where \( J(\tau) = -dN(\tau)/d\tau \). Combining Eq. (3.9) and Eq. (3.12), the general solution for \( S(t) \) is found to be

\[ S(t) = 2n_0D \sum_{i=1}^{\infty} b_i a_i \left[ \frac{e^{-Da_i^2t} - e^{-\Gamma t}}{\Gamma - Da_i^2} \right], \] (3.13)

where \( a_i \) and \( b_i \) are defined in Eq. (3.10). Sometimes it is more appropriate to describe the decay of free-electron population in the BBR with a multi-exponential function. In such cases, the overall population \( S(t) \) can be divided into several groups with \( S(t) = \sum S_j(t) \). Each \( S_j(t) \) has its own decay rate \( \Gamma_j \) (or, equivalently, carrier lifetime) and injection flux \( J_j(t) \). Then Eq. (3.11), (3.12) and (3.13) can simply be used to solve for each individual group and all the groups combine to give the overall population behaviour.

The free electrons in the BBR alter the dielectric constant near the device surface, causing the surface reflectivity to change. The simplest model to describe this relation is the classical Drude theory [10,107], which predicts the complex dielectric constant \( \epsilon(\omega,t) \) as a function of free-carrier density as

\[ \epsilon(\omega,t) = \epsilon_r(\omega) + \frac{e^2 S(t)}{m^* \epsilon_0 \omega w \omega (1 - i\omega \tau_c)} \epsilon_r(\omega), \] (3.14)

where \( e \) is electron charge, \( \omega \) is angular frequency, \( \epsilon_0 \) is vacuum permittivity, \( m^* \) is effective mass of electron, \( \tau_c \) is mean collision time of free electrons, \( \epsilon_r(\omega) \) is the relative dielectric constant due to interband transition, and \( w \) is the effective thickness of the BBR. An important conclusion drawn from Eq. (3.14) is that the transient reflectivity \( \Delta R(t) \) following the excitation of a femtosecond pulse is proportional to the accumulated free-electron population in the BBR \( S(t) \). This establishes the founda-
tion of the PPR technique, i.e., by measuring $\Delta R(t)$ using a pump-probe scheme, one can directly observe the evolution of photoelectron population near the device surface. The result, in turn, can be used to understand transient carrier dynamics such as carrier diffusion and relaxation as suggested by Eq. (3.13). It should be pointed out that the Drude model does have certain limitations. For example, it has been shown that the model works very well far above the bandgap but fails to account for some key carrier effects such as band filling and bandgap renormalization near the bandgap [95]. A comprehensive theory for free-carrier effects near the bandgap is much more complicated and hence out of the scope of the current work [13, 64, 95]. However, the proportionality between $\Delta R(t)$ and $S(t)$ is believed to be a reasonable approximation regardless of the Drude model being valid or not. Thus, the effectiveness of the PPR approach should not be affected by the particular model used here.

3.3.2 Numerical Treatment

To gain quantitative insight into the different dynamic processes, numerical modelling is performed based on the theoretical framework outlined in Section 3.3.1. Particularly, Eq. 3.13 is solved using MATLAB. Several additional factors, specifically pertaining to the experiment have been included in this simulation. For instance, the effect of wavelength-dependent absorption is considered in the simulation by treating different wavelength components in the pump spectrum with different $\alpha(\lambda)$ [90]. The generated photoelectrons, however, are all assumed to thermalize and cool down to the bottom of the conduction band within a negligible time so that their diffusion can
be described by the same equation, regardless of how they are initially generated [26].

In addition, to account for possible multiple decay channels for the free electrons, multi-exponential decay is considered in the simulation. Prior reports have indicated that surface recombination in the BBR leads to a characteristic response time on the order of 1 ps [32] and the photoemission process from photocathodes with a similar active-layer thickness typically taking about tens of picoseconds [13], [32], [34].

Therefore, an important finding through the numerical modelling is that a single exponential decay of the free-electron population was not able to explain the observed transient behaviours of the reflectivity. To address this problem, a bi-exponential decay model is proposed, where the relaxation of the free-electron population in the BBL takes the form of

\[ S(t) \propto A \exp\left(-\frac{t}{\tau_A}\right) + B \exp\left(-\frac{t}{\tau_B}\right). \]  

(3.15)

Here \( \tau_A \) and \( \tau_B \) are the carrier lifetimes of two independent decay processes; \( A \) and \( B \) are constants and satisfy the condition \( A + B = 1 \). With this additional degree of freedom in the form of a second exponential, a much better agreement between the numerical result and the experimental data is expected. Another beauty of Eq. 3.13 is that, \( D \) is directly related to free-electron density near the device surface, which in turn is proportional to the change of reflectivity as indicated by Eq. (3.14). Thus, one should in principle be able to determine \( D \) based on the measured transient behavior of the reflectivity. The electron diffusion coefficient \( D \) is an important figure-of-merit for ultrafast carrier dynamics in GaAs photocathodes and its accurate determination can be of huge importance to shed light on specific photocathode’s performance char-
acterization. The specific choice of parameters and their physical implications will be discussed in Chapters 5 and 6 for the particular type of photocathode used in their respective analysis.
CHAPTER 4

FEW-CYCLE PUMP-PROBE REFLECTOMETER

4.1 Introduction

In this chapter, the effort will be to elucidate on different steps involved in developing a PPR system with both high temporal resolution and broad spectral coverage. The approach is based on a few-cycle femtosecond laser and an ultra-broadband pump-probe system. The latter is the key innovation as it allows the pulse width and the spectrum of the laser to be preserved throughout the beam paths and eventually delivered onto the sample. The result is a simple (oscillator only), compact (small footprint) pump-probe reflectometer that can make time-domain and spectral-domain measurements simultaneously.

4.2 Different Parts of the Reflectometer

Based on the general picture introduced in Ch. 2, Section 2.2.2 for a universal pump-probe scheme, the ensuing sections of this chapter will sequentially expand all steps in detail that are involved in building a ‘Few-Cycle PPR’. Nevertheless, a brief introduction will be provided in this section for the overall reflectometer system setup,
which serves as a precursor for the reader to understand the nitty gritty of how a PPR works.

**Figure 4.1**: Layout of Few-Cycle Pump-Probe Reflectometer

Fig.4.1 shows the layout of our Few-cycle PPR system. The light source is a 6.5-fs Ti:Sapphire oscillator (Venteon Pulse:One PE) with a 540-mW average power and an 83-MHz repetition rate. The details of this femtosecond oscillator will be covered in Section 4.2.1. An external cavity pulse compressor unit ensures the management of dispersion throughout the 3-m pulse transportation path from laser to the sample. This includes a dispersion-compensating mirror (DCM) pair, a CaF$_2$ wedge pair (for dispersion fine tuning), a dispersion-balanced broadband beam-splitter, a periscope pair (PR1 and PR2 for generating a cross-polarized probe beam), and all-reflective beam paths for both the pump and the probe. The details of these optics will be covered in Sections 4.2.2 to 4.2.4. For focusing both beams on the sample, the
system employs off-axis parabolas with focused beam diameters of $\sim 60 \mu m$ (pump) and $\sim 28 \mu m$ (probe). The pump beam is modulated using a chopper, whereby the reflected probe is lock-in detected at various pump delays. The details of linear stage instrument error correction and pulse characterization are covered in Sections 4.2.5 and 4.2.6 respectively. Section 4.3 will introduce the CAD diagram of the actual setup of PPR in the Ultrafast Optics Lab.

4.2.1 Mode-locked Ti:sapphire Laser - The Few-Cycle Pulse Source

Mode-locking is a technique which remains central to the pulsed laser technology. This technique refers to a general practice of locking multiple axial modes in a laser cavity by enforcing coherence between the phases of different modes, whereby establishing a preference for generation of intense ultrashort laser pulses. Ever since its inception in the classic work on the He-Ne laser [108], the implications of this work has been manifold. Owing to multifarious transient phenomenon in nature and a quest to resolve them, the race for ultrashort pulse generation [109] has picked up since then and has gradually matured now to times scales as short as an attosecond [110,111].

With absolute bandwidth of the gain medium, such as titanium doped sapphire crystal (Ti:Al$_2$O$_3$), approaching almost an octave, most of the present-day lasers with a typical repetition rate of 100 MHz are able to lock approximately 2 million of these axial modes. This has resulted in pulses as short as 5 fs - shorter than two optical cycles - at a center wavelength of 800 nm. The mechanism responsible for producing such short pulses is a result of work by Sibbett’s group who generated very short pulses in a single resonator [112] and these results of the self-mode-locked Ti:sapphire
laser is acknowledged as being a key transition point in the field of ultrashort pulse generation. This mode-locking mechanism was recognized as caused by what is now called Kerr–lens mode-locking (KLM) which focuses the high intensity part of the beam by the Kerr–effect, whereas the low-intensity parts remain unfocused. If such a beam is passed through an aperture, the low-intensity parts are attenuated, thereby shortening the pulse.

The oscillator used in this research also belongs to the family of KLM Ti:sapphire lasers, and its design is a slight modification of the work credited to produce a record of about 5 fs [113,114], the shortest pulses ever achieved directly from an oscillator, whereby classifying it as a Few-Cycle Ti:Sapphire laser.

![Figure 4.2](image)

**Figure 4.2:** (a) Schematic optical setup of VENTEON PULSE ONE oscillator. (b) Ti:Sapph oscillator in UAH PULS lab.

As shown in Fig. 4.2 (a), the oscillator cavity comprises of seven DCM mirrors (M1-M7), where DCM stands for Double Chirped Mirrors and their functioning will be further explained in Section 4.2.2. Multiple bounces are made on these mirror pairs per round trip to generate necessary negative dispersion to compensate for the
positive second- and third-order dispersion of the laser crystal (tc), the amount of air inside the 83.3 MHz laser cavity and the 1.7 mm of BaF$_2$ per round trip which is used to fine-tune and balance the dispersion on each side of the laser crystal. The gain medium (tc), located in between mirrors M3 and M4 is highly doped Ti:sapphire crystal (2mm x 3mm x 2.5mm). The crystal is pumped by a 532 nm pump light from a frequency-doubled, diode-pumped Nd:YAG (Laser Quantum Finesse) using pump laser steering mirrors (PM1 and PM2) and is focused with a plano-convex lens (L) with 62.9 mm focal length. The curved mirrors (M3 and M4) have a radius of curvature of 100 mm. The intracavity fine-tuning of the dispersion is further optimized by using BaF$_2$ wedge pairs and can be achieved by simply inserting the BaF$_2$ wedges. This significantly simplifies the handling of the system since one has to control only one degree of freedom. The current design has also two external cavity DCM mirrors pairs (EC1 and EC2), which provides an additional degree of freedom for alignment of the beam towards the sample, which is generally several meters away from the exit point of the oscillator. As a result of using these specialized DCM mirrors and BaF$_2$ wedges, the design renders superiority over previous designs employing prism compressors, both in compactness and achieving shorter pulses directly from the laser, thus making the extracavity pulse compression more successful. In the next couple of sections, the external pulse compressor and methods used to preserve the temporal profile of these few-cycle pulses throughout the experiment will be explained.
4.2.2 The Dispersion Compensating Unit

The first thing that a Few-Cycle pulse train, directly out of an oscillator, is introduced to is an external cavity pulse compressor or a dispersion compensation unit. One of the many perquisites of dealing with Few-Cycle pulses is that it can simultaneously offer an unprecedented temporal window of <5 fs and broad spectral bandwidth i.e., 650-1100 nm. However, the technical challenges to handle such few-cycle pulses are mainly two-fold: First is to prevent pulse broadening due to dispersion effects as briefly introduced in Section 2.3.2. and second is the selection of mirrors which can offer broad reflection bandwidth, supporting almost an octave of frequencies in these pulses. Both of these challenges demands a very special class of optics to be incorporated in our reflectometer.

![Figure 4.3: Bragg Mirror design. Figure adapted from [115].](image)

A Standard Bragg mirror (dielectric mirror) or a quarter-wave stack can be a natural choice in order to support the higher reflection bandwidth in a pump-probe spectroscopy experiment employing few-cycle optical pulses. A schematic of a typical high-reflector Bragg-mirror is as shown in Fig. 4.3 [115]. These mirrors are usually composed of SiO$_2$ and TiO$_2$ alternating layers with high and low refractive index. Each layer has an optical thickness of quarter-wave ($\lambda_B/4$) for the selected center wavelength ($\lambda_B$ - Bragg wavelength at which the mirror is designed to have its high-
est reflectivity). However, due to the limited contrast available in the refractive index of alternate layer materials, these mirrors are not well suited to support the broad reflection bandwidth associated with few-cycle pulses. Moreover, their minimal contribution to GDD is only well suited for the center wavelength for which they are designed. On the contrary, for shorter (longer) frequency components, these structures contribute positive-chirp (negative-chirp) respectively, whereby deteriorating the pulse shape.

Figure 4.4: DCM mirror Pairs and CaF$_2$ wedge pairs.

In order to address these limitations, double chirped mirror (DCM) pairs and CaF$_2$ wedge pairs as shown in Fig. 4.4 were employed as a part of our external cavity dispersion management unit. A chirped mirror is also a Bragg mirror, but with a variable duty cycle, i.e., the ratio of optical thickness of high and low index layers. Fig. 4.5 (a) shows a general concept behind a chirped mirror [116]. In these structures, by slowly increasing the Bragg wavelength from the surface to substrate, the high-reflectivity bandwidth of the mirror can be extended simply by adding more layers. Simultaneously, this design dictates the short wavelengths to be reflected first.
whereby allowing longer wavelengths to penetrate deeper into the mirror and hence introducing necessary negative GDD to compensate for the positive GDD. However, as shown in Fig. 4.5 (b), this design has a limitation in a way that near surface Bragg stacks responsible for reflecting only shorter wavelength, also contribute to partial reflection of longer wavelengths. Hence, an interference between strong reflection from the back of the mirror and these spurious partial reflection from the front end leads to a formation of a Gires-Turnois interferometer [117] for long wavelengths resulting in strong periodic oscillations of the group delay. Furthermore, a refractive index jump from the top mirror layer to the air again introduces another GTI into the mirrors. To avoid these limitations, one has to additionally chirp the top high-index layer apart from the Bragg wavelength as done in the original ‘single’ chirped mirror design. The name ‘double chirped mirror (DCM)’, hence stems from this special optimization performed to overcome these aforementioned limitations [118,119]. Also, the surface of these mirrors is coated with a specially designed broadband anti-reflection coating so as to match the refractive index jump from the top DCM layer to air. These steps are schematically shown in Fig. 4.5 (c) & (d). For the current PPR assembly, commercially available DCM7 GVD-mirror pair from Venteon-Optics are used. The supported wavelength range for these mirrors spans almost an octave (600 - 1200 nm) with a reflectivity of 99.6%. The dimensions of this mirror is 35 x 20 mm, so as to accommodate multiple reflections & with a 10 mm thickness fabricated on a fused silica substrate. The reported GDD/pair is -120 fs². The reason for using a mirror-pair instead of a single mirror lies in the fact that this design, for a single mirror, still introduces dispersion oscillations while handling bandwidths in excess of an octave.
and are difficult to suppress. In order to overcome this challenge, a complimentary pair of DCM is designed in such a way that oscillations from each mirror are out of phase with each other and as a result, when they are added, it produces a smoothly varying group delay across the entire octave. This is shown in Fig. 4.5 (e) [120,121].

A CaF$_2$ wedge pair is inserted after the DCM as shown in Fig. 4.4 (b). This additional element provides extra freedom for continuous dispersion fine-tuning. The basic idea behind wedge pairs is quite analogous to the prism compressors unit as introduced in Chapter 2 Section 2.3.2. The wedge pairs introduce tunable dispersion and optimal pulse compression in combination with dispersion compensating mirrors. For this, one of the wedges is mounted on a translation stage, which allows us to insert variable thickness of the wedge into the beam (introducing positive material
The dispersion characteristics of the DCM mirrors are specially designed to work together with specific glass materials. In our case, DCM7 mirror pairs were designed in comparison to the compensation target of 4.4 mm CaF$_2$. These wedge pairs were mounted at Brewster’s angle to reduce the loss of incident p-polarised light.

4.2.3 vChirp Software - Deciding the Total Beam Path

Now as described in Section 4.2.1, the oscillator used for this thesis is capable of directly producing $\sim$ 8 fs pulses right after the exit point of our laser. Nevertheless, considering the limitations of the experimental setup, such as the space occupied by the pump-probe system and the size of the oscillator, it is not practically feasible to put our reflectometer (interferometer) right at the exit of the oscillator to preserve the temporal resolution of our pulses. This means that the pulse must travel some distance in air before it reaches the sample. It is well documented in literature [122, 123] that second-and third-order dispersion values of air are a finite positive number, meaning that by the time few-cycle pulse train reaches the sample, it has lost its original temporal profile. In order to overcome this difficulty, manufacture provided vChirp software to simulate the pulse shape after it has traveled a certain amount of distance in the air. This helps to estimate the total distance that pulse will travel in air, which includes the distance from oscillator output to the beam splitter plus the distance traveled within the interferometer before reaching the sample. Simultaneously, the software additionally allows one to include the DCM mirror pair & CaF$_2$ wedge pair as a part of the simulation run. Since the compensation with chirped mirrors is discrete in nature (a finite dispersion per bounce on the mirror), one can decide how many
bounces are optimal to cancel the dispersion introduced by air. Also, by controlling the insertion of one window of CaF$_2$ wedge pair, the variable thickness adds positive GDD in a controlled manner, allowing for continuous compensation. The software also allows adding an estimated thickness in the beam path. All in all, these three parameters acts as a precursor in deciding the total footprint of the pump-probe experiment.

Fig. 4.6 shows the collection of simulation runs on dispersion calculation software - vChirp, where we can simulate the pulse broadening towards our experiment and see the effects of a compressor. In the software, one can simply add all optical elements with corresponding thickness the pulses are traveling through plus the amount of air it has to travel before hitting the sample. Fig. 4.6 (a) is the unchirped pulse directly outside the Venteon PE Ti:Sapphire Oscillator. The pulse width is estimated to be around 6 fs Fig. 4.6(b) shows the inclusion of DCM and CaF$_2$ as a part of the pulse compressor unit and an allowance of 2 m of air path travel. However, as it can be seen from the bottom left of the figure that pulse profile has distorted and the pulse width is estimated to be 16 fs This hints to the fact that the amount of air path, considered in this run, is over compensated for by a single bounce on the DCM mirror pairs. Hence the logical thing would be to increase the amount of air path to a value, along with one bounce on the DCM pairs, that can bring back the temporal profile of the pulse to its minimum. This first step, solely from simulation runs, gives us a starting point for deciding the overall footprint of the pump-probe setup so as to design the experiment. Fig. 4.6(c) shows the results of an optimum simulation run with an allowance of 3.8 meters air in the beam path. One bounce on the DCM7
mirror pair has been considered, with an estimated allowance of 1.4 mm of CaF$_2$ material thickness in the beam path. This thickness is based on the manufacture specified value for the middle of wedge pair, however, real-time pulse characterization is done by using SPIDER and fine-tuning of CaF$_2$ wedge pair admittance into the beam path so as to achieve $\sim$ 8 fs pulses at the sample.

### 4.2.4 Dispersion Management

Once the pulses have reached the beam splitter, the next thing to consider is the material dispersion introduced by the beam-splitter itself and all subsequent optics. This was taken care by employing a dispersion-balanced broadband beamsplitter which splits the pump and the probe beams with about the same amount of dispersion in both arms and an all-reflective beam path within our pump-probe system.

Ultrabroadband beam splitters are necessary for pump-probe spectroscopy experiments with few-cycle optical pulses. When the spectral range of interest increases beyond one octave, conventional metallic beam splitters show considerable loss and strong wavelength dependence in reflection and transmission owing to the wavelength-dependent penetration depth into the metal. Conventional dielectric beam splitters based on quarter-wave Bragg stacks cannot support such broad spectra. Therefore it is highly desirable to use a broadband beam splitter based on chirped multilayer dielectric thin-film coatings deposited on a substrate. For efficient ultrabroadband pulse splitting, this class of beam-splitters not only introduce constant reflectance and transmittance over the whole spectral range but also allows well-controlled group-delay dispersion (GDD) [124]. This is generally achieved by matching the GDD for
Figure 4.6: vChirp simulation.
reflection from the coating with the GDD picked up by the transmitted beam for a single pass in the substrate. The beam-splitter for the current assembly is from Venteon-Optics and it is based on the design as reported in [124]. It is a 50:50 beam splitter covering the spectral range of 600-1500 nm. The design is carried out for p-polarized light with a 45° angle of incidence. The dielectric multilayer thin-film coating is deposited on a fused-silica substrate with a thickness of 650 µm. For the rest of the pump-probe system, silver mirrors with enhanced reflectance are used in order to employ an all reflective path throughout the assembly so as to minimize pulse broadening due to material dispersion.

Moving on further into the details of the reflectometer design, one important parameter to consider is the relative polarization state of pump and probe beams. As mentioned in Ch.2, for a degenerate geometry, such as the one reported in this research, both pump and probe wavelengths are same. This makes isolating the transmitted or reflected probe beam from the scattered pump beam after the sample difficult and leads to a significant background signal on the detector. In such cases, the polarization state of the pump and probe beams can play an important role in order to reduce the background noise. One way to flip the polarization of either pump or probe by 90° with respect to the other beam is by using a half-wave plate. After either reflection or transmission from the sample and before this signal reaches the detector, a polarizing cube beam splitter or broadband linear polarizer can be used to further sanitize the signal from the pump background. However, the thickness of the half-wave plate can significantly broaden the pulse and this is even before the pump/probe beam reaches the sample.
Hence in order to avoid any further pulse broadening due to material dispersion, a periscope assembly was employed to flip the polarization of probe beam w.r.t to pump beam by 90° instead of using a half-wave plate. The concept is shown in Fig. 4.7 (a) & (b) and for the sake of clarity, it is described as follows. For the incoming beam (probe), the resulting polarization depends mainly on two factors: 1) the input polarization, 2) the angles of incidence on the two periscope mirrors. As shown in Fig. 4.7 (a), a horizontally-polarized (or p-polarized) probe beam is propagating parallel to the surface of a table and when this beam is incident on a mirror oriented face-up at 45° (such that the beam will be directed straight up at 90°) the polarization state for the purposes of the mirror is actually s-polarized (not p-polarized). This is because polarization is defined in relation to the incident surface and hence if you change the angle of your interface then the polarization of the beam changes for the purposes of calculating the interaction. In this case, while the polarization is parallel to the table, the polarization is perpendicular to the mirror interface, so the calculation of the reflection must be treated using the boundary conditions/Fresnel coefficients corresponding to s-polarization, not p-polarization. This is why the angle of the top mirror is so critical: if the top mirror is angled such that the beam exits perpendicularly from the periscope (Fig. 4.7 (a)), the plane of incidence rotates by 90°, so the polarization rotates. But if the mirrors are arranged as shown in Fig. 4.7 (b), then the polarization is the same because the plane of incidence is the same for both mirrors. Hence the second periscope is not only used to bring back the height of the "polarization-flipped" probe beam to its original height of 4" with respect to the
surface of the table, but it also maintains the “flipped polarization state” as facilitated by the first periscope.

![Figure 4.7: Polarizing flipping periscope assembly.](image)

4.2.5 Spatial Overlap Error: Considerations of Inherent Motion Errors in Linear Stage

Another important factor that must be considered for any PPR setup is runout of the linear stage (both linear and angular runout) which affects the position accuracy of the focused pump and probe beams at the sample and is an important factor associated with the motion system of the delay line. Runout is the departure of the moving functional point (linear stage/delay line) from the desired ideal straight-line motion. Flatness and straightness (linear runout) represent the deviation from the ideal straight-line motion and these are perpendicular to the direction of the
travel in horizontal and vertical planes respectively. Pitch and yaw are rotations around the axis perpendicular to linear motion (perpendicular to the direction of travel) in the horizontal and vertical planes respectively. Roll is the rotation around an axis in the direction of travel. In any time-resolved measurements (pump-probe scheme) the pump and probe beams are spatially overlapped at the target sample and the temporal overlap is altered by scanning the linear stage. Runout of the stage (especially angular runout - Angular runout is the rotation of the moving linear stage/delay line) is an important factor as it is an indication of how the spatial overlap is preserved during the scan of temporal overlap. The pitch and yaw become even more critical in configurations where the target sample at which the beam should be overlapped spatially, is far from the delay stage. In such cases, the linear off-axis errors introduced by the angular deviations of the stage and amplified by the distance are the main components of runout which are called Abbe Error. In the current setup, the delay line is introduced in the pump beam path and the distance between the pump beam (starting from beam splitter) to the sample is $\sim 1150$ mm. Because of the inherent (manufacturer) linear/angular runouts in the delay line, as described in this section, the pump spot on the sample has a linear error (Abbe Error) of $\sim 10$ µm on either side ($\pm 12$ mm) of the zero position of the linear stage. This amounts to a total of $20$ µm shift of the pump spot on the sample for the entire scan of the delay line. This creates a background signal, as depicted in Fig. 4.8 (a), which must be subtracted from the pump-probe signal in order to get the correct relaxation dynamics of the sample under investigation.
4.2.6 Characterization of Ultrashort Pulses: SPIDER

Spectral Phase Interferometry for Direct Electric field Reconstruction (SPIDER) is a well-established method for ultrashort pulse characterization and can be reviewed in various publications [125, 126]. The effort in this section will be briefly review the main measurement principle behind this technique.

Interferometry provides a very sensitive and accurate means to measure the phase of an optical field. SPIDER is a specific implementation of spectral shearing
interferometry for the complete temporal characterization (or more specifically the spectral phase) of ultrashort optical pulses. Spectral shearing interferometry is similar in concept to lateral shearing interferometry, except the shearing is performed in the frequency domain. The spectral shear is generated by upconverting the test pulse with two slightly different monochromatic frequencies, where the difference in their frequencies is equal to the spectral shear. The basic concept is that two pulse replicas that are delayed in time by an amount $\tau$ and spectrally shifted with respect to each other by an amount $\Omega$ are interfered on a spectrometer. The resulting interferogram (or SPIDERgram) can thus be written as,

\[ S(\omega) = I(\omega) + I(\omega - \Omega) + 2\sqrt{I(\omega)I(\omega - \Omega)} \cos[\phi(\omega) - \phi(\omega - \Omega) + \omega\tau], \]

where $I(\omega) = |E(\omega)|^2$ is the spectral intensity of the individual pulses and $\phi(\omega)$ is the spectral phase. The time delay results in fringes that are nominally spaced by $\delta\omega \approx 2\pi/\tau$ and enables the interferometric term (last term in the equation above), that contain the phase information, to be extracted. The phase information can be extracted by a phase retrieval procedure introduced by Takeda et. al. [127]. All this complicated math of phase retrieval from SPIDERgram is accomplished in the lab by the using the venteon SPIDER (vSPIDER) unit and its supporting software. The first step in characterizing the pulse shape is providing careful alignment of the test pulse withing the SPIDER unit such that you can observe a decent interference signal on the vSPIDER software. The rest of the procedure is quite redundant in terms of alignment of the main beam until you observe a stable sub 10 fs pulse on the vSPIDER software. The Pulse characterization results will be discussed in the next section.
4.3 PPR System description

Our PPR system is built around a 6-fs Ti:Sapphire oscillator (Venteon Pulse:One), which offers 500 mW of average power at an 83-MHz repetition rate. The laser is integrated into a portable pump-probe platform as depicted in Fig. 4.10. Special measures are taken to manage pulse dispersion throughout the beam paths so that the optimum pulse shape can be achieved on the sample surface. These include the use of a pair of dispersion compensating mirrors (DCM) at the output of the laser to pre-compensate the group-velocity dispersion introduced by air and glass during pulse transmission. A CaF$_2$ wedge pair inserted after the DCM provides fine dispersion tuning. An ultrabroad-band, dispersion-balanced beamsplitter (DBB) splits the laser output into pump and probe beams. The beamsplitter has a 1-mm thickness. Its special coating produces low group-delay dispersion in both transmission and reflection with similar spectral profiles, which allow simultaneous dispersion compensation for both pump and probe pulses. Except for the DCM, the CaF$_2$ wedge and the DBB, all the optics used in the beamline prior to the sample are reflective components with protected silver coatings. The pump beam, which has an average power of 270 mW, passes through a motorized tunable delay line (Newpot VP-25XA) and a beam chopper before being focused onto the sample near-normal incidence by an off-axis parabolic (OAP) mirror. The probe beam has an average power of 20 mW. Its polarization is rotated by 90° through a periscope, as seen in Inset (a). A second OAP then focuses the beam onto the sample at 15°. The probe spot size on the sample surface is about 1/3 of the pump spot size. The reflected probe beam off the
sample surface is focused onto a Si photodetector and the detector output feeds into a lock-in amplifier (SRS SR830). Wavelength-selectivity is introduced to the probe measurement through the addition of a tunable optical bandpass filter in front of the photodetector. A polarizer is inserted prior to the bandpass filter to remove residual pump light in the reflected probe signal. A zoom-in view of the detection section is shown in Inset (b). The overall footprint of the setup (excluding the laser) is 72 cm × 45 cm.

Figure 4.9: SPIDER characterization of the few-cycle pulses. (a) Time-domain trace shows a 6.5 fs FWHM duration for the pump pulses. (b) Spectrum of the laser shows a 300-nm spectral coverage.

The pump pulses are characterized at the location of the sample using spectral phase interferometry for direct electric-field reconstruction (SPIDER). The time-domain and frequency-domain results are shown in Fig. 4.9 (a) and (b) respectively. A 6.5-fs full- width-at-half-maximum (FWHM) pulse duration and a 300-nm spectral width at 20 dB below the peak have been obtained. A portion of the probe beam is split off by the beam sampler and is coupled into a spectrometer (Ocean Optics
USB2000) to make a real-time measurement of the probe spectrum. This spectral information is used to normalize the measured reflectivity spectra to take into account the different incident powers at different wavelengths. The probe pulse width is estimated to be about 10 fs.

Figure 4.10: Layout of the PPR setup. Inset: (a) polarization rotation by periscope; (b) a close view of the detection system.
CHAPTER 5

PRE-EMISSION CHARACTERIZATION OF NEA GaAs/AlGaAs PHOTOCATHODES

5.1 Introduction

In this chapter, primary focus will be on ultrafast transient carrier dynamics in different structure reflection-mode GaAs/AlGaAs NEA photocathodes. The experimental approach is based on PPR system as detailed in Chapter 4. One important aspect of this study is to show the feasibility of using femtosecond PPR measurements to characterize these devices and to offer a direct picture of electron diffusion/drift inside NEA photocathodes, something the traditional dc approaches has been unable to provide so far. In order to quantitatively verify the physical understanding of various processes happening in these devices, numerical modelling results will be presented for some of these devices based on the carrier-diffusion model presented in Chapter 3. This will further explain the transient behaviors of reflectivity of these devices, with an ultimate aim to draw conclusions regarding the photoemission performance based on the different doping structure and different growth method used for these photocathodes.
5.2 Overall PPR measurement of GaAs/AlGaAs photocathodes: An Overture to NEA Photocathode Characterization.

In order to verify the effectiveness of our PPR system, first measurements were taken on GaAs substrate as the sample. The substrate is p-doped at $1 \times 10^{16} \text{cm}^{-3}$ level, with a thickness of 370 µm. The measured relative-reflectivity evolution is shown in Fig. 5.1, where “Time” represents the relative delay between the probe and the pump pulses. This result agrees with typical PPR behaviors for GaAs [94,128], where a sharp increase of reflectivity is followed by an exponential decay. The comparably longer carrier lifetime ($\sim 20$ ps) in the current case is believed to be due to the use of a GaAs substrate, which has a much lower concentration of defects than epitaxial GaAs. The result demonstrates the capability of our PPR system in studying transient carrier dynamics in semiconductor devices.

![Figure 5.1: PPR trace measured with a GaAs substrate ($1 \times 10^{16} \text{cm}^{-3}$).](image)

Moving on to actual photocathodes, the first study focuses on two GaAs/AlGaAs photocathodes device structures. Fig. 5.2 shows the schematics of the two devices.
Device #1 uses Si-doped GaAs (370 µm) as the substrate. A 0.7-µm layer of p-Al_{0.57}Ga_{0.43} with a doping concentration of $3 \times 10^{18} cm^{-3}$ is directly grown on the substrate to serve as the buffer layer. Grown on top of the buffer layer is the active layer, which is 1.7 µm of p-GaAs uniform-doped at $1 \times 10^{19} cm^{-3}$. Device #2 is built upon the same substrate as Device #1, with a 0.5-µm buffer layer made of p-GaAlAs doped at $1 \times 10^{19} cm^{-3}$. The active layer is 1.2 µm of p-Al_{0.63}Ga_{0.37}As as active layer, gradient-doped from $1 \times 10^{19} cm^{-3}$ (buffer layer side) to $1 \times 10^{18} cm^{-3}$ (cap layer side). The device is capped by 0.1-µm layer of p-GaAs with a doping concentration of $1 \times 10^{18} cm^{-3}$. Both photocathodes are surface-activated by means of a Cs-O layer on the front surface.

The PPR measurements on the two devices are performed under similar experimental conditions. Fig. 5.3 (a) and (b) show the measured transient reflectivity...
Figure 5.3: PPR measurement results for NEA GaAs/AlGaAs photocathodes: (a) uniform-doped structure; (b) gradient-doped structure

responses for Device #1 and Device #2, respectively. Comparing the two traces, several similarities and differences can be drawn.

First of all, after the excitation of the pump pulse, it takes about 3 ps for the reflectivity to reach its maximum in both devices. Moreover, in both cases, the reflectivity experiences a sharp initial rise within the first picosecond following the excitation. After that, the increase gradually slows down until the reflectivity maximizes. All these behaviors suggest that there is a carrier transportation process after the pump pulse impinges onto the sample. The initial rise of the reflectivity is likely caused by the photo-generated free electrons near the surface. The electrons generated deeper inside the active layer diffuse toward the surface, causing the reflectivity to continue to rise, albeit at a gradually reducing rate. The gradient-doped sample (Device #2) achieves a higher peak value of $\Delta R/R$ ($2.85 \times 10^{-4}$ vs. $1.75 \times 10^{-4}$), indicating possibly more efficient carrier transportation. This is in agreement with prior
reports on similar doping structures [101,102,104], where gradient doping is found to improve electron diffusion length. Upon reaching their peak values, the reflectivities of both devices begin to decrease as carrier relaxation begins to dominate. However, the relaxation characteristics of the two photocathodes are markedly different. Device #1 exhibits a relatively faster relaxation (Fig. 5.3(a)), with $\Delta R/R$ falling to less than one half of its peak value within 50 ps (maximum measurable delay). The reduction rate of $\Delta R/R$ is nearly constant, with a slight increase toward larger delays. This kind of behavior suggests that multiple processes may take place simultaneously during this period and some of them counter balance the relaxation of free electron concentration near the surface. One possible scenario is that thermalized free electrons from deeper inside the device continue to diffuse toward the surface while carrier relaxation occurs near the surface. Meanwhile, Device #2 exhibits a much slower relaxation process as shown in Fig. 5.3(b). Extrapolation of the experimental curve shows that it would take about 300 ps for $\Delta R/R$ to fall to one half of its peak value (assuming the decay rate remains the same). This distinction between the two photocathodes likely stems from their difference in doping structures. The gradient-doped structure in Device #2 apparently leads to stronger electron population buildup near the surface. In the meantime, the lower doping level near the surface of Device #2 results in longer carrier lifetime. Overall, the gradient-doped structure appears to create a more favorable condition for the operation of a photocathode than the more traditional uniform-doped structure. This distinction between the two photocathodes likely stems from their difference in doping structures. The gradient-doped structure in Device #2 apparently leads to stronger electron population buildup near
the surface. In the meantime, the lower doping level near the surface of Device #2 results in longer carrier lifetime. Overall, the gradient-doped structure appears to create a more favorable condition for the operation of a photocathode than the more traditional uniform-doped structure. This conclusion does not come in surprise as many reports in the past have shown the effectiveness of gradient-doping in enhancing quantum efficiency \[101,102,104\]. Also, the results of this section have shown that femtosecond PPR measurement is able to offer a direct picture of electron diffusion inside NEA photocathodes, something traditional dc approaches unable to provide. The majority of the studies on GaAs/AlGaAs NEA photocathodes so far focus on steady-state characterization, where the photocathodes are under the excitation of continuous-wave (CW) light sources such as halogen lamps \[129,130\]. However, this preliminary work paves a way for completely different approach in making the comparison from the perspective of transient carrier dynamics in these photocathodes.

5.3 Comparative Study of GaAs Photocathodes Grown by MOCVD and MBE

The overarching conclusions of previous section indicated that gradient doping not only leads to more efficient electron transportation but also results in better electron accumulation (i.e. higher concentration and longer lifetime) near device surface. The introduction of a gradient (or exponential) doping structure in the active layer of such devices have shown to balance the requirements for long electron diffusion lengths and narrow surface band bending regions \[100–102\] and has shown promising results for enhancing the quantum efficiencies and spectral response in both transmission mode
(t-mode) photocathodes [103] and reflection mode (r-mode) photocathodes [104]. Although, the majority of these prior reports have employed molecular beam epitaxy (MBE) as the preferred epitaxial growth method due to its virtue of atomic dimensional precision, precise control over the layer thickness and doping concentration which are generally demanded by these exponential doped GaAs photocathodes, owing to their unique doping architecture. However, in the past, there has been some work pointing to the fact that particular epitaxial growth technique employed to grow this AlGaAs/GaAs heterojunction based negative electron affinity (NEA) photocathodes has also played an important role in their performance [131–134]. More recently, similar comparison has been reported, specifically on the exponentially doped photocathode indicating that photocathodes grown by MOCVD generally have better spectral response and quantum efficiency [135, 136]. On one hand, these reports indicated that photocathodes grown by MOCVD generally have better spectral response and quantum efficiency based on steady-state analysis and measurement. On the other hand, there has been little prior work comparing the dynamic response of devices fabricated with different technologies. In this section, we further expand our investigation of these devices and report a comparative study of the ultrafast response of two gradient-doped GaAs photocathodes fabricated using two different methods, viz. MBE and MOCVD.

The study focuses on comparing the dynamic response of two reflection mode GaAs/AlGaAs photocathodes structures grown by different epitaxial growth methods, viz. metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). Fig. 5.4 shows the schematics of these two devices. Both the devices employs
a similar gradient doping structure for the GaAs active layer by means of a high-to low graded doping concentration from the bulk to surface. This type of doping promotes a built-in electric field to enhance the photoelectron diffusion and drift towards the surface [104], whereby significantly improving the photocathode quantum efficiency. Both devices use n-doped GaAs as the substrate. A 1-\(\mu\)m layer of p-Al\(_{0.6}\)Ga\(_{0.4}\)As with a doping concentration of \(1 \times 10^{19} cm^{-3}\) is directly grown on the substrate to serve as the buffer layer. The purpose of this layer is to serve as an electron potential barrier that can reflect the back diffusion electrons towards the device surface. Grown on top of the buffer layer is the active layer, whose total thickness of 2 \(\mu\)m is divided into 4 sections, with the doping concentration distributed gradiently from \(1 \times 10^{19} cm^{-3}\) to \(1 \times 10^{18} cm^{-3}\). Both photocathodes are surface-activated by means of a Cs/O layer on the front surface.

**Figure 5.4:** Doping structure diagram of the two GaAs/AlGaAs photocathodes. (blue) Device #1 (MBE grown): gradient-doped p-GaAs as active layer. (yellow) Device #2 (MOCVD grown): gradient-doped p-GaAs as active layer.
Figure 5.5: Pump-Probe measurement results for NEA GaAs/AlGaAs photocathodes: (a) PPR measurements for Device #1 (MBE grown) & Device #2 (MOCVD grown): gradient-doped photocathodes. (b) Estimated total electron accumulation near device surfaces over certain time spans.

The PPR measurements on the two devices are performed under similar experimental conditions. Fig. 5.5 (a) show the measured transient reflectivity responses for Device #1: MBE (black plot) and Device #2: MOCVD (red plot). Following similarities and differences can be drawn by comparing the two traces. In both cases, a sharp initial rise of the reflectivity is seen following the injection of the pump pulse, which indicates a surge of free-electron population near the device surfaces. Reflectivities of both devices peaks at about 700 fs. After that, they first engage in a fast decay over several picoseconds and then gradually settle into a slower decay. The peak reflectivity of Device #2 (MOCVD), however, is markedly higher than that of Device #1 (MBE) (by $\sim$ 83%). To physically understand these results in more detail, we resort to the fact that transient reflectivity is directly proportional to the free-electron concentration near the sample surface. Hence, the above result can be viewed as the time evolution of photoelectron populations accumulated on the surfaces of the photocathodes. From the higher peak reflectivity observed with Device
one overarching observation can be made that the MOCVD grown device is able
to transport more photoelectrons to the surface than the MBE grown device. Also,
throughout the entire time span, the pump-probe trace of Device #2 stays above that
of Device #1, as is evident from Fig. 5.5 (a). To further support these claims, PPR
curves were integrated over time for both devices. Such an integration reflects the
total amount of free electrons being accumulated near device surface across a certain
time span. As shown in Fig. 5.5 (b), total electron accumulation near device surface is
estimated at three representative times, viz., 1 ps, 3 ps and 60 ps. For all these times,
Device #2 (MOCVD) has respective higher values as compared to Device #1 (MBE)
viz., ∼ 125%, ∼ 88% and ∼ 32%. This clearly suggests that MOCVD grown device
help photoelectrons migrate faster toward device surface. One possible explanation
for such behaviour can be inferred from the classic work by Zhang et.al. [135]. In
their study, they have estimated the electric field intensity of each band-bending re-
gion (BBR) for similar exponentially doped, MOCVD and MBE grown GaAs/AlGaAs
photocathodes. They found that, both the interfacial and surface electric fields values
for MOCVD samples are greater than that of the MBE sample, which suggests that
more powerful electric field in the MOCVD sample could improve the photo-excited
electrons moving towards surface more effectively. In order to quantitatively verify
the above physical understanding, numerical modelling results will be presented for
both devices based on a carrier-diffusion model of chapter 3 to further explain the
transient behaviors of reflectivity.

Fig. 5.6 shows the experiment and theory comparison for MBE and MOCVD
grown devices. Excellent agreement between theoretical predictions and measured
Figure 5.6: Theoretical model is fit to experimental data (a) Device #1 (MBE grown), (b) Device #2 (MOCVD grown), to determine the diffusion coefficient $D$ and relaxation lifetimes $\tau_A$ and $\tau_B$.

Table 5.1: The Optimum Parameters for Theory-Experiment Comparison

<table>
<thead>
<tr>
<th>Device</th>
<th>Diffusion Coefficient: $D$ (cm$^2$/s)</th>
<th>Relaxation time: $\tau_A$ (fs)</th>
<th>Relaxation time: $\tau_B$ (ps)</th>
<th>Constant: $A$</th>
<th>Constant: $B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device #1 (MBE)</td>
<td>255</td>
<td>930</td>
<td>72</td>
<td>0.91</td>
<td>0.09</td>
</tr>
<tr>
<td>Device #2 (MOCVD)</td>
<td>260</td>
<td>870</td>
<td>37.5</td>
<td>0.94</td>
<td>0.06</td>
</tr>
</tbody>
</table>

data not only validates the numerical model but also allows various device parameters to be evaluated quantitatively. Invoking the arguments made in section 3.3.2, numerical modelling of free electrons was performed and the relevant parameters, namely $D$, $\tau_A$, $\tau_B$, $A$ and $B$, as shown in Table 1, were chosen so that the theoretical curves agree with the experimental traces for these two devices as shown in Fig. 5.6. It should be pointed out that this theoretical model is primarily considering diffusion as the only responsible mechanism for electron transport towards the device surface after laser excitation. On the other hand, both of these devices has a gradient doping architecture in their active region. The diffusion coefficients estimated via theoretical modelling is little high as compared to the diffusion coefficient for undoped GaAs.
is only 200 cm²/s. This serves as further evidence that other electron transportation mechanisms, likely carrier drift under directional build-in field, also contribute in gradient-doped devices. One possible argument for higher $D$ values also rests upon fact that these gradient doped NEA photocathodes are meant to increase the electron diffusion lengths, whereby increasing the quantum efficiency of these devices. To further verify this argument, we refer to the work of Niu et. al [102], where they have deduced the mathematical expression of the electron diffusion and drift length of an exponential doped photocathode and is written as:

$$L_{DE} = \frac{1}{2}(\sqrt{A^2L^4_D + 4L^2_D + AL^2_D})$$

(5.1)

Here, $L_D$ is the diffusion length of a uniformly doped photocathode and is given by $L_D = \sqrt{D\tau}$. Based on their analysis, they propose that the exponential doped photocathodes could be looked at as uniformly doped photocathodes whose electron diffusion lengths are greatly increased. This is only possible if their $D$ values are higher as compared to its uniformly doped counterpart [137], since $\tau$, which is the mean life time of the electron is relatively high for gradient doped structures, owing to their smaller average doping concentration [101]. Hence, the respective values of $D$ for MBE and MOCVD devices of 255 cm²/s and 260 cm²/s appears to be reasonable. This also validates the feasibility of our diffusion only model to characterize gradient doped devices.

In summary, PPR measurements on NEA GaAs/AlGaAs photocathodes with two different doping structures were presented. These result indicates that gradient doping not only leads to more efficient electron transportation but also results in bet-
ter electron accumulation (i.e. higher concentration and longer lifetime) near device surface and hence the gradient-doped structure appears to create a more favorable condition for the operation of a photocathode than the more traditional uniform-doped structure. Moreover, it is shown that femtosecond PPR measurement is able to offer a direct picture of electron diffusion inside NEA photocathodes. Furthermore, a comparative study of the ultrafast response of two gradient-doped GaAs photocathodes fabricated using two different methods, viz. MBE and MOCVD is presented. While past research has indicated that photocathodes grown by MOCVD generally have better spectral response and quantum efficiency, these reports are all based on steady-state analysis and measurement. Utilizing a totally different approach, which is based on femtosecond pump-probe reflectometry (PPR), significant insight was obtained by comparing the dynamic response of devices by measuring their transient reflectivity and it was found out that MOCVD grown, exponentially doped photocathodes have indeed better performance as compared their MBE grown counterpart. The carrier-diffusion model of chapter 3 was used to analyze photoelectron transport, accumulation, and decay in the active layer. Excellent agreement between theoretical predictions and measured data not only validates the numerical model but also allows various device parameters to be evaluated quantitatively.
CHAPTER 6

WAVELENGTH-RESOLVED STUDY OF PHOTOELECTRON DYNAMICS IN GaAs PHOTOCATHODES

6.1 Introduction

As asserted in previous chapters, PPR is a versatile and well established characterization technique to study ultrafast dynamics in materials and devices [17]. However, depending on specific research goals, various groups have exploited PPR systems either to make time-domain measurements [12, 138] or time-resolved spectral domain measurements. [15, 17]. In chapter 5, the sole emphasis was on time-domain PPR measurements and to showcase its effectiveness in characterizing NEA photocathode devices and to offer a direct picture of electron diffusion/drift inside these devices. The carrier diffusion model of Chapter 3 was also seen to be in excellent agreement with these results based only on time-domain analysis. In this Chapter, a wavelength resolved pre-emission investigation of photoelectron transport and population decay in a uniformly doped NEA GaAs/AlGaAs photocathode will be presented by means of same PPR apparatus as detailed in chapter 4. This method is just one step further to add the capability of making wavelength-resolved measurement to the system. This is done by inserting a tunable bandpass filters in front of the photodetector to
select the probe wavelength that is detected. By changing the center wavelength of the filter (typically with a 10-nm bandwidth), the same time-domain measurement can be made at a series of wavelengths. This offers an extra dimension to PPR for comprehensive characterization of these photocathodes. In order to further validate these wavelength resolved experimental findings, a numerical treatment is performed based on same carrier diffusion model of chapter 3, and the theoretical results once again shows excellent agreement with experiment results, whereby allowing the determination of important parameters such as diffusion coefficient and the free-electron population decay times near the surface through such wavelength-resolved comparisons.

6.1.1 Transient Behaviors of Reflectivity

The validity of wavelength-resolved experimental and theoretical approach is attested by taking PPR measurements on one of the NEA GaAs photocathodes. More specifically, these measurements were taken on a uniformly doped photocathode as shown in Fig. 3.7 at a number of probe wavelengths. As a first step in this direction, PPR measurements on uniformly doped photocathode were compared with the transient reflectivity measurements of a standard GaAs substrate in order to provide the experimental evidence that validates the applicability of the diffusion model at different wavelengths.

Fig. 6.1 shows the measurement results at three representative wavelengths: one far above the GaAs band gap at 750 nm, one right above the band gap at 830 nm, and one below the band gap at 880 nm. Also shown in Fig. 6.1 are three reference
traces taken at the same wavelengths with a GaAs wafer. The wafer is \( p \)-doped at \( 3 \times 10^{18} \ \text{cm}^{-3} \) with a thickness of 0.35 mm. The PPR traces for both devices show a sharp initial change after the excitation of the pump pulse (at time zero), followed by a gradual decay. The initial changes of reflectivity are positive at 750 nm and 830 nm and negative at 880 nm for both devices. Such a characteristic is consistent with theoretical predictions based on the concepts of band filling and bandgap renormalisation in GaAs \([64, 65]\) and is commonly observed in transient reflectivity of GaAs \([94, 139]\).

In a nutshell, the sign change across the band gap is a result of the sign change of carrier-induced optical absorption (imaginary part of dielectric constant) across the band gap, which is related to the refractive index (real part of dielectric constant) through the Kramers-Kronig relation. However, a notable difference between the two devices can be seen in the decay portion of the traces, where the photocathode displays a much slower relaxation than the GaAs wafer at all three wavelengths. This is a strong indication that the transient-reflectivity behaviours of the photocathode are likely dominated by the electron transport process. The reason is very simple. The main difference between the two devices is the unique doping structure of the photocathode (see Fig. 3.7), which is designed to facilitate photoelectron transport toward the device surface. Relaxation processes solely associated with material properties would not be able to account for the considerable difference between the two cases because they exist in both devices. This serves as the experimental evidence that validates the necessity of particular diffusion model used in this thesis.

A closer look at the traces in Fig. 6.1 shows that the reflectivity rises to 80% of its peak value in a period of about 500 fs. After that, the increase gradually
Figure 6.1: PPTR traces measured with the photocathode (black) and a GaAs wafer (blue) at three different wavelengths, (a) 750 nm, (b) 830 nm, and (c) 880 nm.

slows down. At about 2 ps, the reflectivity reaches its peak value. It then begins a gradual decay, dropping to half of its peak value within 30 ps. The above behaviors of reflectivity appear to be qualitatively consistent with a simple physical picture. The initial rise of the reflectivity is likely caused by the photo-generated free electrons near the surface. The electrons generated deeper inside the active layer diffuse toward the surface, causing the reflectivity to continue to rise. On the other hand, once the free-electron population reaches a certain level, bulk and surface recombination take over as the dominant processes, causing the free-electron population to decline and leading to a gradual reduction of reflectivity. However, this decline appears to be more complicated than a simple exponential decay, which indicates that there may be multiple mechanisms involved. One such mechanism has to do with the
wavelength dependence of absorption coefficient $\alpha$. Since the pump-pulse spectrum is quite broad, there is a diverse distribution of absorption length $\alpha^{-1}$ within the pump spectrum [140]. As a result of this $\alpha(\lambda)$ relation, longer wavelengths can penetrate deeper into the active layer and the generated photoelectrons need more time to diffuse into the surface region, potentially slowing down the decay of free-electron population on the surface. Another possible mechanism unique to NEA photocathodes is surface emission, which allows free electrons on the device surface to escape out of the device. It may provide an additional channel for the device to lose free electrons.

6.1.2 Bi-exponential Decay.

The direct correlation between $S(t)$ and $\Delta R(t)$ allows Eq. (3.13) to be directly compared with the experimentally measured transient reflectivity. This has been done by applying material and device parameters to Eq. (3.13) with proper assumptions to the electron decay rate $\Gamma$. Once again, invoking the arguments made in section 3.3.2, it was indeed found through such comparisons that a simple exponential decay of the free electron population is unable to explain the observed transient behaviors of the reflectivity. This is illustrated in Fig. 6.2, where two special cases of the theoretical curve are plotted against an experimental trace (measured at 750 nm).
Figure 6.2: Measured transient behaviours of reflectivity along with theoretical predictions based on single-exponential (dashed) and bi-exponential (solid) population-decay models.

Both theoretical curves are obtained with a single decay rate $\Gamma$, the first one (fast) chosen to match the experimental trace at the peak reflectivity and the second one (slow) at the tail end. Evidently, neither curve can properly describe all the characteristics of the measured reflectivity. To address this problem, the biexponential decay model (Eq. 3.15) was incorporated in the MATLAB code. Here $\tau_A$ and $\tau_B$ are the carrier lifetimes of two independent decay processes; $A$ and $B$ are constants and satisfy the condition $A + B = 1$. With the additional degrees of freedom, a much better agreement between the numerical result and the experimental data has been achieved, as demonstrated by the solid red trace in Fig. 6.2. The specific choices of parameters and their physical implications will be discussed next.
6.1.3 Diffusion Coefficient and Carrier Lifetimes.

Past efforts to experimentally measure $D$ based on the emitted electron bunches have led to widely scattered results, with values ranging from $20 \text{ cm}^2/\text{s}$ to about $200 \text{ cm}^2/\text{s}$ [23,24,62,63]. PPR offers a completely different approach to experimentally access $D$, potentially via a more straightforward avenue. Fig. 6.3 shows a simple demonstration of such comparisons, where some of the previously reported values of $D$ are plugged into the model and the resulted theoretical predictions are compared with the experimental trace. It is evident from these results that the optimum value of diffusion coefficient is close to $D = 155 \text{ cm}^2/\text{s}$. It should be pointed out that in chapter 5, the value of $D$ for gradient doped device is found to be $D = 260 \text{ cm}^2/\text{s}$. This value makes sense because these devices have longer diffusion lengths and hence larger $D$ as compared to their uniformly doped counterparts. Therefore, $D = 155 \text{ cm}^2/\text{s}$ is not an unreasonable guess.
**Figure 6.3:** Measured transient reflectivity in comparison with simulation results based on various choices of diffusion coefficient $D$. The inset shows a zoom-in view of peak of the plot.

**Figure 6.4:** Theoretical model is fit to experimental data measured at three different wavelengths, (a) 750 nm, (b) 830 nm, and (c) 880 nm, to determine the diffusion coefficient $D$ and free-electron lifetimes $\tau_A$ and $\tau_B$. Pearson correlation function $R$ is calculated in each case to evaluate theory-experiment agreement. (d) The difference between the theoretical and experimental traces, denoted as $\delta R(t)$, is plotted over the entire time span for all three wavelengths. The corresponding RMS errors are also included.
In order to make more accurate evaluations of \( D \) as well as the bi-exponential lifetimes \( \tau_A \) and \( \tau_B \), numerical modelling of the free-electron population is performed and the relevant parameters, namely \( D, \tau_A, \tau_B, A \) and \( B \), are chosen so that the theoretical curves agree with the experimental traces at all three wavelengths shown in Fig. 6.4, i.e., 750 nm, 830 nm and 880 nm. The resulted experiment-theory comparisons are shown in Fig. 6.4(a)-(c). The corresponding optimum parameter values are: \( D = 160 \text{ cm}^2/\text{s}, \tau_A = 1.56 \text{ ps}, \tau_B = 21.60 \text{ ps}, A = 0.76 \) and \( B = 0.24 \). In all three cases, excellent agreement between theory and experiment is achieved as evident from the computed Pearson correlation function \( R \). Furthermore, the difference between the experimental and the theoretical results across the full time span is plotted in Fig. 6.4(d). At all three wavelengths, this difference remains small over the entire span, as evident from the corresponding root-mean-square (RMS) errors.

Several important conclusions can be drawn from the above results. The bi-exponential behaviour of reflectivity indicates that there are at least two independent processes causing the reduction of free-electron population in the surface region, and their corresponding lifetimes are on the order of 1 ps and 20 ps, respectively. This characteristic of two decay times appears to agree with previous observation based on temporal measurement of emitted electron bunches [63]. Given the complexity of potential processes involved, the specific mechanisms underlying the two decay times are not completely clear based on the current experimental results. Prior reports have indicated that surface recombination in the BBR leads to a characteristic response time on the order of 1 ps [62] and the photoemission process from photocathodes with a similar active-layer thickness typically takes about tens of picoseconds [24, 62, 81].
Therefore, it is reasonable to conceive that surface recombination in the BBR and photoemission may have been the key processes underlying the bi-exponential behaviour of reflectivity. Further research is needed to verify such an assessment. Meanwhile, the PPR-measured diffusion coefficient appears to agree with prior observation by Hartmann et al. [23], but larger than some other previously reported $D$ values [24,62,63]. Given the pre-photoemission nature of PPR measurement, it is believe that this result indeed makes a strong case for considering greater free-electron diffusion in actual GaAs photocathodes. Finally, it should be noted that temperature change caused by pump power injection may also induce refractive index change on the device surface [141]. This effect, however, does not affect the observation of transient reflectivity since temperature-induced index change only depends on the average optical power of the pump beam, which remains constant in the experiment and can be easily removed during data processing. Similar argument can be made with regard to the incident angle of the probe beam, which is set at about 15° in the experimental setup. Although changing this angle may affect the reflected spectrum, it would not change the measured transient behaviors shown in Fig. 6.1 and Fig. 6.4 since it is a steady-state effect. The impact of intraband scattering and relaxation on the diffusion model requires a closer look. Historically, the study of hot-carrier scattering and cooling in GaAs has shown a spectrum of lifetimes, ranging from tens of femtoseconds [142] to hundreds of femtoseconds [143] and further up to several picoseconds [144,145]. In the particular case of semiconductor photocathodes, most dynamic models consider this cooling process to be very fast and hence neglect it in the diffusion process [23,24,62]. Such a treatment has been adopted in a number of reports and has been successful in
explaining post-emission characteristics of photoelectrons [63,81]. Meanwhile, recent Monte Carlo simulation of III-V semiconductor photocathodes by Karkare et al. has considered all the intraband, intervalley scattering processes and has also shown good agreement with experiment [79,90]. Current assessment pertaining to this question is based upon the most recent study of the momentum and energy relaxations of hot photoinjected electrons in GaAs, which has demonstrated, both theoretically and experimentally, an inverse relationship between energy relaxation time and electron excess energy (i.e. energy above conduction band minimum) in the high excess energy regime [146,147]. Considering the peak of of the pump spectrum at 720 nm, the average intraband relaxation time in photocathode device is estimated to be about 200 fs based on these reports. This is significantly faster than the carrier build-up time in the BBR, which is about 2 ps. It is thus concluded that the assumption of a negligible carrier cooling time in the diffusion model is indeed a valid one.

In conclusion, this chapter reports wavelength-resolved pump-probe transient-reflectivity measurements of uniformly dope GaAs/AlGaAs NEA photocathodes. The technique offers insights into transient carrier dynamics that otherwise would not be available. These results demonstrate the feasibility of performing both time domain and spectral domain PPR simultaneously and the effectiveness of such an approach in characterizing broadband optoelectronic devices. These results once again testifies the robustness of the two layer carrier diffusion model to be applied for the analysis of these devices across their band gap at different wavelengths.
CHAPTER 7

TIME-FREQUENCY REFLECTOMETRY SPECTROSCOPY OF GaAs

7.1 Introduction

The rapid development of new photonic materials calls for simple yet effective approaches to characterize ultrafast dynamics in materials and devices. Chapter 4 demonstrated a system capable of simultaneously offering broad spectral range (300 nm) and fine temporal resolution (10 fs), and it required only a femtosecond oscillator. With this unique capability, this chapter reports the first 2D time-frequency spectroscopic study of the transient dispersion of GaAs near its band gap. The results maps important carrier dynamics such as carrier cooling, carrier decay, band filling, and band gap renormalization on a single 2D graph, offering a comprehensive picture about these processes and revealing new details unattainable with conventional methods.

7.2 Transient Dispersion in GaAs

Ultrafast carrier dynamics in GaAs has long been a focus of research due to its potential impact on the performances of photonic devices. One important aspect of such dynamics is carrier-induced transient dispersion (TD), which characterizes
the ultrafast change of refractive index near the band gap due to the injection and relaxation of photo-carriers [64,65,148]. Fundamentally, TD serves as a manifestation of several important many-body effects in semiconductors, including band filling, band gap renormalization, free carrier absorption, and plasma screening [13,95,128,149]. Practically, TD has proved to be a key mechanism underlying some of the dynamic properties of optoelectronic devices [150–152]. A complete characterization of TD requires time-frequency measurement of the transient reflectivity. However, despite continued effort in both the time domain [94,139,153,154] and the frequency domain [16,17], there has not been any report on direct observation of time-frequency behaviors of TD near the GaAs band gap.

7.2.1 PPR Measurements

Few-cycle PPR offers a comprehensive approach to study the TD of GaAs. Using the reflectometer shown in Fig. 4.10, measurements have been made for the transient reflectivity of GaAs at a series of probe wavelengths over a span of >200 nm across the band gap. The sample used in this measurement is a 0.35-mm Si-doped GaAs wafer (110) with a doping concentration of $3 \times 10^{18}$ cm$^{-3}$. Fig. 7.1(a) shows several representative PPR traces at various wavelengths. The wavelength selection is accomplished by changing the center wavelength of the tunable bandpass filter in front of the detector. The PPR traces show diverse behaviors of the refractive index at different wavelengths, highlighted by their different peak values as well as the corresponding rise times. Such differences become even more obvious when the traces are plotted on a semi-log scale, as shown in Fig. 7.1(a) inset. The transient reflectivity switches
sign across the band gap. This is due to refractive index nonlinearity near the GaAs band gap [64], and is consistent with prior observations [153, 154]. A bipolar behavior of index is observed near the band gap (810 – 860 nm), which is also consistent with theoretical predictions [65].

By assembling all these individual PPR traces of different wavelengths together, a full time-frequency map of the transient reflectivity $\Delta R(\lambda, t)$ is obtained, as shown in Fig. 7.1(b). A 10-nm wavelength increment has been used in the measurement. This wavelength resolution is limited by the available bandpass filters but should be able to easily improve with continuously tunable optical bandpass filters [155]. Since $\Delta R(\lambda, t)$ is proportional to the refractive index $\Delta n(\lambda, t)$ [154], Fig. 7.1(b) effectively represents a time-frequency spectrogram of TD. Compared to conventional PPR [17, 94, 139, 153, 154], time-frequency measurement offers a comprehensive picture of the ultrafast evolution of dielectric constant due to carrier injection and relaxation.

### 7.2.2 Discussion

The time-frequency spectrogram shown in Fig.7.1(b) can be better analyzed by projecting the distribution of $\Delta R(\lambda, t)$ onto a 2D contour plot as shown in Fig. 7.2(a). The resulted topographic map features a prominent “arch” region that spans diagonally across the middle, indicating a rise of reflectivity (and hence refractive index) above the steady-state value. It begins to emerge at about 200 fs and extends to over 10 ps. The diagonal pattern suggests that the refractive index for longer wavelengths peaks at later times. Meanwhile, a “sag” region can be seen at the lower right, sig-
Figure 7.1: (a) PPR traces at various probe wavelengths show a range of peak reflectivities and rise times. (b) A 2D time-frequency spectrogram of GaAs covers a 200-nm spectral range and almost 4 decades of time scales (10 fs – 50 ps).
nifying a dip of the index function below its steady-state values. This region has a similar diagonal pattern but begins to appear at a much earlier time (40 fs). The existence of these two regions indicates a bipolar nature of carrier-induced index change $\Delta n(\lambda)$ as a function of wavelength. This becomes more evident by plotting $\Delta n(\lambda)$ at several different time delays as shown in Fig. 7.2(b). Such a characteristic agrees well with theoretical models based on the combined effects of band filling and band gap renormalization [64,65]. In particular, the early appearance of the sag region below the band gap appears to be consistent with theory and prior experiment, which shows that the negative change of index below the band gap is more prominent than the positive change above the band gap [64]. It should be noted here that, although the above results are obtained with one particular sample, similar characteristics have been observed on several other GaAs samples with different orientations and doping levels.

The above TD spectrogram also reveals some interesting details about the behaviors of the transition edge. The transition edge is seen in Fig. 7.2(a) as the narrow strip between the arch and the sag regions. It is where the index change crosses zero (see Fig. 7.2(b)) and is an important indicator of the carrier dynamics. To highlight the time-evolution of the transition edge, a rough guideline is added in Fig. 7.2(a). Immediately following the injection of the pump pulse, no visible change of the refractive index is detected. It is only after about 50 fs that index change begins to appear. From 50 fs to 200 fs, this change is primarily in the form of a depression below the band gap. Judging from the boundary of this sag region, it is reasonable to conceive that the transition edge experiences a blue shift within this
Figure 7.2: (a) A time-frequency map of the transient dispersion $\Delta n(\lambda, t)$ of GaAs under few-cycle excitation. Dash-dotted curve outlines the evolution of the transition edge. (b) Cut-out views of the index function at different delay times.

time span. At about 200 fs, the index function above the band gap begins to grow while its counterpart below the band gap continues to decrease. A clear transition edge is formed. What is interesting about this transition edge is that it turns to the opposite direction and begins to veer toward longer wavelengths. The red shift lasts for about 5 ps and covers a wavelength span of 810 – 860 nm. After that, the transition edge stabilizes at 860 nm, which is very close to the steady-state band gap of the sample.

While a thorough theoretical analysis is beyond the scope of this thesis, it is instructive to put the above observation into the context of carrier relaxation and decay. According to semiconductor theories [43, 156, 157], ultrafast carrier dynamics upon the excitation of a femtosecond laser pulse includes three key processes.
The first one is momentum randomization, where carrier-carrier scattering allows the photo-excited carriers to thermalize into a Fermi-Dirac distribution. This process typically occurs within the first tens of femtoseconds. The second one is energy relaxation (or carrier cooling). This is when carrier-phonon scattering causes energy exchange between the "hot" carriers and the lattice. The carriers eventually reach thermal equilibrium with the lattice and relax to the bottom (top) of the conduction (valence) band. This process typically occurs on a time scale of several picoseconds. The third one is carrier decay. During this process, various decay mechanisms (e.g., recombination, capture, diffusion, etc.) cause the population of photo-excited carriers to reduce. Depending on which mechanism dominates, the time scale of this process can range from sub-picosecond to nanoseconds.

Putting the above behaviors of TD into this theoretical framework leads to a phenomenological picture of the underlying physics, which can be viewed from two aspects: i) the magnitude of the index modulation, and ii) the spectral shift of the transition edge. The peak value of the index modulation is an indication of free-carrier density [64]. Within the first few femtoseconds following the pump pulse, the hot photo carriers are in a highly nonequilibrium state with large kinetic energies [146,158]. It is only after they fully thermalize and start to reach equilibrium with the surroundings that they begin to contribute to the dielectric properties of the material. This is why in Fig. 7.2, measurable index modulation appears about 50 fs after the pump excitation. As more and more carriers cool down and fill up the lower energy states, the index modulation continue to grow (from 50 fs to 1 ps), signifying a growing population of equalibrated photo carriers. The freecarrier density peaks
at about 1 ps. After that, carrier decay and, possibly, carrier diffusion [137] take over and gradually lower the free-carrier population, as evident from the reducing modulation to the index function after 1 ps (see Fig. 7.2(b)). The carrier-induced index modulation eventually tapers off after about 10 ps.

Meanwhile, the spectral shift of the transition edge indicates changes occurred to the band gap. It is worth noting here that the transient behaviors of the band gap is under the influence of two competing processes: band filling (BF), which causes the band gap to grow (blue shift), and band gap renormalization (BGR), which leads to band-gap shrinkage (red shift). Now the GaAs sample under consideration for this study was optically pumped with an approximate average power of 270 mW. The pump beam was focused on the sample with pump beam diameter of $\sim 80 \mu m$, which translates to an incident fluence of $0.64472 J/m^2$. For these parameters, the excited carrier density in GaAs sample was estimated to be $\sim 3 \times 10^{19} cm^{-3}$. It is well documented in literature [65] that for concentrations above $\sim 10^{18} cm^{-3}$, bandfilling and plasma effects dominate. Also, prior report [13] have suggested that the effects of change in bandgap due BGR in GaAs are negligible at carrier injection in the range from $1 \times 10^{16} cm^{-3}$ to $5 \times 10^{16} cm^{-3}$, which is consistent with observation [65] that $\Delta E_{\text{BGR}} \to 0$ as the carrier density falls below $1 \times 10^{17} cm^{-3}$. With this understanding, the initial blue shift of the transition edge between 50 fs and 200 fs appears to indicate that, between the two processes, BF takes effect first and dominates in the early stage of carrier cooling. Then BGR gradually sets in and eventually becomes the prevailing effect. This is evident from the reversal of the band gap shift after 200 fs. The delayed appearance of BGR relative to BF suggests that BGR demand a higher
degree of carrier equilibrium to commence, which takes longer time to develop. This is conceivable because BGR relies on the collective effect of Coulomb screening of many particles to establish [65]. Such a state requires a build-up time typically on the order of 50-200 fs according to both theoretical predictions [159, 160] and experimental observations [161]. From this point of view, the reversal of the band-gap shift offers direct evidence of different onset times between BF and BGR when carrier state transitions from nonequilibrium to equilibrium.

In conclusion, this chapter reports the unique capability of compact, few-cycle pump-probe reflectometer. As a proof-of-concept demonstration, time-frequency spectroscopy of the transient dispersion of GaAs near its band gap was performed. The time-frequency spectrogram maps key carrier dynamics onto a single 2D graph, showing a movie-like chronicle of transient carrier behaviors in GaAs with a 10-fs resolution. It reveals a reversal of band-gap shift within the first few hundred femtoseconds after pump excitation, showing evidence of different characteristics of BF and BGR during the process of carrier equilibration, which, to the best of our knowledge, has not been previously reported in experiments. This highlights the unique capability of few-cycle PPR, viz even for a material as well studied as GaAs, the technique can offer new insights into its ultrafast dynamics.
CHAPTER 8

CONCLUSIONS

In summary, this research achieved following objectives. A novel design of a compact, few-cycle pump-probe reflectometer (PPR) is proposed and detailed development is undertaken. It is then shown, both experimentally and theoretically, that few-cycle PPR offers a new and original approach to resolve the long standing problem of time resolved photoemission from Negative Electron Affinity (NEA) photocathodes. It is also demonstrated that few-cycle PPR can offer new insights into the ultrafast carrier dynamics of GaAs by experimentally studying its transient dispersion near the band gap.

For the development of a few-cycle pump-probe reflectometer system (PPR), only a single femtosecond oscillator is used in order to achieve broad spectral range (300 nm) and fine temporal resolution (10 fs) simultaneously. A much simpler and low-cost experimental system is built by utilizing the widely spread fourier components of few cycle pulses of a femtosecond oscillator for broadband pump-probe reflection measurements. It is shown that the temporal resolution and spectral range of the few-cycle PPR scheme are dictated by the laser itself circumventing such requirements as detection of probe pulses through a narrow-band filter e.g. a monochromator or an
OMA or the requirements on sample itself of other schemes. It also circumvents the requirements of high baseline cost and high system complexity of a multi-stage optical amplifier chain for achieving spectral-domain pump-probe reflectometry. Moreover, by employing just an oscillator along with standard lock-in detection technique, efficient wavelength-resolved pump-probe measurements are made. It is shown that this system is capable of probing weak index modulations generated by pump pulses as small as of the order of $10^{-4}$ - $10^{-5}$.

Using the PPR setup, this research also reports the first pre-photoemission characterization of ultrafast photoelectron dynamics in GaAs photocathodes. A diffusion model based on a two-layer assumption proves to be effective in explaining the experimental results. The free-electron population inside the band-bending region is found to experience bi-exponential decay. The diffusion coefficient in the active layer and the bi-exponential electron lifetimes are evaluated by comparing the theoretical model with the PPR measurement at multiple wavelengths. The result shows that the evaluated diffusion coefficient $D = 160 \text{ cm}^2/\text{s}$ is close to the diffusion coefficient of undoped GaAs (200 cm$^2$/s), but is larger than some other previously reported $D$ values. Given the pre-photoemission nature of PPR measurement, it is concluded that this result indeed makes a strong case for considering greater free-electron diffusion in actual GaAs photocathodes. The bi-exponential nature of the decay accounts for two separate lifetimes, which are on the orders of 1 ps and 20 ps. It is concluded that the two independent processes causing the reduction of free-electron population in the surface region, associated with these times, are surface recombination in the BBR and photoemission respectively. Hence, the PPR method and its results offer
an alternative avenue toward understanding the temporal response of GaAs photocathodes and can potentially provide physical insight unattainable with conventional post-photoemission approaches.

Furthermore, a comparative study of the ultrafast response of two gradient-doped GaAs photocathodes fabricated using two different methods, viz. MBE and MOCVD is presented. While past research has indicated that photocathodes grown by MOCVD generally have better spectral response and quantum efficiency, these reports are all based on steady-state analysis and measurement. Utilizing a totally different approach, which is based on pump-probe reflectometry (PPR), significant insight was obtained by comparing the dynamic response of devices by measuring their transient reflectivity and it was found out that MOCVD grown, exponentially doped photocathodes have indeed better performance as compared their MBE grown counterpart.

Finally, to demonstrate the unique capability of this reflectometer, a time-frequency spectroscopy of the transient dispersion of GaAs near its band gap is reported. The time-frequency spectrogram mapped key carrier dynamics onto a single 2D graph, showing a movie-like chronicle of transient carrier behaviors in GaAs with a 10-fs resolution. It revealed the spectral shift of the transition edge and indicated that changes occurred to the band gap. The transient behaviors of the band gap is generally under the influence of two competing processes: band filling (BF), which causes the band gap to grow (blue shift), and band gap renormalization (BGR), which leads to band-gap shrinkage (red shift). The initial blue shift of the transition edge between 50 fs and 200 fs indicated that, between the two processes, BF takes effect
first and dominates in the early stage of carrier cooling. Then BGR gradually sets in and eventually becomes the prevailing effect. This is evident from the reversal of the band gap shift (red shift) after 200 fs. Hence, the reversal of the band-gap shift offered direct evidence of different onset times between BF and BGR when carrier state transitioned from nonequilibrium to equilibrium.

All in all, this dissertation reports on a pump-probe reflectometer (PPR) based on few-cycle laser pulses. The technique constitutes a nice example of what one can achieve with the state of the art few-cycle lasers. The primary direction of this research is to showcase the capability of this “single” system to conduct comprehensive study and characterize ultrafast carrier dynamics in novel devices. As a proof of concept, a broadband reflective spectroscopy with femtosecond-scale temporal resolution was carried out on widely studied GaAs semiconductor. The ensuing full dielectric function characterization results offered new insights into the underlying rich physics in this semiconductor. This simple, yet elegant study has opened up various possibilities of where the future research can be propelled. Recently, there is lot of advances in novel materials such as two-dimensional (2D) materials, metamaterials, plasmonics etc. where the current PPR technique can offer similar comprehensive analysis of various ultrafast processes happening in these materials. However, one possible improvement to the current PPR setup could be the wavelength resolution, which is currently limited by the available bandpass filters. This can be easily improved by employing continuously tunable optical notch filter and bandpass filter systems that cover the visible to near-infrared spectral ranges. Also, a potential application that was spun-off from this research project was to apply PPR method to photocathode
materials. This study has shown the possibility of characterizing these materials with high reproducibility and throughput using PPR. However, the current theoretical analysis supporting this part of research is primarily based on carrier diffusion model. Hence, it can be apt for analyzing uniformly doped photocathodes. However, in order to increase the adaptability of this model for the investigation of exponentially doped photocathodes, where apart from diffusion, there is also an additional carrier drift, future research efforts can potentially contribute by optimizing the current model by incorporating carrier drift.

Another potential area that the future efforts can be directed is ultrafast nano-photonics. Research interest has grown rapidly in the last few years in this area, where the combination of highly spatially confined carriers and ultrafast electromagnetic excitation leads to rich physics and many potential applications. One major area of study in ultrafast nano-photonics is the coherent interaction between electromagnetic excitations and the nano structures, which preserves the phase information between the EM wave and the electric carriers (electrons and/or holes). Knowing such a phase can not only help us understand the carrier dynamics in the material but also learn about the transient characteristics of the optical pulse. However, due to the very fast de-phasing time ($\sim 10^{15}$ s) in bulk materials, such coherent interaction can only be detected in highly spatially confined nano structures (i.e. Quantum Dots (QD)) with extremely short probing pulses. The pathway for fabricating quantum dot sensors for supporting this research has already been identified. It remains for the future efforts to explore the possibility of using current PPR setup and the quantum dot sensors for directing the thrust towards ultrafast nanophotonics research.
It is hoped that the experimental and theoretical foundations laid by this thesis research will serve as a precursor for many potential applications in the coming years.
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