Ultrafast photoelectron transportation in GaAs and GaAs-based devices

Rui Zhou

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ULTRAFAST PHOTOELECTRON TRANSPORTATION IN GaAs AND GaAs-BASED DEVICES – FROM THEORY TO EXPERIMENT

Rui Zhou

A DISSERTATION

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

August 2023

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Gallium Arsenide (GaAs) is one of the most important semiconductors in the field of photonics and has been the focus of extensive studies since the 1960s. In particular, GaAs photonic devices such as GaAs diode lasers and GaAs photocathodes have attracted tremendous interest owing to their superb features and wide ranges of applications. Despite the success of past research, the advancement of new theoretical models and experimental techniques continues to offer new insights into the properties of GaAs and the potentials of GaAs photonic devices. The work presented in this dissertation represents our most recent effort towards understanding the ultrafast photoelectron dynamics in GaAs wafers and GaAs photocathodes. Theoretically, analytical and numerical models are established to describe photoelectron transportation in GaAs photocathodes with different doping structures following the photoexcitation of femtosecond laser pulses. Experimentally, the time-resolved transient reflectivity of actual devices is measured with the few-cycle pump-probe reflectometry. The excellent agreement found in the theory-experiment comparisons validates the effectiveness of the theoretical models and helps determine some key parameters of the tested sam-
ples. Furthermore, time- and wavelength-resolved spectrograms of GaAs wafers with different doping methods are obtained and analyzed. The observed carrier-induced band gap shifts indicate that the transient dispersion measurements are capable of revealing some hidden details of GaAs material and may be considered a potential tool for future semiconductor property studies.
Acknowledgements

Finishing this dissertation is a milestone in my life, and this work would not have been possible without the support and help of amazing people around me. I am deeply grateful to my advisor Dr. Lingze Duan, who introduced me to the field of ultrafast optics, and has guided and encouraged me at every important moment throughout my Ph.D. research. In addition to research, he is also a great mentor in life, his optimism and sparkling smiles always cheer me up to embrace all kinds of possibilities in life.

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Last, but most importantly, I would like to thank my whole family, especially my parents, for their unconditional love, understanding, and support, not only during my Ph.D. journey but every single second of my life. They encourage me to be free and chase a better version of myself.
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<th>Description</th>
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<tr>
<td>$A$</td>
<td>gradient doping coefficient</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient</td>
</tr>
<tr>
<td>$E$</td>
<td>built-in electric field induced by doping</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi level energy</td>
</tr>
<tr>
<td>$E_g$</td>
<td>intrinsic band gap energy</td>
</tr>
<tr>
<td>$E_{opt}$</td>
<td>optical band gap</td>
</tr>
<tr>
<td>$J(t)$</td>
<td>electron injection flux from the sublayer AL into the sublayer BBR</td>
</tr>
<tr>
<td>$N(t)$</td>
<td>total electron population in the BBR</td>
</tr>
<tr>
<td>$N_C$</td>
<td>effective density of states in the conduction band</td>
</tr>
<tr>
<td>$N_f(t)$</td>
<td>total number of photoelectron injected from the AL into the BBR</td>
</tr>
<tr>
<td>$N_V$</td>
<td>effective density of states in the valence band</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$W$</td>
<td>width of the band bending region</td>
</tr>
<tr>
<td>$\Delta R(t)$</td>
<td>transient reflectivity change</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>absorption coefficient in the AL</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\epsilon_0$</td>
<td>vacuum permittivity</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>relative permittivity</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>reduced Planck constant</td>
</tr>
<tr>
<td>$\mu_n$</td>
<td>electron mobility</td>
</tr>
<tr>
<td>$\tau$</td>
<td>photoelectron lifetime</td>
</tr>
<tr>
<td>$d$</td>
<td>thickness of the AL</td>
</tr>
<tr>
<td>$k_0$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$m_e^*$</td>
<td>effective mass of electron</td>
</tr>
<tr>
<td>$m_h^*$</td>
<td>effective mass of hole</td>
</tr>
<tr>
<td>$n(x,t)$</td>
<td>photoelectron concentration (as a function of location and time)</td>
</tr>
<tr>
<td>$q$</td>
<td>elementary charge</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$v_d$</td>
<td>drift velocity</td>
</tr>
</tbody>
</table>
There is a crack, a crack in everything.
That’s how light gets in.

- Leonard Cohen
Chapter 1. Introduction

1.1 Overview

As one of the most well-known III-V compound semiconductors, gallium arsenide (GaAs) has long been considered a superior electronic and photonic material over silicon, and has been widely used in communication and optoelectronic industries. One particularly important application of GaAs is to serve as the substrate material for the epitaxial growth of p-n junction diode structures, which leads to a variety of GaAs-based devices. These devices play critical roles in electronics and photonics, especially in the fields requiring good high-speed and high-frequency performances. For example, GaAs-based high speed metal-oxide-semiconductor field-effect transistors (MOSFETs) have led to the non-silicon MOSFET (NSMOSFET) technology and made important contributions to all-electronic-based industries and new communication technologies [1, 2]; GaAs-based photocathodes have been widely used in night vision, polarized-electron generation, ultraviolet detection, and photon-enhancement in emission tubes due to their high quantum efficiency and low dark emission [3, 4, 5].

Tremendous interest has been attracted toward GaAs and GaAs-based devices in recent years, and a lot of studies have been conducted to improve the material properties and device performances. In the particular case of GaAs
photocathodes, one major achievement is that techniques have been developed to realize the negative electron affinity (NEA) condition, which greatly helps improve the photoemission efficiency and therefore the overall performance [6, 7]. Meanwhile, there have been a number of reports dedicated to improving the performance of GaAs photocathodes by optimizing their inner structures. One important aspect of these efforts is the use of specifically tailored doping structures. For example, gradient doping profiles have been introduced to enhance photoelectron transportation toward the device surface by creating drift-assisted photoelectron migration. This method balances the requirements of long electron diffusion lengths and narrow band-bending regions [8, 9, 10, 11], and demonstrates great potential in improving quantum efficiencies and spectral responses in both transmission mode (t-mode) photocathodes [12] and reflection mode (r-mode) photocathodes [13].

In prior research, theoretical models have been developed to describe photoelectron transportation in NEA GaAs photocathodes. However, some of the existing models are based on steady-state analysis, which assumes the tested samples are under a constant illumination of light [10, 14]. These models are restricted to the steady-state condition and are inadequate to describe dynamic photoelectron transportation processes induced by time-dependent excitation, for example, ultrafast laser pulses. Other time-dependent models are designed for the conventional uniform doping structure, where the only transportation process involved is photoelectron diffusion [15, 16, 17]. As a result, they fail to include the impact from other possible photoelectron transportation mechanisms caused
by the doping structure. Given the current state of the field, a comprehensive description of the dynamic behaviors of GaAs photocathodes under pulsed excitation is still needed. This is the primary motivation for this dissertation research.

Meanwhile, significant progress has been made in the generation of ultra-short laser pulses in the past fifty years [18, 19, 20]. The availability of ultrafast lasers with a wide range of pulse widths, wavelengths, pulse energies, and pulse repetition rates makes it possible to investigate a broad range of physical phenomena using ultrafast spectroscopy techniques [21]. Pump-probe spectroscopy is one of these techniques and has been widely used to study the optical properties of semiconductor materials and devices. Of particular interest to the current research is pump-probe reflectometry (PPR) which has been developed and demonstrated in our lab at UAH. PPR is based on a mode-locked Ti:Sapphire laser operating at a center wavelength of 800 nm with a nominal pulse width of 6.5 fs. The ultra-short few-cycle pulses generated by the laser allows the PPR system to achieve a sub-10 femtosecond temporal resolution, which makes it suitable to conduct ultrafast time-resolved measurements and obtain experimental data from samples such as GaAs materials and devices. The availability of this advanced research capability provides a solid foundation for the experimental part of this research.

With both the theoretical model and the experimental setup ready, a comprehensive study of the photoelectron dynamics in GaAs-based materials and devices becomes feasible. Such a research is both unique and significant. It is unique because prior experimental studies on GaAs photocathode dynamics were
all based on the measurement of emitted electron bunches [15, 16, 22]. Such a post-emission approach is not only complex and costly (due to the use of vacuum systems and streak cameras) but with lower time resolution (ps) as well. It is significant because a growing list of new applications is relying on the ultrafast dynamics of GaAs devices [23, 24, 25, 26]. For example, the new-generation highly-coherent X-ray sources based on linear accelerators use femtosecond laser pulses to excite GaAs photocathodes to produce seed electron pulses [27]. Understanding the pre-emission photoelectron behaviors inside the photocathodes is critical to the design and optimization of these photocathodes.

Under this context, the objective of my dissertation research is to conduct a comprehensive analysis of ultrafast photoelectron transportation dynamics in GaAs wafers and GaAs photocathodes using few-cycle pump-probe reflectometry. Theoretically, I aim for developing analytical and numerical models that can describe GaAs photocathodes with more complicated doping profiles, such as gradient doping and step-wise doping. Experimentally, the research goal is to leverage the few-cycle time resolution (∼10 fs) and the ultrabroad spectrum (∼300 nm) of the PPR system to achieve time-wavelength two-dimensional (2D) mapping of the transient dynamics.

1.2 Outline of Research

Based on the subtopics, the dissertation can be divided into several chapters as explained below:
Chapter 2 is devoted to the background knowledge which is necessary and essential to understanding the theoretical and experimental work described later in this dissertation. It starts with the basic property of GaAs material and the resultant advantages and applications followed by the various types of devices based on GaAs material and their applications. GaAs photocathodes feature with the negative electron affinity (NEA) condition will be introduced in detail specifically, as they will be used as the primary samples for the GaAs devices in this research. The process of photoemission from an NEA GaAs photocathode will be explained via Spicer’s three-step model among which transportation of photoelectrons will be discussed extensively with related concepts such as diffusion and drift. The current common methods used in evaluating photoelectron transportation in GaAs photocathodes will be talked through, with respect to their applicable conditions, and pros and cons. At the end of Chapter 2, ultrafast pump-probe spectroscopy and the few-cycle pump-probe reflectometry (PPR) setup that has been used to conduct experimental measurements in this dissertation will be introduced.

Chapter 3 presents a comprehensive study on ultrafast photoelectron transportation in NEA GaAs photocathodes with the gradient doping structure. At the beginning of the chapter, the two-layer model of photoelectron transportation will be introduced, which will be used as the foundation for all theoretical analyses throughout this dissertation. Then relying on the two-layer concept, a theoretical model including effects of both diffusion and drift will be derived to describe the photoelectron behavior inside an NEA GaAs photocathode following the photoexcitation by femtosecond laser pulses. Two gradient-doped photocathodes will be
tested with the few-cycle PPR. The experimental data will be compared to the results predicted by the theoretical model. Some key parameters of the photoelectron transport will be determined via the comparison, such as the diffusion coefficient, the drift velocity, and the lifetime of the photoelectron. A further comparison will be carried out between gradient-doped samples and conventional uniform-doped samples to reveal the impact of the doping structure.

Chapter 4 is a further extension of Chapter 3, with the hope to make the theoretical model more accurate in representing actual photocathode devices. Considering the fact that the so-called “gradient-doped” devices available now are typically made up by several uniformly-doped sublayers, which can be more precisely referred to as the stepwise doping structure, a detailed evaluation of the stepwise doping structure will be conducted in this chapter. A theoretical model of photoelectron transportation will be established specifically based on the stepwise doping profile, starting with calculating the built-in electric field generated by the doping structure. The effectiveness of the model will be examined by comparing the theoretical results to the experimentally collected pump-probe transient reflectivity data of real devices. Comparisons will be also made between this stepwise doping model and the conventional gradient doping model discussed in Chapter 3.

While Chapters 3 and 4 are focused on time-dependent photoelectron transportation, Chapter 5 will extend the research into both time and wavelength domains. By incorporating proper wavelength filters into the experimental PPR setup, the time-wavelength resolved pump-probe transient reflectivity data of the
tested GaAs wafers will be obtained and plotted in 2D and 3D time-wavelength spectrograms. From the plotted results, some hidden hints of carrier induced phenomena will be noticed and investigated. Particularly, the Burstein-Moss effect – the carrier induced optical band gap shift in heavily doped GaAs material – will be discussed in detail. Additional observations will also be discussed.

Finally, Chapter 6 will provide a brief summary of this dissertation, the main contribution of this research to the field, and some possible future work that can be carried out to extend this dissertation research.

Some of the MATLAB codes used to fulfill the theoretical simulations in this dissertation research will be provided in Appendix A. All other relevant data and sources are available upon request.
1.3 List of Publications

1.3.1 Journal Articles


1.3.2 Refereed Conference Papers


1.3.3 Conference Presentations


2.1 GaAs and GaAs-based Devices

When the word “semiconductor” is mentioned, silicon (Si) and germanium (Ge) may be the first names that come to your mind, as they are the two most well-known semiconductors. However, apart from these elemental semiconductors, a class of synthetic semiconductors – the compound semiconductors, which are made up of two or more elements from different groups, draw particular attention. Among all compound semiconductors, III-V compounds are the most intensely studied and widely used. Back in 1926, Huggins pointed out that elements from groups III and V when melted together and re-solidified should crystallize with structures similar to those of Si and Ge [28]. This prediction of III-V compounds was confirmed later in 1929 by Goldschmidt [29], and then Welker’s work in the early 1950s [30] started the era of III-V compound semiconductors.

Generally speaking, elemental semiconductors are easier to grow, purify and process as compared to compound semiconductors [31]. As a result, Si and Ge were the dominant semiconductor materials for a long time. On the other hand, compound semiconductors provide the possibility to combine elements from different groups and the flexibility to control or modify some of the properties of the material, for example, the band structures [32]. Thus, the development
of novel manmade III-V compounds enables semiconductors with various band structures. This extension in the diversity of band structures drives the improvement of compound semiconductor properties, such as carrier mobility and light emission capability since all these important material properties are affected by the material band structure [33].

As one of the most well-known III-V semiconductors, GaAs has attracted lots of interest because of its outstanding optoelectronic properties. Small band gap, low effective mass, high mobility of electrons at the conduction band minimum, and sharp optical absorption are among its favourable properties [34]. In particular, GaAs has a direct band gap, which means the minimum of the conduction band is directly in line with the maximum of the valence band in the momentum space, as shown in Figure 2.1(a). In this case, transitions between the valence band and the conduction band only require a change in energy, and no change in momentum [36]. This property permits GaAs higher light emission efficiency than indirect band gap semiconductors, for example, silicon (as shown in Figure 2.1(b)).

Furthermore, the band gap energy of GaAs at 1.42 eV (~870 nm) is located in the highly useful visible-near infrared wavelength region (see Table 2.1). This makes GaAs a very important material in the manufacture of light emitting diodes (LEDs) and semiconductor lasers [37]. In addition, with the advantage of the small direct band gap, GaAs is used extensively in photodetectors and space solar cells since an incident photon can excite an electron from the valence band to the conduction band directly [35].
Figure 2.1: Band structures of (a) GaAs and (b) silicon. GaAs is a direct band gap semiconductor, while Si is an indirect band gap semiconductor. Figure adapted from [35].
<table>
<thead>
<tr>
<th>Material*</th>
<th>Symbol</th>
<th>Band gap type</th>
<th>Band gap energy (eV)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>germanium</td>
<td>Ge</td>
<td>indirect</td>
<td>0.67</td>
</tr>
<tr>
<td>gallium antimonide</td>
<td>GaSb</td>
<td>direct</td>
<td>0.72</td>
</tr>
<tr>
<td>silicon</td>
<td>Si</td>
<td>indirect</td>
<td>1.12</td>
</tr>
<tr>
<td>gallium arsenide</td>
<td>GaAs</td>
<td>direct</td>
<td>1.42</td>
</tr>
<tr>
<td>cadmium selenide</td>
<td>CdSe</td>
<td>direct</td>
<td>1.74</td>
</tr>
<tr>
<td>cadmium sulfide</td>
<td>CdS</td>
<td>direct</td>
<td>2.4</td>
</tr>
<tr>
<td>gallium nitride</td>
<td>GaN</td>
<td>direct</td>
<td>3.4</td>
</tr>
</tbody>
</table>

*Ordered by band gap energy.
**Under room temperature $T = 300K$. 

Table 2.1: Band gap type and energy for some common semiconductors
One particularly important application of GaAs is to serve as the substrate material for the epitaxial growth of other III-V semiconductors, and more commonly for p-n junction diode structures, which leads to a variety of GaAs-based devices. GaAs devices can be roughly divided into two categories – electronic devices and light-based (photonic) devices. Both categories of GaAs devices have found important commercial applications.

GaAs electronic devices cover three basic types of devices based on p-n junction structures: heterojunction bipolar transistors (HBTs), field effect transistors (FETs) and diodes. Their superior high-frequency and high-speed performance over silicon devices have developed them great markets in cellular phone technology, fiber-optic communications, electronic test equipment and military applications [38, 39].

Meanwhile, GaAs-based photonic devices have found high-volume applications in LEDs and lasers. LEDs are the biggest market for GaAs devices, and the vertical-cavity surface-emitting lasers (VCSEL) are predominantly GaAs-based devices at present. Furthermore, the advancement of growth technology has great impacts on GaAs devices. Today’s dominant growth methods, including molecular beam epitaxy (MBE), metal organic vapor-phase epitaxy (MOVPE) and vertical gradient freeze (VGF), feature the ability to grow semiconductor thin films with high purity, which is impossible to achieve with older techniques such as liquid-phase epitaxy (LPE) and vapor-phase epitaxy (VPE) [40, 41]. This improvement allows the growth of thin, uniform active regions and ultimately leads
2.2 NEA GaAs Photocathodes

GaAs photocathode is a particular branch of GaAs devices. A photocathode is basically an electrode made from a photoemissive material to convert incident light (photon) into electrons using the photoelectric effect. The electrons emitted from the photocathode can be collected by an anode to form photocurrent. Although a photocathode is usually a very small piece of device, it is an essential part of a photoemissive cell in optoelectronic systems, such as phototubes and photomultipliers [42]. Figure 2.2 shows a real photocathode sample in our lab used for the experiment and a sketch of a typical photoemissive cell consisting of a photocathode and an anode. Many different photocathode mate-
rials have been developed, and the selection of the material depends mainly on the required performance parameters. Spectral response and quantum efficiency (QE) are two main performance parameters. Compared to traditional metal- or alkali-based photocathodes, GaAs photocathodes can cover a wider spectral response range with higher QE, and are popular in optoelectronic applications, such as night vision, ultraviolet detection, polarized-electron generation, and photon-enhancement in emission tubes [3, 4, 5, 43].

Since QE is one of the key parameters in evaluating photocathode performance, considerable research has been carried out to improve the QE of GaAs photocathodes. The most successful approach among the different schemes is attaining the so-called negative electron affinity (NEA) condition on the GaAs photocathode surface [44, 45].

The NEA condition can be best explained via the band diagrams in Figure 2.3. Figure 2.3(a) shows a typical $p$-type semiconductor/vacuum interface, with the conduction band minimum (CBM) $E_C$, the valence band maximum (VBM) $E_V$, the Fermi level $E_F$, and the band gap $E_g$. The separation in energy between the CBM and the vacuum level $E_0$ at the surface is the electron affinity $\chi$, and the distance from $E_F$ to $E_0$ is the work function $\varphi$ of the material. Conventionally the electron affinity is positive ($\chi > 0$) as shown in Figure 2.3(a), and is usually referred as the positive electron affinity (PEA) condition. To escape into the vacuum, electrons in the CBM of the semiconductor must gain enough energy to overcome the positive barrier $\chi$ in the PEA condition [46].
Figure 2.3: Band diagrams for (a) positive electron affinity (PEA) and (b) negative electron affinity (NEA) conditions. $E_C$ and $E_V$ define the conduction band minimum (CBM) and the valence band maximum (VBM), respectively. $E_F$ is the Fermi level, $E_g$ is the band gap, and $\varphi$ is the work function of the material. The position of the vacuum level $E_0$ with respect to the CBM at the surface and in the bulk is defined by the electron affinity $\chi$ and the effective electron affinity $\chi_{eff}$, respectively.

Through some special treatments of certain semiconductor surfaces, the vacuum level $E_0$ can be shifted to a position lower than the CBM of the bulk, as illustrated in Figure 2.3(b). In this case, though the actual electron affinity $\chi$ is still positive, since the vacuum level $E_0$ lies below the CBM of the bulk, the negative effective electron affinity ($\chi_{eff} < 0$) condition is formed, and this is referred as the negative electron affinity (NEA) condition. Given the NEA condition, electrons with energy greater than or equal to $E_C$ encounter no work function barrier at the surface of the device, and therefore they can escape into the vacuum much easier than those facing the conventional PEA condition. This fact makes NEA photocathodes feature higher quantum efficiency, better performance and eventually bigger application market [47, 48, 49, 25].

NEA photocathodes are of two basic types: the transmission mode (t-mode) photocathode and the reflection mode (r-mode) photocathode, depending
Figure 2.4: Schematic diagram of (a) a transmission mode (t-mode) photocathode and (b) a reflection mode (r-mode) photocathode.

on the difference of the direction of the incident light, as illustrated in Figure 2.4. For the t-mode photocathode, the incident light is irradiated on the substrate or the back of the photocathode, and for the r-mode photocathode, the incident light and the emitted photoelectrons are located on the same side of the photocathode. The r-mode photocathodes are considerably simpler to fabricate, but both types of photocathodes have found wide applications. The r-mode photocathodes are primarily employed in photodiodes and photomultipliers, whereas the t-mode photocathodes are required for image and TV camera tube applications [50, 51].

The most commonly used semiconductors for NEA photocathodes are silicon and III-V compounds, among which GaAs is the most popular one. For GaAs photocathodes, the NEA condition is usually achieved by activating the device surface with monolayers of cesium and oxygen (Cs:O) [6, 7]. NEA GaAs photocathodes have been widely applied in photomultipliers, low-energy electron microscopes, and night-vision image intensifiers due to their ability to achieve high quantum efficiency and low dark emission [52, 26]. Lots of interest has been
put into NEA GaAs photocathodes, and research related to them has always been continued. In this dissertation, studies about the GaAs devices will be focused on the r-mode NEA GaAs photocathodes.

### 2.3 Photoelectron Transportation in NEA GaAs Photocathodes

Based on the widely accepted Spicer’s three-step model [53, 54], photoemission from an NEA emitter can be divided into three steps: (I) photoexcitation of electrons from the valence band to the conduction band, (II) electron transport action to the surface, and (III) escape across the surface and emission into the vacuum. Figure 2.5 interprets these three steps of photoemission in a $p$-type NEA GaAs photocathode. This model has not only provided a way of understanding the photoemission process in detail, but has also aided researchers for an efficient
photocathode design. Based on this three-step model, increasing the efficiency of any step would improve the overall performance of a photoemitter. The efficiency of step I (the photoexcitation) is usually determined by the material intrinsic properties, for example, the band gap. And in step III, the photoemission efficiency can be greatly increased with the realization of the NEA condition (as discussed above in Section 2.2). Therefore, for an NEA GaAs photocathode, improving the efficiency of step II (the transportation of the photoelectrons) becomes the key factor in optimizing the device performance.

Photoelectron transportation in photocathodes usually involves photoelectron decay and photoelectron motion. Photoelectron decay includes all the physical mechanisms that cause the loss or reduction of photoelectrons throughout the transport process, for example, recombinations induced by surface defects or the Auger effect. Photoelectron motion contains two main mechanisms – diffusion and drift. A graphic explanation of the concepts is given in Figure 2.6. Diffusion is the thermal random motion induced by the gradient in particle concentration,
i.e., photoelectrons move from regions with higher concentration to regions with lower concentration. The tendency of diffusion is to reach a uniform concentration of particles. Diffusion is usually quantitatively characterized by diffusion coefficient. It is highly dependent on particle and material properties and has to be experimentally determined for any individual material and any diffusing particle. On the other hand, drift is a directional motion driven by an external field or force [56]. The parameter for drift is the drift velocity, which is not only related to the particle’s own character, for instance, the effective mass of the particle, but also ruled by the external field or force that drives the drift process. In a photocathode, electron drift is typically driven by a built-in electric field generated by an intentionally designed doping structure. Diffusion and drift are in general two independent mechanisms as the causes for them are independent of each other, yet their parameters, the diffusion coefficient and the drift velocity are internally linked via the Einstein relation, and we will discuss this in detail later in Chapter 3 and Chapter 4.

Understanding photoelectron transportation in NEA GaAs photocathodes is necessary as well as important for seeking better designs to further improve the device performance. And this leads to an important branch of the NEA GaAs photocathodes research, concentrating on the photoelectron transportation inside the devices. In prior studies, there has been a lot of work dedicated to improving the design of NEA GaAs photocathodes to achieve better photoelectron transportation. Most of the designs are focused on introducing novel doping structures in the active layer of the devices to improve the photoelectron motion inside the
photocathodes [9, 10, 57, 8, 12, 58]. Some of the designs are given as examples in Figure 2.7. In this dissertation, the photoelectron transportation, including diffusion, drift and decay of NEA GaAs photocathodes will be thoroughly examined through ultrafast laser spectroscopy, and the key parameters such as the diffusion coefficient and the drift velocity will be determined for the tested devices. The impact of doping structure in the active layer of the devices on photoelectron transport will be evaluated as well.

2.4 Current Methods to Experimentally Study NEA GaAs Photocathodes

Current approaches to experimentally study NEA GaAs photocathodes can be divided into two main families – those based on the steady-state measurements and those relying on the post-photoemission evaluations.
The steady-state measurements analyze photoelectron behaviors based on the spectral response of the tested photocathode under constant illumination, i.e., illuminated by a continuous-wave (cw) light source. Previously, both theoretical and experimental researches have been well developed under the steady-state condition. Theoretical models have been established to describe photoelectron transportation, and the theoretical results can very well match the experimental measurements [14, 10]. The limitation of these studies is that they are restricted to the steady-state condition. Once the steady-state is interrupted by external factors, for example, a sudden change in illumination, the theories are no longer applicable. Therefore, the steady-state method is insufficient to offer time-dependent information on photoelectron transportation.

Meanwhile, the post-photoemission approach is capable of characterizing time-dependent photoelectron transportation, by analyzing time-resolved profiles of the emitted electron bunches. Typical resolution can reach several picoseconds [15, 16]. The basic concept of the post-emission method, as reported in prior studies [22, 16], is to project the longitudinal emitted electron bunches in a transverse direction onto a screen, thus the temporal profile of the electron bunches can be recorded. Since the temporal response of the device is dominated by the photoelectron transportation [16], the temporal profile of the emitted electron bunches can be employed to evaluate the photoelectron transportation behavior inside the device. A typical layout of the experimental setup for the temporal response measurement is illustrated in Figure 2.8. There are two essential components in this setup – the photogun and the deflection cavity. The photogun is

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Figure 2.8: Layout of a typical experimental setup for the temporal response measurement of an NEA GaAs photocathode. Figure adapted from [22].

Figure 2.9: Schematic of (a) a conventional DC photogun chamber and (b) a dipole mode RF deflection cavity. Figure adapted from Ref [59] and [16], respectively.
an injector built around the photocathode to provide high quality electron beam based on the emitted electrons from the photocathode [60, 61, 62]. It is a complicated system, and an example of a conventional design of the chamber is given in Figure 2.9(a). The deflection cavity is used to convert the profile of the electron beam from longitudinal to transverse, and it can be realized with a dipole mode radio-frequency (RF) deflection cavity as shown in Figure 2.9(b).

From Figures 2.8 and 2.9 we can see that the post-photoemission approach employs specific components. Moreover, it requires ultra high vacuum environment and high bias voltage (> 100 kV) to make the photogun system properly operate [63, 60]. Such demanding conditions are not easily achievable. This prevents the post-emission method from being widely applied. Another drawback of this method is that it only offers indirect information of photoelectron transportation inside a photocathode. This is because the electron emission from an NEA photocathode strongly depends on the condition of the device surface, such as the scattering caused by the chemical depositions left from the Cs:O activation in acquiring the NEA condition [64, 7]. As a result, the true properties of the photoelectron transportation inside the device may be masked and failed to be revealed in the temporal response of the emitted electron bunches from the post-emission measurements. Therefore, a technique that can provide a direct picture of the photoelectron transportation inside a photocathode device is needed. In this dissertation, this will be realized with the pre-photoemission measurements performed with the few-cycle pump-probe method, which is much simpler and easier to conduct as compared to the post-photoemission approach.
2.5 Few-Cycle Pump-Probe Reflectometry

Many techniques have been developed to investigate the optical properties of semiconductors using ultrafast lasers, among which pump-probe spectroscopy is the most common form. It is the preeminent method for time-resolved studies [21, 65] and has led to many developments in numerous scientific fields especially in material science [66, 67]. A general pump-probe system contains two essential elements: a pump to excite the sample under investigation and a probe to track the sample responses. There are two broad types of pump-probe techniques – degenerate and non-degenerate pump-probe spectroscopy. In the former case, the pump and the probe are split from a single laser output [68, 69]. Whereas, in the latter one, the pump and the probe come from different sources, such as two synchronized lasers at different wavelengths or a laser and a synchronized white light source [70, 71, 72]. For both types of pump-probe schemes, the basic idea behind them is similar to the principle of optical sampling. As explained in Figure 2.10, the pump pulses excite the sample from equilibrium and generate transient responses. Then the probe pulses are used as optical gates to probe the signal, allowing the detector to collect data only within that certain time window. As a result, a slice containing the instantaneous information (e.g. reflectivity, absorption, Raman scattering, luminescence) of the optical signal at the moment when the gate is open is collected. By changing the location of the gate to scan throughout the signal and repeating the measurements, the whole profile of the
Figure 2.10: Operating principle of a pump-probe system. Figure adapted from [73].
signal can be reconstructed. The change of the timing of the gate is usually realized by introducing a tunable delay line in either the pump or the probe arm.

From the above described procedure, it is clear that for suitably thin samples, the time resolution in degenerate pump-probe spectroscopy is limited only by the width of the optical gate, \( i.e., \) the duration of the probe pulses. The duration of the pulses generated by a few-cycle laser is only a small multiple of the optical cycle, which is about 2.7 fs at a central wavelength of 800 nm. Thus, pump-probe methods based on few-cycle laser pulses can easily achieve temporal resolutions of sub-10 fs level. They are one of the most sophisticated techniques to study ultrafast phenomena.

The setup that will be used in this project is a homemade degenerate pump-probe reflectometer, as illustrated in Figure 2.11. It measures the change in the reflected probe pulse energy induced by the pump as a function of the time delay between the pump and the probe pulses. The whole system is built around a 6.5-fs Ti:Sapphire laser operating at a center wavelength of 800 nm, with an average power of 500 mW and a repetition rate of 83 MHz. To manage the dispersion introduced by air and glasses during the transmission, a pair of dispersion compensation mirrors (DCM) and CaF\(_2\) wedges are placed at the output of the laser to provide dispersion pre-compensation and dispersion fine-tuning, respectively. An ultrabroad-band, dispersion balanced beamsplitter (DBB) is used to split the laser output into the pump and the probe beams. Except for the DCM, the CaF\(_2\) wedges, and the DBB, all other optics used in the optical path before the sample are reflective components with silver coatings. The pump beam, which
Figure 2.11: (a) The schematic layout of the experimental setup – the PPR system, which features (b) the ultrashort pulse and (c) the ultrabroad spectrum simultaneously.
has an average power of 270 mW, passes through a motorized delay stage and a beam chopper and is focused onto the sample by an off-axis parabolic (OAP) mirror. The probe beam has an average power of 20 mW. A pair of periscopes (PR1 & PR2) are used to rotate the polarization of the probe beam to make it cross-polarized with respect to the pump beam, and a second OAP mirror is used to focus the probe beam onto the sample. The reflected probe beam from the sample is detected by a Si photodetector and the output of the photodetector is fed into a lock-in amplifier. A tunable bandpass filter can be inserted before the photodetector if wavelength-resolved analyses are necessary. The unique design of this pump-probe system allows the pulse width and the spectrum of the laser to be preserved throughout the beam paths and eventually delivered onto the sample. As a result, the whole system features simultaneously a broad spectra range (300 nm) and a fine temporal resolution (< 10 fs) [73, 74].
Chapter 3. Dynamic Photoelectron Transportation in Gradient-Doped GaAs Photocathodes

3.1 Introduction

Negative-electron-affinity (NEA) III-V semiconductor photocathodes have been widely used in night vision, ultraviolet detection, polarized-electron generation, and photon-enhancement in emission tubes [3, 4, 5]. Compared to the traditional metal- or alkali-based photocathodes, III-V photocathodes are able to achieve higher quantum efficiency (QE) [47, 49], which is one of the key metrics to evaluate the performance of photocathodes [47]. Recent studies have further indicated that the use of exponential doping structures in the active layer of a III-V photocathode can help enhance the QE [8, 13, 75]. It has been suggested that such enhancement is due to the built-in electric field caused by the gradient of doping concentration in the active layer. As a result, in such photocathodes, the photoelectrons can be transported toward the surface through both diffusion and directional drift [9, 10]. In prior studies, theoretical models have been developed to describe the impacts of drift on key specifications of NEA GaAs photocathodes, such as diffusion length and QE [10, 14]. However, all the existing theories are based on steady-state analysis, which assume the photocathode is under a constant illumination of light.
Meanwhile, an important application of III-V photocathodes is the generation of electron bunches using pulsed lasers [15, 16, 22, 76]. Pulsed lasers have also been utilized to investigate the carrier-diffusion dynamics in GaAs photocathodes [15, 16, 17]. The existing steady-state theories are incapable of describing photoelectron transportation in these cases, and a time-dependent, dynamic model has become necessary. In our previous studies, a diffusion model has been developed to explain the behaviors of the photoelectrons in a uniform-doped GaAs photocathode following its excitation by a femtosecond laser pulse [17, 77]. In this chapter, a generalization of this theory has been made to incorporate a built-in electric field and thereby include carrier drift. As such, the model is capable of describing devices with arbitrary doping gradients. We further verify the model by comparing it with experimental results from femtosecond pump-probe reflectometry (PPR) measurements [17, 74]. Good experiment-theory agreements are realized, demonstrating the effectiveness of the theory in modeling real devices. Comparisons are also made between uniform doping and gradient doping to examine their differences in electron transportation dynamics, and the impact of doping gradient on surface charge accumulation is discussed.

3.2 Two-Layer Model for GaAs Photocathodes

In previous research, a diffusion model based on a two-layer concept has been developed to describe the photoelectron transportation in a uniform-doped GaAs photocathode [17, 77]. As the validity of the two-layer model has been fully proved by the excellent agreement previously achieved between the theoretical
predictions and the experimental data, it will be used again in my research here to provide a solid foundation for the new theoretical models.

In the two-layer model, the actual active layer – the heavily p-doped GaAs layer – is divided into two distinct sublayers: an active layer (AL), where most of the photoelectron generation and transportation take place, and an infinitely thin band-bending region (BBR) near the surface, where the photoelectrons accumulate and decay. In both AL and BBR, the electron concentration should satisfy the one-dimensional (1D) continuity equation, which can be derived from the general continuity equation and written as

$$\frac{\partial n(x, t)}{\partial t} = G(x, t) - \frac{\partial J(x, t)}{\partial x} - \Gamma_t n(x, t), \quad (3.1)$$

where $n(x, t)$ is the photoelectron concentration as a function of space $x$ and time $t$, $G(x, t)$ is the electron generation caused by all external factors, $J(x, t)$ is the electron flux, and $\Gamma_t$ is the total electron decay rate which includes all the effects leading to the reduction of the electron population [17]. Due to the different electron behaviors in the AL and the BBR, separate analyses need to be applied to them.

In the AL, the photoelectron generation $G(x, t)$ can be combined into a proper initial condition since the photoelectron generation caused by a femtosecond pulse can be considered an instantaneous process. Secondly, for simplicity, we can lump all the electron decay and loss into the BBR and treat the AL as a decay-free layer, which eliminates the last term $\Gamma_t n(x, t)$ in Equation 3.1. Thirdly, the electron flux in this study is caused by diffusion and/or drift, thus the term
$J(x, t)$ can be written in forms related to diffusion coefficient and/or drift velocity accordingly. Taking all the above aspects into account, the general continuity equation Equation 3.1 can be simplified into the governing equation in the AL, which can be written as

$$\frac{\partial n(x, t)}{\partial t} = D \frac{\partial^2 n(x, t)}{\partial x^2} + \frac{\partial [v_d n(x, t)]}{\partial x}, \quad (3.2)$$

where $D$ is the diffusion coefficient and the drift velocity $v_d$ is introduced and defined as $v_d = \mu_n |E|$, here $\mu_n$ is the electron mobility and $E$ is the built-in electric field created by the doping structure. $E$ may have different forms depending on the doping structures of different devices, thus Equation 3.2 can be further simplified into different shapes. The initial condition of Equation 3.2 is $n(x, 0) = n_0 e^{-\alpha x}$, where $\alpha$ is the absorption coefficient in the AL and $n_0$ is a scale factor for the electron population density. For simplicity, $n_0$ has been chosen in our model to make $\int_0^d n_0 e^{-\alpha x} dx = 1$, where $d$ is the thickness of the AL. Let us further assume the BBR acts as an electron “sink” where all the electrons are trapped in it without returning back to the AL, and the back interface of the AL is an impenetrable “wall” where all the electrons bounce onto it and get reflected back. This leads to a Dirichlet boundary condition $n(0, t) = 0$ on the AL-BBR interface and a Neumann boundary condition $\frac{\partial n(x = d, t)}{\partial x} = 0$ on the back interface.

In the BBR, due to the infinitesimal thickness, all the spatial dependence is neglected. Thus, the continuity equation Equation 3.1 reduces to

$$\frac{\partial N(t)}{\partial t} = J(t) - \Gamma N(t), \quad (3.3)$$
where \( N(t) \) is the total electron population in the BBR, \( J(t) \) is the electron injection flux, and \( \Gamma \) is the electron decay rate, which combines all the effects that lead to the reduction of the photoelectron population. \( J(t) \) can be related to the AL electron concentration \( n(x, t) \) by

\[
J(t) = \frac{dN_I(t)}{dt} = \frac{d}{dt} \left[ 1 - \int_0^d n(x, t) dx \right], \tag{3.4}
\]

where \( N_I(t) = 1 - \int_0^d n(x, t) dx \) is the total number of photoelectron injected from the AL into the BBR.

Above is the basic concept of the two-layer model. By solving the AL continuity equation Equation 3.2, the photoelectron concentration \( n(x, t) \) can be obtained and plugged into the BBR continuity equation to solve for the device surface photoelectron density, which can be directly related to the experimentally measured device surface reflectivity change based on the classical Drude theory [78, 79].

### 3.3 Carrier Transportation in Gradient-Doped GaAs Photocathodes

#### 3.3.1 Theoretical Model

The gradient-doping structure is also known as the exponential-doping, which means the doping concentration varies exponentially with the depth, i.e.,

\[
N_d(x) = N_{d0} \exp(Ax),
\]

where \( N_{d0} \) is the doping concentration on the surface of the photocathode, \( A \) is the gradient doping coefficient, and \( x \) is the depth from the surface. Figure 3.1 illustrates the typical band scheme of a gradient-doped GaAs
Figure 3.1: The band scheme of a typical gradient-doped GaAs photocathode with the illustration of the two sublayers: the active layer (AL) and the band-bending region (BBR).

The drift velocity $v_d$ according to the definition is therefore

$$E = -\frac{d}{dx} \left( \frac{k_0 T}{q} \ln \frac{N_{d0}}{N_d(x)} \right) = \frac{k_0 T A}{q},$$

where $k_0$ is the Boltzmann constant, $T$ is temperature, and $q$ is the elementary charge.
\[ v_d = \mu_n \left| \frac{k_0 TA}{q} \right| = DA, \]  

(3.6)

and here the Einstein relation \( D = \mu_n \frac{k_0 T}{q} \) has been used to simplify the equation.

Because of the constant built-in electric field as given in Equation 3.5, the continuity equation in the AL for the gradient doping structure can be derived from Equation 3.2 and written as

\[
\frac{\partial n(x, t)}{\partial t} = D \frac{\partial^2 n(x, t)}{\partial x^2} + DA \frac{\partial n(x, t)}{\partial x}. \]  

(3.7)

By solving Equation 3.7 with initial condition and boundary conditions as given in Section 3.2, the general solution can be found as

\[
n(x, t) = 2n_0 e^{-\gamma x} \sum_{i=1}^{\infty} b_i \sin (a_i x) e^{-\beta_i D t}, \]  

(3.8)

where \( \beta_i \) and \( \gamma \) have been introduced to simplify the expression and are defined as

\[
\beta_i = \frac{A^2}{4} + a_i^2, \quad \gamma = \frac{A}{2}. \]  

(3.9)

The expansion coefficients \( a_i \) and \( b_i \) are ruled by the boundary conditions and the initial condition, respectively. Applying the Neumann boundary condition at the back interface to the general solution Equation 3.8 results in a transcendental equation.
\[ \tan(a_i d) = \frac{2}{Ad} (a_i d), \]  
\hspace{1cm} (3.10)

which gives a set of discrete solutions for \( a_i \). Equation 3.10 has to be solved numerically in general, although analytical solutions are attainable approximately for small \( A \) values. This case will be discussed in detail later in Section 3.4.1.

Figure 3.2 shows the time evolution of \( n(x, t) \) in an AL of 2 \( \mu \text{m} \) thickness for (a) \( A = 0 \) (uniform-doped) and (b) \( A = 5 \ \mu \text{m}^{-1} \) (gradient-doped). In both cases, \( \alpha = 0.85 \ \mu \text{m}^{-1} \) has been assumed. Comparing Figure 3.2(a) and 3.2(b), it immediately becomes clear that a positive doping gradient pushes the peak concentration further toward the device surface while lowering the \( n(x, t) \) profile at a faster pace. Both facts indicate accelerated photoelectron transportation toward the BBR.
Figure 3.3: The impact of doping gradient to photoelectron accumulation on the device surface: (a) the growth of the total number of electrons injected from the AL into the BBR for different doping gradients, and (b) the time evolution of the injection flux under various doping gradients ($d = 2 \ \mu m$). Note that $A = 0$ indicates uniform doping.

The impact of the doping gradient can be further evaluated by examining the time evolution of $N_I(t)$ and $J(t)$ with various values of $A$ for a fixed AL thickness $d$. As shown in Figure 3.3(a), larger doping gradients lead to quicker buildups of the electron population inside the BBR. With $A = 5 \ \mu m^{-1}$, the electron population injected from the AL to the BBR is about 25-30% higher than it is in a uniform-doped device over a time range of 20-100 ps. Meanwhile, the injection flux $J(t)$ is generally 20-50% higher in a gradient-doped device of $A = 5 \ \mu m^{-1}$ than in a uniform-doped device, as shown in Figure 3.3(b).

In the BBR, by plugging the general solution of $n(x, t)$ given in Equation 3.8 into the BBR continuity equation Equation 3.3, the surface charge density $N(t)$ can be obtained as
\[ N(t) = 2n_0 D \sum_{i=1}^{\infty} b_i \left[ a_i - \frac{\gamma \sin(a_i d) + a_i \cos(a_i d)}{\gamma^2 + a_i^2} e^{-\gamma d} \right] \frac{\beta_i}{\Gamma - \beta_i D} \left( e^{-\beta_i D t} - e^{-\Gamma t} \right), \]

where, again, the coefficients \( a_i \) and \( b_i \) are determined by the boundary conditions and the initial condition of \( n(x, t) \) in the AL.

In Figure 3.4, \( N(t) \) is plotted for four different electron decay times, \( \tau = 1 \) ps, 10 ps, 50 ps and 200 ps, with \( \tau \) defined as \( \tau = 1/\Gamma \). In each case, uniform doping and several gradient-doping cases are plotted to showcase the impact of the doping profile. According to Figure 3.4, upon the injection of the laser pulse, the electron population near the device surface first experiences a sharp rise. This is then followed by an exponential population decay. The peak population is influenced by both \( A \) and \( \tau \). Larger doping gradients generally lead to higher peak populations, especially for large decay times. Such a behavior once again demonstrates the positive impact of the doping gradient on electron accumulation near the device surface.

### 3.3.2 Theory-Experiment Comparison

The above theoretical model can be experimentally verified using femtosecond PPR measurement, which probes the transient variation of the surface reflectivity following the injection of an ultrafast laser pulse. According to the well-known Drude theory [78, 79], the accumulation of free electrons on the surface of a semiconductor causes a slight change in the surface reflectivity, and the
Figure 3.4: The injection and decay of the electron population in the BBR leads to a transient behavior of $N(t)$ that features a sharp peak and an exponential tail, as seen here for four different decay lifetimes, $\tau = 1, 10, 50, \text{ and } 200 \text{ ps}$. ($A = 0$ corresponds to uniform doping.)
amount of this change is proportional to the area density of the electrons [17], which is directly correlated to the total electron population $N(t)$ in our 1D model as mentioned earlier. Thus, transient evolutions of $N(t)$ such as those shown in Figure 3.4 should be indicative of the behaviors of the transient reflectivity $\Delta R(t)$ measured by the PPR. This allows us to directly compare our theory to experiments. In doing so, not only the theoretical model can be verified, but also the key parameters of the tested devices are able to be determined, such as their diffusion coefficients $D$, drift velocities $v_d$, and electron decay times $\tau$.

Some practical aspects need to be clarified before proper comparisons can be made. In deriving Equation 3.11, it has been assumed that all the photo-electrons in the BBR share the same decay rate $\Gamma$ (or decay time $\tau$). However, previous studies have shown that multiple decay mechanisms with vastly different decay rates may coexist in actual devices [17, 15, 16]. In particular, a bi-exponential behavior of $\Delta R(t)$ has been found in the GaAs photocathodes studied in this work, indicating two distinctive electron decay rates. To account for the possibility of two decay processes, let us generalize the theoretical model by dividing the electron population in the BBR into two independent groups, each following Equation 3.11 with its own decay rate. The overall transient behavior of $\Delta R(t)$ hence can be modeled by

$$\Delta R(t) \propto N(t) = C_1 N_{\Gamma_1}(t) + C_2 N_{\Gamma_2}(t), \quad (3.12)$$
where $N_{\Gamma_1}(t)$ and $N_{\Gamma_2}(t)$ are the populations of the two electron groups with the decay rates $\Gamma_1$ and $\Gamma_2$, respectively. $C_1$ and $C_2$ represent the partition of the total electron population and satisfy the condition $C_1 + C_2 = 1$.

Experimental measurement of $\Delta R(t)$ has been performed using our home-built PPR system. Samples being tested in this part are two gradient-doped devices, one fabricated with metal organic chemical vapor deposition (MOCVD) and the other fabricated with molecular-beam epitaxy (MBE). The two devices share the same doping structure: a 1-µm buffer layer of $p$-$\text{Al}_{0.6}\text{Ga}_{0.4}\text{As}$ with a doping concentration of $1 \times 10^{19}$ cm$^{-3}$ directly grown on the $n$-type GaAs substrate, and a 2-µm gradient-doped active layer made of $p$-doped GaAs, with a doping concentration changing from $1 \times 10^{19}$ cm$^{-3}$ near the buffer layer to $1 \times 10^{18}$ cm$^{-3}$ on the surface. The doping structure is shown in the inset of Figure 3.5(a).

Figure 3.5(a) and (b) show the PPR-measured transient reflectivity for the MOCVD and the MBE devices, respectively. In both cases, $\Delta R(t)$ experiences an initial sharp rise followed by a decay process. This general behavior indeed resembles the behavior of $N(t)$ as shown in Figure 3.4. A closer look at Figure 3.5 further reveals that the decay of $\Delta R(t)$ includes a quick drop immediately following the peak and a long, slowly-decreasing tail, indicating the existence of two decay mechanisms with markedly different decay rates. Using the bi-exponential model given in Equation 3.12, excellent agreements between theory and experiment are achieved for both devices, as shown in Figure 3.5. The corresponding fitting parameters are given in Table 3.1. These parameters suggest that the fast decay process has a decay time of about 1 ps, whereas the slow decay process is
Figure 3.5: Comparisons between the theoretical model and experimental data show good agreement for two gradient-doped photocathode samples, fabricated with (a) MOCVD and (b) MBE. Inset: The doping structure of the tested photocathodes.

Table 3.1: Device parameters used in theoretical model in Figure 3.5

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>$D$ (cm$^2$/s)</th>
<th>$v_d$ (cm/s)</th>
<th>$C_1$</th>
<th>$\tau_1$ (ps)</th>
<th>$C_2$</th>
<th>$\tau_2$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOCVD</td>
<td>160</td>
<td>$1.84 \times 10^6$</td>
<td>0.942</td>
<td>1.3</td>
<td>0.058</td>
<td>80</td>
</tr>
<tr>
<td>MBE</td>
<td>160</td>
<td>$1.84 \times 10^6$</td>
<td>0.911</td>
<td>1.5</td>
<td>0.089</td>
<td>180</td>
</tr>
</tbody>
</table>

typically 100 times slower. In both devices, over 90% of the photoelectrons are lost due to the fast decay process. Although the exact underlying physical mechanisms are not clear solely based on these results, the fast and the slow decay times appear to agree with the typical time scales of surface recombination and photoemission, respectively, according to prior studies on similar GaAs photocathodes [16, 17, 27, 76].
3.4 Discussions

3.4.1 Small Doping Gradient – A Special Case

As mentioned in Section 3.3.1, the expansion coefficients $a_i$ and $b_i$ in the solution of $n(x,t)$ Equation 3.8 in general cannot be solved analytically due to the transcendental equation Equation 3.10. However, in the special case of a small doping gradient, an approximate analytical solution can be developed. This becomes clear by converting Equation 3.10 into a set of parametric equations with $u = \tan(y)$ and $v = \frac{2}{Ad}y$, where $y = a_id$, and seeking the intersections between $u(y)$ and $v(y)$. When the slope $\frac{2}{Ad}$ in $v(y)$ is greater than 1, i.e., when $Ad < 2$, the intersections are very close to $y = (i - 1/2)\pi$, where $i$ is a positive integer. This leads to a set of approximate solutions for $a_i$

$$a_i = \frac{2i - 1}{2d}\pi, \quad i = 1, 2, 3, \cdots.$$  \hfill (3.13)

Further applying the initial condition $n(x,0)$ to Equation 3.8 and completing the Fourier expansion, the coefficient $b_i$ is found to be

$$b_i = \frac{a_i + (-1)^i(\alpha - \gamma)e^{-(\alpha - \gamma)d}}{d[(\alpha - \gamma)^2 + a_i^2]}.$$ \hfill (3.14)

Finally, substituting Equations 3.13 and 3.14 into Equation 3.11, a full analytical expression for the total electron population in the BBR (i.e., surface charge density) can be written as
Figure 3.6: Comparisons between numerical results (line) and analytical predictions (marker) for (a) $n(x, t)$ and (b) $N_I(t)$ validate the analytical solution (Equations 3.13, 3.14, and 3.15) for small doping gradients.

\[ N(t) = 2n_0D \sum_{i=1}^{\infty} b_i a_i + \left(-1\right)^i \gamma e^{-\gamma d} \frac{\beta_i}{\gamma^2 + a_i^2} \left( e^{-\beta_iDt} - e^{-\Gamma t} \right). \] (3.15)

Note that, with a typical AL thickness of $d = 2 \, \mu m$, the solution Equation 3.15 is valid when $A < 1 \, \mu m^{-1}$. To verify the validity of this approximate solution, some comparisons have been made between the results obtained with the numerical method and the analytical formula for the case of $A = 0.5 \, \mu m^{-1}$. Figure 3.6(a) shows the AL electron concentration $n(x, t)$ versus $x$ at three different delay times. The matching between the numerical results and the analytical predictions is very good for short time scales (e.g., $< 10 \, ps$), although at longer delay times, slight deviations can be seen near the back interface of the device. Figure 3.6(b) shows a similar comparison for the AL-to-BBR electron injection
$N_i(t)$. Once again, excellent agreement is achieved between the analytical and the numerical results.

### 3.4.2 Uniform-Doping vs. Gradient-Doping

Another interesting aspect worthy of further consideration is the comparison between uniform doping and gradient doping. As pointed out in Section 3.3.1 based on the numerical results, gradient doping generally enhances photoelectron transportation from the AL to the BBR, resulting in a faster buildup of the free-electron population on the device surface. But now let us revisit this comparison from a more generic point of view and gain a deeper understanding about the underlying physics.

Let us first consider the case of uniform doping. By setting $A = 0$ in Equation 3.8 and Equation 3.9, the general solution for $n(x, t)$ in a uniformly-doped device can be written as

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

(3.16)

where $a_i$ is given by Equation 3.13 and

$$b_i = a_i + (\frac{\gamma}{2}) \frac{\alpha e^{-\alpha d}}{d(\alpha^2 + a_i^2)},$$

(3.17)

according to Equation 3.14 with $\gamma = 0$. Note that Equation 3.16 is an exact solution, and it agrees with the previously reported result based on a diffusion-only model [17].
Now, consider a gradient-doped device. By substituting the coefficients defined in Equation 3.9 into the general solution Equation 3.8 and moving the drift-related terms to the left-hand side of the equation, the following relation is obtained,

\[ n(x, t) e^{4(x + \frac{1}{2} \nu d t)} = 2 n_0 \sum_{i=1}^{\infty} b_i \sin (a_i x) e^{-a_i^2 D t}. \] (3.18)

If we define the left-hand side as an “effective electron concentration”

\[ n_{\text{eff}}(x, t) = n(x, t) e^{4(x + \frac{1}{2} \nu d t)}, \] (3.19)

then Equation 3.18 can be rewritten as

\[ n_{\text{eff}}(x, t) = 2 n_0 \sum_{i=1}^{\infty} b_i \sin (a_i x) e^{-a_i^2 D t}. \] (3.20)

Comparing Equation 3.20 with Equation 3.16, it immediately becomes clear that \( n_{\text{eff}}(x, t) \) shares the same general solution as the pure diffusive electron concentration in a uniform-doped device, albeit with a different set of initial and boundary conditions, which can be derived according to Equation 3.19 and the initial and boundary conditions for \( n(x, t) \). In other words, solving a gradient-doped device in general can be converted into solving a uniform-doping problem for \( n_{\text{eff}}(x, t) \) and then multiplying the result with \( \exp \left[ -\frac{4}{2} \left( x + \frac{1}{2} \nu d t \right) \right] \). This global exponential term can be viewed effectively as a descending exponential envelope propagating at a speed of \( \frac{1}{2} \nu_d \) toward the device surface \( (i.e., \) the \(-x\) di-
Figure 3.7: PPR traces (solid) measured with uniform-doped photocathodes show good agreement with the theoretical traces (dash-dotted) given by Equations 3.15 and 3.12 with $A = 0$ for both (a) MOCVD and (b) MBE samples. Inset: The doping structure of the tested photocathodes. Parameters used in theoretical simulations are given below in Table 3.2.

rection). It is the embodiment of the so-called drift-assisted carrier transportation [80], which accelerates the accumulation of photoelectrons on the device surface.

To verify the applicability of our model to uniform-doped devices, PPR measurements have been performed on uniform-doped photocathodes and have been compared with theoretical predictions based on Equation 3.15 and Equa-

Table 3.2: Device parameters used in theoretical simulation in Figure 3.7

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>$D$ (cm$^2$/s)</th>
<th>$C_1$</th>
<th>$\tau_1$ (ps)</th>
<th>$C_2$</th>
<th>$\tau_2$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOCVD</td>
<td>120</td>
<td>0.935</td>
<td>1.3</td>
<td>0.065</td>
<td>46</td>
</tr>
<tr>
<td>MBE</td>
<td>120</td>
<td>0.9</td>
<td>1.3</td>
<td>0.1</td>
<td>30</td>
</tr>
</tbody>
</table>
tion 3.12 under the condition of $A = 0$. As shown in Figure 3.7, good theory-
experiment agreements can also be achieved, proving the effectiveness of the model
over both uniform and gradient doping profiles.

### 3.4.3 Influence of Einstein Relation

In Section 3.3.1, the Einstein relation $D = \mu_n \frac{k_0 T}{q}$ has been used to simplify
the drift velocity $v_d$ (as in Equation 3.6) and the theoretical analysis based on
Equation 3.2. However, it has been shown that, when the doping concentration is
comparable or even greater than the effective density of valance/conduction-band
states, as in the current case, it is more accurate to use a generalized Einstein
relation between $D$ and $\mu_n$ [33, 81], which takes the form of

$$D = \mu_n \frac{k_0 T}{q} \left( 1 + 0.35355 \frac{p}{N_V} \right),$$

(3.21)

where $p$ is the doping concentration and $N_V$ is the effective density of states in the
valence band. Under this generalized Einstein relation, the diffusion coefficient $D$
is no longer a constant across the AL since it is now dependent upon the doping
concentration, which can be written as

$$D(x) = \mu_n \frac{k_0 T}{q} \left( 1 + 0.35355 \frac{N_d(x) e^{Ax}}{N_V} \right) = D_0 \left( 1 + 0.04 e^{Ax} \right),$$

(3.22)

where the doping concentration is specified using the gradient doping profile
$N_d(x) = N_{d0} \exp(Ax)$, and $D_0$ represents the constant diffusion coefficient when
the simple Einstein relation is considered. Under this condition, the continuity equation in the AL Equation 3.7 must be modified to include an extra term proportional to $\frac{\partial D(x)}{\partial x}$

$$\frac{\partial n(x,t)}{\partial t} = D(x) \frac{\partial^2 n(x,t)}{\partial x^2} + \frac{\partial D(x)}{\partial x} \frac{\partial n(x,t)}{\partial x} + D(x) A \frac{\partial n(x,t)}{\partial x}. \quad (3.23)$$

The impact of this extra term in the current context is investigated and the results are summarized in Figure 3.8. In Figure 3.8(a), the photoelectron concentration $n(x,t)$ in the AL is obtained with both the Einstein relation (solid) and the generalized Einstein relation (dashed lines with markers) for $t = 1$ ps, $t = 10$ ps and $t = 100$ ps. And in Figure 3.8(b), the AL-to-BBR injection population $N_I(t)$ is plotted against the time delay for both versions of the Einstein

![Figure 3.8](image-url)
relation. In both plots, the differences between the simulation results given by the generalized Einstein relation and those predicted by the original constant $D$ model are minute. Thus, for simplicity, the simple form of the Einstein relation, \textit{i.e.}, the constant $D$ model can be kept in this research.

3.5 Conclusion

In conclusion, in this chapter, a general theory describing photoelectron transportation dynamics in GaAs photocathodes has been developed. The time-dependent electron concentration distribution is obtained by solving, both numerically and analytically, a generalized diffusion equation incorporating directional drift caused by gradient doping. Surface charge density is derived to link the theoretical model to the experiment via the measurable carrier-induced surface-reflectivity change. The transient reflectivity behaviors of both uniform-doped and gradient-doped GaAs photocathodes are characterized using femtosecond pump-probe reflectometry. Theory-experiment comparisons show excellent agreement, thereby validating the effectiveness of the model in explaining experimental observations. Bi-exponential decay of free-electron population is found in all photocathode samples. The corresponding decay times and partition ratios are derived through curve fitting. Comparisons are made between uniform doping and gradient doping for their characteristics in photoelectron transportation. The impact of doping gradient on the acceleration of electron migration and surface accumulation is discussed based on both numerical results and analytical solutions. Overall, the methodology presented in this chapter is complementary to
the existing steady-state models and can potentially open a new avenue toward the experimental characterization of key device parameters.
Chapter 4. Dynamic Photoelectron Transportation in
Stepwise-Doped GaAs Photocathodes

4.1 Introduction

As discussed previously in Chapter 3, semiconductor photocathodes with
gradient doping structures have attracted lots of interest in recent years due to
their improved performances over the conventional, uniform-doped devices, such
as higher quantum efficiencies, longer diffusion lengths, and better spectral re-
sponses [9, 13]. However, it is necessary to point out the fact that the true
gradient-doping profile with continuously varying doping concentrations is very
difficult to fabricate with the current manufacturing technology. The so-called
“gradient-doped” devices are typically made up of multiple uniformly doped sub-
layers with a stepwise doping profile. On the other hand, it has been a common
practice in the field to use continuous doping models to describe such stepwise-
doped devices [57, 75], and this approximation has been widely adopted without
any in-depth study on its validity. Due to the intrinsic difference between a
continuous doping profile and a stepwise doping profile, certain important char-
acteristics of real devices are missing in a simplified model based on a continuous
doping profile. For example, the built-in electric field induced by a stepwise dop-
ing profile only appears within narrow regions across the sublayer boundaries
rather than uniformly distributed throughout the active layer of the device. This leads to a different electron-population distribution inside the active layer and ultimately affects electron transport. The potential impact of such a difference has been pointed out [82], but has not been carefully studied in the past.

In this chapter, a theoretical model is specifically developed to analyze the dynamic transport of photoelectrons following a femtosecond pulse excitation in a stepwise-doped GaAs photocathode. This work is built upon my previous studies of GaAs photocathodes with continuous gradient-doping profiles as described in Chapter 3. To validate the theoretical predictions, numerical results based on the model are compared with experimental results from pump-probe reflectometry measurements. Moreover, comparisons are made between the stepwise doping model (SDM) and the gradient doping model (GDM), which offer valuable insights into the validity of the GDM as well as its limitations.

4.2 Theoretical Model

The theoretical analysis rests again upon the “two-layer” concept, which has been explained in detail in Section 3.2 and has been experimentally verified in prior reports [17, 82, 83]. To help you recall it, the main idea of the “two-layer” concept is to divide the actual active layer of a photocathode into two distinct sublayers based on the difference in electron behaviors: a thick active layer (AL), where most of photoelectron generation and transportation take place, and a very thin band-bending region (BBR) near the surface, where photoelectrons transported from the AL accumulate and become trapped. For simplicity, the sublayer
Figure 4.1: The band scheme of a 4-layer stepwise-doped GaAs photocathode with the illustration of the two sublayers: the active layer (AL) and the band-bending region (BBR). Darker shading indicates higher doping concentrations.

AL is assumed to be loss-free, and all carrier decay processes are lumped into the sublayer BBR. Figure 4.1 illustrates the band scheme of a 4-layer stepwise-doped GaAs photocathode as well as the definitions of the two sublayers. At the surface of the photocathode, the conduction band and the valence band naturally bend downward as a result of the activation of the $p$-doped GaAs [8, 10, 84]. Downward band bending also occurs between adjacent doping layers due to their doping concentration difference, which forms a stepwise band profile in the AL [85], as shown in Figure 4.1. Such a band profile creates strong, constant electric fields within narrow regions across the doping boundaries, while leaving the majority of each doping layer free of electric field [10, 82, 86]. Mathematically, the field distribution in the AL can be written as
\[ E(x) = \begin{cases} 
0 & \text{within each doping layer} \\
\frac{\Delta E_F}{qW} & \text{on doping boundaries} 
\end{cases} \] (4.1)

where \( \Delta E_F \) is the difference between the Fermi levels of the adjacent doping layers, \( q \) is the elementary charge, and \( W \) is the width of the downward bending region. \( W \) can be obtained through the relation [87, 88]

\[ W = \sqrt{\frac{2\varepsilon_0\varepsilon_r \Delta E_F}{q^2(N_h - N_l)}}, \] (4.2)

where \( \varepsilon_0 \) and \( \varepsilon_r \) are the permittivity of vacuum and the relative permittivity of GaAs, respectively, and \( N_h \) and \( N_l \) are the higher and lower doping concentrations of the adjacent doping layers, respectively.

For each doping layer, the position of the Fermi level can be calculated through [33, 81]

\[ E_F = k_0T \left( \ln \frac{p}{N_V} + 0.35355 \frac{p}{N_V} \right), \] (4.3)

where \( k_0 \) is the Boltzmann constant, \( T \) is temperature (\( T = 300 \) K is used in all calculations in this chapter), \( p \) is the doping concentration, and \( N_V \) is the effective density of states in the valence band. Note that, in heavily doped \( p \)-GaAs, the doping concentration \( p \) is usually comparable or even higher than the value of \( N_V \), which is \( 7 \times 10^{18} \) cm\(^{-3}\) for GaAs. Therefore, the second term in Equation 4.3 cannot be neglected as with non-degenerate semiconductors [55, 89]. It is then
Figure 4.2: The electric field generated inside a sample with the 4-layer stepwise-doped structure. The (orange) lines between adjacent doping layers indicate the strengths of the electric fields in those regions. The widths $W$ of these regions are also labeled.

It is straightforward to write the Fermi level difference between adjacent doping layers as

$$
\Delta E_F = k_0 T \left( \ln \frac{N_h}{N_l} + 0.35355 \frac{N_h - N_l}{N_V} \right)
$$

(4.4)

Now, the electric field distribution in the AL can be determined by substituting Equations 4.2 and 4.4 into Equation 4.1. An example of such a field distribution is shown in Figure 4.2, where the doping parameters of an actual GaAs photocathode sample are given, along with the calculated values of $E$ and $W$ on each doping layer boundary.

In the sublayer AL, the governing equation is the simplified one-dimensional continuity equation [82]
\[
\frac{\partial n(x,t)}{\partial t} = D \frac{\partial^2 n(x,t)}{\partial x^2} + \mu_n \frac{\partial [E(x)n(x,t)]}{\partial x},
\]

(4.5)

where \( n(x,t) \) is the photoelectron concentration in the AL, \( D \) is electron diffusion coefficient, \( \mu_n \) is electron mobility, and \( E(x) \) is the built-in electric field induced by the doping structure. Note that the \( E(x) \) here is given by Equation 4.1, and \( \mu_n \) and \( D \) are related through the Einstein relation \( D/\mu_n = k_0 T/q \). The initial condition for Equation 4.5 is \( n(x,0) = n_0 e^{-\alpha x} \), where \( \alpha \) is the absorption coefficient in the AL, and \( n_0 \) is a scale factor representing the initial photoelectron concentration on the device surface. Such an initial condition is the result of an instantaneous-excitation assumption, which is valid when the photoelectrons are generated via injection of femtosecond pulses [17]. For simplicity, \( n_0 \) has been chosen in this model so that \( \int_0^d n_0 e^{-\alpha x} dx = 1 \), here \( d \) is the thickness of the AL. A Dirichlet boundary condition \( n(x = 0, t) = 0 \) is applied to the AL-BBR interface, while a Neumann boundary condition \( \frac{\partial n(x = d, t)}{\partial x} = 0 \) is applied to the back interface against the buffer layer.

According to Equations 4.1 and 4.5, in a stepwise-doped photocathode, electron diffusion exists throughout the entire AL, whereas electron drift only occurs on the boundaries between different doping layers. Using the device shown in Figure 4.2 as an example and numerically solving the differential equation Equation 4.5, the time evolution of the electron concentration \( n(x,t) \) inside the AL can be obtained. Figure 4.3(a)–(d) show the distribution of \( n(x,t) \) (solid lines) across the AL at four different delay times after the pulse excitation: 1 ps, 10 ps, 50 ps and 150 ps, respectively. Evidently, abrupt changes in the electron
Figure 4.3: The distribution of electron concentration $n(x, t)$ in the sublayer AL at different values of the time delay $t$, predicted by the SDM (solid) and the GDM (dashed) with a doping profile as shown in Figure 4.2 and a diffusion coefficient $D = 20 \text{ cm}^2/\text{s}$. 
concentration are caused by the built-in electric fields on the boundaries between different doping layers. Such “sawtooth-shape” distributions are in stark contrast to the smooth $n(x, t)$ profiles predicted by the GDM, as illustrated by the dashed lines in Figure 4.3 for the same device [82]. When time delays are small, the GDM appears to result in fairly close predictions on the “average” trends of $n(x, t)$, as shown in Figure 4.3(a) and (b). As time progresses, however, the discrepancies between the GDM and the SDM grow larger, as evident from Figure 4.3(c) and (d). For example, at the back interface ($x = 2 \mu m$), the electron concentration given by the GDM is 39% higher than that given by the SDM when $t = 50$ ps (see Figure 4.3(c)), and this difference grows to 56% when $t = 150$ ps (see Figure 4.3(d)).

The value of the diffusion coefficient $D$ also appears to affect the accuracy of the GDM. There has been a wide range of $D$ values reported in the literature for GaAs photocathodes, ranging from 20 cm$^2$/s to 160 cm$^2$/s [15, 16, 17, 22, 76, 82]. The results shown in Figure 4.3 are obtained with $D = 20$ cm$^2$/s. If $D$ is set to 160 cm$^2$/s, the difference between the SDM and the GDM is considerably more pronounced, as demonstrated in Figure 4.4(a)–(d).

Based on the above comparisons, it is evident that the SDM and the GDM in general predict different photoelectron distributions in the AL. Although the GDM is able to capture the average trend of the electron behaviors within small delay times, for devices with large diffusion coefficients or for cases involving long delay times, the GDM apparently tends to underestimate the rate of electron migration toward the BBR, which leads to noticeable errors. Such errors can
Figure 4.4: Similar comparisons between the SDM and the GDM as in Figure 4.3 with $D = 160 \text{ cm}^2/\text{s}$.
be quantitatively assessed by studying the total number of photoelectrons $N_I(t)$ transported from the AL into the BBR, where $N_I(t)$ is defined as $N_I(t) = 1 - \int_0^d n(x, t) dx$. Figure 4.5(a) and (b) show the time evolution of $N_I(t)$ with both the SDM (solid) and the GDM (dashed) for $D = 20 \text{ cm}^2/\text{s}$ and $160 \text{ cm}^2/\text{s}$, respectively. In both cases, the SDM predicts a faster overall AL-to-BBR injection rate than the GDM, indicating a trend of underestimation by the latter. To numerically gauge this error, a comparison has been made between the two models when the SDM-predicted $N_I(t)$ reaches 0.5, i.e., when 50% of the total generated photoelectrons transport from the AL into the BBR. The result shows that, for both Figure 4.5(a) and (b), the GDM yields a prediction about 9.7% lower than the SDM.
4.3 Theory-Experiment Comparisons

Given the different photoelectron behaviors predicted by the two models, it is interesting to investigate the impact of stepwise doping on the transient reflectivity change of actual devices. Previously in Chapter 3, I have shown you how the pump-probe transient reflectivity (PPTR) measurements offer great insight into the dynamic behaviors of photoelectrons and help determine key device parameters, such as diffusion coefficient and carrier lifetimes, if a proper theoretical model is used. However, at that time, the GDM was used as the theoretical model. Here let us apply the SDM to the experimental data and seek to compare the outcome with results from the GDM.

The specific approach is quite similar to that in Section 3.3.2. Based on the Drude model, the transient change of surface reflectivity $\Delta R(t)$, which can be experimentally characterized through a PPTR measurement, is proportional to the device surface charge density $N(t)$, which is described in this numerical model by the electron population density in the BBR. The governing equation for electron population in the BBR can be written as

$$\frac{\partial N(t)}{\partial t} = J(t) - \Gamma N(t), \quad (4.6)$$

where $J(t)$ is the AL-to-BBR injection flux and $\Gamma$ is the electron decay rate. Note that $J(t)$ is related to $N_I(t)$ through $J(t) = dN_I(t)/dt$, and $\Gamma$ combines all the effects that lead to the decay of the photoelectron population in the AL and the BBR. Numerically solving Equations 4.5 and 4.6 with an instantaneous initial
excitation results in a solution of $N(t)$ that represents the transient evolution of the surface charge density upon the injection of a femtosecond pulse. By comparing such a theoretical prediction with an experimental PPTR trace, key device parameters can be determined.

The PPTR measurements are performed with our home-built pump-probe reflectometry, which is based on a 6.5-fs Ti:sapphire laser operating at a center wavelength of 800 nm and a repetition rate of 83 MHz [74]. Two stepwise-doped GaAs photocathodes have been tested, one fabricated with metal organic chemical vapor deposition (MOCVD) and the other fabricated with molecular-beam epitaxy (MBE). The two devices share the same doping structure, which is illustrated in Figure 4.6(a) inset. The measured PPTR traces for the two devices are shown in Figure 4.6(a) and (b). Both traces are normalized to their peak values. A sharp rising edge is featured in both figures at $t = 0$, which correspond to the injection of the pump pulse. A quick decay of the reflectivity is seen immediately following the peak, but it is quickly replaced by a slow, steady decay after about 10 ps.

The above general behaviors of the transient reflectivity bear the feature of a bi-exponential decay [17, 82]. It is well known that multiple decay channels exist in GaAs photocathodes [16]. In the current model, the total electron population accumulated in the BBR experiences two independent decay processes, which cause the bi-exponential decay of the transient reflectivity. This can be incorporated into the model by first invoking the Drude model $\Delta R(t) \propto N(t)$ and then writing $N(t)$ as $N(t) = C_1 N_{r1}(t) + C_2 N_{r2}(t)$, where $N_{r1}$ and $N_{r2}$ rep-
Figure 4.6: Theoretical predictions based on the SDM show excellent agreement with the experimentally measured PPTR traces for GaAs photocathode samples fabricated with (a) MOCVD and (b) MBE. Inset: The doping structure of the tested photocathodes.

represent the populations of two separate groups of electrons. The two groups of electrons each independently follows Equation 4.6 with their own decay rates of \( \Gamma_1 \) and \( \Gamma_2 \), respectively, and \( C_1 \) and \( C_2 \) are the corresponding weighting factors under the restraint of \( C_1 + C_2 = 1 \). By setting proper values of the parameters \( \Gamma_1, \Gamma_2, C_1, C_2, \) and \( D \), and solving Equation 4.6, theoretical predictions of the transient reflectivity \( \Delta R(t) \) can be made.

Such theoretical predictions based on the SDM have shown excellent agreement with the experimentally measured PPTR traces, as demonstrated in Figure 4.6 for both the MOCVD and the MBE devices, provided that proper device parameters are chosen. This validates the effectiveness of the SDM. The corresponding device parameters used in the theoretical model are listed in Table 4.1 and Table 4.2, respectively. To highlight the differences between the SDM and
Table 4.1: Device parameters used in the theoretical computation for the MOCVD device in Figure 4.6(a).

<table>
<thead>
<tr>
<th>Model Type</th>
<th>$D$ (cm$^2$/s)</th>
<th>$C_1$</th>
<th>$\tau_1$ (ps)</th>
<th>$C_2$</th>
<th>$\tau_2$ (ps)</th>
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<tbody>
<tr>
<td>SDM</td>
<td>110</td>
<td>0.9739</td>
<td>1.55</td>
<td>0.0261</td>
<td>80</td>
</tr>
<tr>
<td>GDM</td>
<td>160</td>
<td>0.942</td>
<td>1.3</td>
<td>0.058</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 4.2: Device parameters used in the theoretical computation for the MBE device in Figure 4.6(b).

<table>
<thead>
<tr>
<th>Model Type</th>
<th>$D$ (cm$^2$/s)</th>
<th>$C_1$</th>
<th>$\tau_1$ (ps)</th>
<th>$C_2$</th>
<th>$\tau_2$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDM</td>
<td>120</td>
<td>0.9477</td>
<td>1.8</td>
<td>0.0523</td>
<td>180</td>
</tr>
<tr>
<td>GDM</td>
<td>160</td>
<td>0.911</td>
<td>1.5</td>
<td>0.089</td>
<td>180</td>
</tr>
</tbody>
</table>
the GDM, Table 4.1 and Table 4.2 also include the device parameters extracted from the GDM using the same devices [82]. Comparing the results from the two models, it is evident that, while the SDM and the GDM give similar assessments on the carrier decay parameters, the GDM consistently leads to greater values of the diffusion coefficient $D$ than the SDM. This finding appears to support the conclusion made in the Section 4.2, which suggests that the GDM tends to underestimate the rate of photoelectron transportation in a stepwise-doped device. As such, when the GDM is used to predict the experimental result based on a stepwise-doped device, a greater-than-normal value of $D$ has to be used to compensate the underestimation of electron drift. From this point of view, it is reasonable to conclude that, while the GDM is capable of capturing the main characteristics of photoelectron transportation in a stepwise-doped photocathode, it does suffer the drawback of inaccurate assessment of the diffusion coefficient.

4.4 Discussions

4.4.1 The Assumption of a Decay-Free AL

So far, in the two-layer model, the sublayer AL has been assumed to be decay-free, as indicated by Equation 4.5. In reality, however, carrier decay may exist in the AL. It is thus interesting to investigate how the inclusion of electron decay in the AL impacts the applicability of the two-layer model. To consider the decay, the governing continuity equation Equation 4.5 is modified to
Figure 4.7: Impact of photoelectron decay in the AL on the distribution of $n(x,t)$ at (a) $t = 10$ ps and (b) $t = 150$ ps, with $\tau_e = \infty$ (solid) and $\tau_e = 3$ ns (dashed/markers).

\[
\frac{\partial n(x,t)}{\partial t} = D \frac{\partial^2 n(x,t)}{\partial x^2} + \mu_n \frac{\partial [E(x)n(x,t)]}{\partial x} - \frac{n(x,t)}{\tau_e},
\]

where $\tau_e$ is electron lifetime in the AL. The impact of this new decay term can be qualitatively estimated via the following assessment. On one hand, prior research has shown that the lifetime of minority carrier in $p$-doped GaAs is generally above 1 ns [90, 91]. On the other hand, for the devices studied here, the majority of the generated photoelectrons ($> 50\%$) are transported from the AL into the BBR within the first 150 ps, as shown in Figure 4.5. Therefore, it is believed that the inclusion of electron decay in the AL should not significantly alter the photoelectron behaviors inside the AL. To verify this assessment, numerical simulations based on Equation 4.7 have been carried out and the results are shown in Figure 4.7. In Figure 4.7(a), the photoelectron concentration $n(x,t)$ is calculated at a delay time of $t = 10$ ps with $\tau_e = \infty$ (decay free) and $\tau_e = 3$ ns. In Figure 4.7(b), similar comparisons are made at a delay time of $t = 150$ ps. In both cases,
the difference introduced by the electron decay is negligible, which justifies the assumption of a decay-free AL in the current context. Note that $\tau_e = 3$ ns has been chosen here as a representative value of the AL electron lifetime based on a recent study of GaAs with similar doping concentrations [91].

### 4.4.2 The Impact of Einstein Relation

In Section 4.2, the Einstein relation $D = \mu_n k_0 T / q$ has been used to simplify the theoretical analysis based on Equation 4.5. However, it has been shown that, for $p/n$-type semiconductors, when the doping concentration is comparable or even greater than the effective density of valance/conduction-band states, as in the current case, it is more accurate to use a generalized Einstein relation between $D$ and $\mu_n$ [33, 81], which takes the form of

$$D = \mu_n \frac{k_0 T}{q} \left( 1 + 0.35355 \frac{p}{N_V} \right),$$

where $p$ is the doping concentration and $N_V$ is the effective density of states in the valence band. Under this generalized Einstein relation, the diffusion coefficient $D$ is no longer a constant across the AL since it is now dependent upon the doping concentration. The continuity equation in the AL must be modified to

$$\frac{\partial n(x, t)}{\partial t} = D \frac{\partial^2 n(x, t)}{\partial x^2} + \frac{\partial D}{\partial x} \frac{\partial n(x, t)}{\partial x} + \mu_n \frac{\partial [E(x)n(x, t)]}{\partial x},$$

where an extra term proportional to $\partial D/\partial x$ is introduced.
Figure 4.8: The effect caused by the generalized Einstein relation on (a) the electron distribution $n(x, t)$ in the AL at different delay times and (b) the AL-to-BBR electron injection $N_I(t)$. Results obtained using the Einstein relation are represented by solid lines. Results obtained using the generalized Einstein relation are represented by dashed lines with circular markers.

The impact of this extra term in the current context is investigated using the doping configuration shown in Figure 4.2 as an example, and the results are summarized in Figure 4.8. In Figure 4.8(a), the photoelectron concentration $n(x, t)$ in the AL is obtained with both the Einstein relation (solid) and the generalized Einstein relation (dashed lines with markers) for $t = 1$ ps and $t = 150$ ps. For small time delays, e.g., $t = 1$ ps, the correction caused by the generalized Einstein relation has no apparent effect on the overall distribution of $n(x, t)$. As the time delay increases, discrepancies begin to appear but nevertheless remain small. The overall effect of such discrepancies can be further evaluated by computing the BBR injection rate, which is shown in Figure 4.8(b), where the injection population $N_I(t)$ is plotted against the time delay for both versions of the Einstein relation. The generalized Einstein relation appears to result in a
slight increase in $N_f(t)$, which is less than 2% across all delay times. Therefore, for the devices under study here, the original Einstein relation is considered a valid approximation. Finally, it is worth mentioning here that, because of the intimate relation between $D$ and $\mu_n$ through the Einstein relation, the justified use of the Einstein relation also suggests that electron mobility can be treated as a constant in the current model.

4.5 Conclusion

In conclusion, in this chapter, the photoelectron transport dynamics in stepwise-doped GaAs photocathodes is thoroughly investigated using the SDM, with a special focus on its improvement from the conventional GDM. By solving the one-dimensional continuity equation with a distinctive field distribution caused by the stepwise doping profile, the time-dependent electron concentration distribution in the AL is obtained. The resulted ultrafast evolution of the electron population in the BBR is compared with experimental PPTR measurements. Excellent agreements are achieved, and key device parameters, such as the diffusion coefficient and the electron decay lifetimes, are extracted. Comparisons with the GDM indicate that the continuous-doping treatment causes the photoelectron transport rate in the AL being underestimated in the theoretical model and the diffusion coefficient $D$ being overestimated during theory-experiment comparisons. Finally, the validity of a decay-free AL and the suitability of the Einstein relation are examined and verified. The work establishes the importance and
the effectiveness of the SDM, which offers a more accurate theoretical tool for analyzing III-V semiconductor photocathodes.
Chapter 5. Experimental Investigation of the Burstein-Moss Effect in GaAs Wafers

5.1 Introduction

Burstein-Moss (BM) effect, also known as the BM shift, is a phenomenon observed in degenerate semiconductors, where the optical band gap blue shifts as the doping concentration increases \[92, 93, 94\]. It was first observed in indium antimonide (InSb), which is believed to be attributed to the small effective mass of electrons in InSb and the relatively low degenerate concentration of InSb. Then, as the improvement in doing techniques made it easier to achieve heavily doped samples, the BM effect was observed in many other semiconductors at much higher carrier concentrations, such as zinc oxide (ZnO), gallium nitride (GaN) and gallium arsenide (GaAs) \[95, 96, 97, 98, 99\].

The BM effect is generally understood as a consequence of band filling. In an intrinsic semiconductor, the Fermi level lies near the center of the forbidden band gap between the conduction band and the valence band, which is known as the intrinsic Fermi level \(E_{Fi}\) as shown in Figure 5.1(a). And at moderate doping levels, the impurities introduce discrete donor (or acceptor) energy states in the \(n\)-type (or \(p\)-type) semiconductor. These types of semiconductors are called nondegenerate semiconductors. The Fermi level position under this condition is
Figure 5.1: Simplified energy band diagrams for different types of semiconductors.
deflected from the intrinsic Fermi level toward the conduction or valence band depends on the doping method, but still within the band gap, as shown in Figure 5.1(b) and (c). However, if the impurity concentration is high enough, the donor states interact to form a band which overlaps the bottom of the conduction band. As a result, the Fermi level will end up inside the conduction band. This type of semiconductor is referred to as a degenerate \textit{n}-type semiconductor (as in Figure 5.1(d)). In a similar way, as the acceptor doping concentration increases in a \textit{p}-type semiconductor, the discrete acceptor energy states widen into a band of energy and may overlap the top of the valence band. The Fermi energy will then lie in the valence band and leads to a degenerate \textit{p}-type semiconductor (Figure 5.1(e)) [100, 101]. Considering the fact that the optical band gap of a material is determined by energy separation between the filled valence band and unfilled conduction band, and that Fermi level restricts the highest possible level of electrons, under degenerate doping conditions, the change of the Fermi level position results in the optical band gap widening effect or the BM shift [95, 96, 97, 102]. On the other hand, under conditions of very heavy doping, band gap narrowing starts to happen due to the correlated motions of the charge carriers and their scattering against ionized impurities [103, 104, 105]. The observed apparent band gap is then the result of the counteracting between the BM shift and the band gap narrowing.

Meanwhile, light-induced photoelectrons can also cause a similar band-filling effect [106]. The associated band gap blue shift, which sometimes is referred to as the dynamic BM effect, has been observed by driving semiconductors with
strong laser pulses [107, 108]. Although the BM effect caused by doping (steady-state) and the BM effect caused by photo-excitation (dynamic) are both well studied, little attention has been given to their combined effects under the same context. The Fermi level in a degenerate semiconductor is intimately related to Coulomb screening, which in turn affects the dynamics of the photo-induced band shift [107, 109]. Thus, a careful investigation into the dynamic BM effect under various levels of heavy $n$-type doping is of fundamental interest.

Previously, a preliminary study has demonstrated transient dispersion measurement using a few-cycle pump-probe reflectometry (PPR) [74]. Transient dispersion (TD) refers to the rapid change of wavelength-dependent refractive index $n(\lambda)$ following an ultrafast photoexcitation [110]. TD is a result of several important many-body effects in semiconductors, such as band filling, bandgap shrinkage (renormalization) and free carrier absorption [106]. It can be characterized by measuring the slight variation of surface reflectivity over a range of wavelengths using broadband (few-cycle) laser pulses as probes [82]. Since the photo-induced reflectivity change $\Delta R(\lambda, t)$ switches sign at the optical band gap [74, 106], a two-dimensional (2D) map of $\Delta R(\lambda, t)$ obtained through transient dispersion measurement offers a direct visualization of band gap behaviors as carrier populations evolve.

In this chapter, the transient dispersions of four $n$-GaAs wafer samples with different doping levels were examined. Clear evidence of both steady-state and dynamic BM effects is observed, and a link between them is identified.
5.2 Experiments and Results

The GaAs wafer samples (MTI) are single-side polished with thicknesses ranging between 0.35–0.625 mm. Three n-type GaAs samples are chosen with doping concentrations of $4 \times 10^{17}$ cm$^{-3}$ (Te-doped), $8 \times 10^{17}$ cm$^{-3}$ (Si-doped), and $3 \times 10^{18}$ cm$^{-3}$ (Si-doped), respectively. To provide a baseline reference, an undoped GaAs wafer is also tested.

The home-built few-cycle PPR system is again used to obtain experimental data. The pump-probe setup is originally designed to measure time-resolved reflectivity change. In this chapter’s experiments, specifically, a series of band-pass filters with center wavelengths ranging from 650 nm to 950 nm are incorporated into the detection system to provide wavelength-resolved measurements. Such a design allows the PPR to perform time-frequency spectroscopy with an $\sim 10$-fs temporal resolution and a $>200$-nm wavelength span, which covers the nominal band gap for GaAs at 1.42 eV ($\sim 870$ nm).

Figure 5.2 shows the PPR-measured relative reflectivity change $\Delta R(\lambda, t)$ as functions of wavelength and time delay (from the pump pulse) in a 3D spectrogram for all four GaAs wafer samples. A clear sign change can be seen occurring across the apparent band gap in all 4 cases. But the detailed time-wavelength profiles of $\Delta R$ are different in each case. A better view of these spectrograms is illustrated in the 2D contour maps in Figure 5.3, obtained by projecting the 3D plots on a 2D plane. The color contour represents the transient change of the surface reflectivity relative to its steady-state value, which in turn signifies
Figure 5.2: 3D time-wavelength spectrograms of the transient dispersion in GaAs wafers, measured by the few-cycle PPR system. Four samples with different doping concentrations are used: (a) undoped; (b) $4 \times 10^{17}$ cm$^{-3}$ Te-doped; (c) $8 \times 10^{17}$ cm$^{-3}$ Si-doped; and (d) $3 \times 10^{18}$ cm$^{-3}$ Si-doped.
Figure 5.3: Projected 2D contour maps of the 3D spectrograms in Figure 5.2 of the transient dispersion in the GaAs wafers. Doping concentrations are listed at the bottom left corner of each figure. The steady-state and blue-shifted band gaps are labeled at the top and the bottom of each figure, respectively.
Figure 5.3: Projected 2D contour maps of the 3D spectrograms in Figure 5.2 of the transient dispersion in the GaAs wafers. (cont.)
the transient change of refractive index. Comparing Figure 5.3 to Figure 5.2, it is clear to see that a positive change (yellow region) in Figure 5.3 indicates a rise of the refractive index above the steady state value, whereas a negative change (blue region) suggests a dip in refractive index below the steady state value. The variations of these index changes vs. wavelength provide the so-called transient dispersion. Mapping the evolution of the dispersion over time offers insight into the ultrafast carrier dynamics inside the material and the impacts of such dynamics on material properties.

5.3 Discussions

Based on previous studies, the reflectivity of GaAs switches its sign near the band gap due to the refractive index nonlinearity [106, 111]. Thus, the time-evolution of the optical band gap can be identified in a 2D transient dispersion map as the transition edge between the positive and the negative regions [74]. For a clearer view, dashed trend lines are added in Figure 5.3 to indicate the approximate locations of the transition edge for each GaAs sample.

5.3.1 The Dynamic Bertein-Moss Effect

At first glance, a common feature across all these samples is that the optical band gap appears to experience a relaxation process, red-shifting from a shorter wavelength of about 500–700 fs after the excitation pulse and eventually stabilizing at a longer wavelength after about 10 ps. Such an observation agrees with the general picture of photocarrier-induced band gap shift, i.e., the sudden
increase of the photoelectron population in the first few hundred femtoseconds after excitation causes a blue shift of the optical band gap through the dynamic BM effect, but then, as the photoelectron population gradually decays (due to various decay channels such as recombination), the band filling effect slowly weakens until the band gap eventually shifts back to the steady-state level. The clear transition edges in Figure 5.3 prove that the transient dispersion measurement has allowed us to show both dynamic and steady-state BM effects on the same graph.

To achieve more detailed numerical evaluations, the blue-shifted and the steady-state band gap wavelengths (energies) are labeled for each sample in Figure 5.3. Based on these values, it is evident that higher doping levels lead to larger steady-state band gaps, which is the original (steady-state) BM effect. Furthermore, the extent of the dynamic BM effect depends on the doping level. For example, the band gap shift caused by the dynamic BM effect in the undoped sample (Figure 5.3(a)) is about 15 nm (from 886 nm to 871 nm), while for the Te-doped sample (Figure 5.3(b)), this shift increases to 29 nm. Similar trends are also seen in the two Si-doped samples (Figure 5.3(c) and (d)). The underlying physics for this dependence is still under investigation. However, the experimental results highlight the potential of transient dispersion measurement in studying photonic material properties.
Figure 5.4: Schematic energy band model for (a) undoped GaAs where the Fermi level $E_F$ locates near the center of the band gap between the valence band (VB) and the conduction band (CB); and (b) heavily $n$-doped GaAs with the $E_F$ pushed up into the CB.

5.3.2 The Steady-State Burstein-Moss Effect

As mentioned before in Section 5.1, the Fermi level is pushed up into the conduction band in degenerate $n$-type semiconductors, and the location of the Fermi level rises up rapidly with increasing doping concentration, as illustrated in Figure 5.4. The optical absorption involves transitions from the filled level in the valence band to the lowest unfilled level $E_m$ in the conduction band. Therefore the optical band gap $E_{opt}$ is determined by the energy separation between $E_m$ (which lies approximately $4kT$ below the Fermi level) and its corresponding level.
in the valence band (which locates \((m_e^*/m_h^*)E_m\) below the top of the valence band) [92]. Thus the rise of the Fermi level leads to the change of the location of \(E_m\) and eventually to the optical band gap widening in degenerate semiconductors. Mathematically, the optical band gap widening due to the BM effect \(\Delta E_{g}^{BM}\) can be written as [98, 112]

\[
\Delta E_{g}^{BM} = \left(1 + \frac{m_e^*}{m_h^*}\right) E_M \\
= \left(1 + \frac{m_e^*}{m_h^*}\right) (E_F - E_C - 4kT) \\
= \left(1 + \frac{m_e^*}{m_h^*}\right) \frac{\hbar^2}{2m_e^*} (3\pi^2 n)^{2/3},
\] (5.1)

where \(E_F\) is the Fermi level relative to the top of the valence band, \(T\) is temperature, \(\hbar\) is the reduced Planck constant, \(m_e^*\) and \(m_h^*\) are the effective masses of electrons and holes in GaAs, respectively, and \(n\) is the carrier concentration in the unit of \(\text{cm}^{-3}\). The optical band gap \(E_{opt}\) is then defined as

\[
E_{opt} = E_g + \Delta E_{g}^{BM},
\] (5.2)

with \(E_g=1.424\) eV representing the intrinsic band gap of GaAs in room temperature.

Consider the special situation where \(E_F - E_C - 4kT = 0\), i.e., \(E_M\) lies right at the bottom of the conduction band, the BM shift is then equal to zero according to Equation 5.1. This happens at the electron concentration \(n_{crit} = 2.38 \times 10^{18}\)
cm$^{-3}$ for GaAs as calculated from Equation 5.1. Therefore, for $n$-type GaAs, no BM shift is expected and $E_{opt} \approx E_g$ when $n \leq n_{crit}$.

Now, let’s compare the above theoretical calculations to the experimental data. In Figure 5.3(a), for the undoped sample, the observed steady-state band gap is $\sim 1.4$ eV, which roughly matches the nominal value of the intrinsic band gap of GaAs under room temperature.

In Figure 5.3(b), for the Te-doped sample, no blue shift of the band gap is observed in the experimental data. The reason is that the doping concentration of the sample ($4 \times 10^{17}$ cm$^{-3}$) is lower than the effective density of states in conduction band for GaAs ($N_C = 4.7 \times 10^{17}$ cm$^{-3}$), so the sample does not qualify for the degenerate doping condition. Therefore the BM shift is not expected. Instead, a tiny band gap shrinkage of 0.03 eV ($=1.424$ eV-1.394 eV) is noticed in Figure 5.3(b). This value matches the ionization energy of the shallow donor Te [113, 114], hence, the shrinkage is very likely a natural result introduced by the dopant.

With a higher doping concentration, the degenerate GaAs sample is obtained, as given in Figure 5.3(c). Noticing that the doping concentration here ($8 \times 10^{17}$ cm$^{-3}$) is though high enough to make the sample degenerate, still lower than the value of $n_{crit} = 2.38 \times 10^{18}$ cm$^{-3}$ to have the BM effect occurred. This is verified by the experimental data of the sample as shown in Figure 5.3(c). The observed optical band gap (1.418 eV) is close to the intrinsic band gap of undoped GaAs, and shows no sign of carrier induced shift. The observed minor band gap
shrinkage of 0.006 eV (=1.424 eV-1.418 eV) is, again, likely due to the nature of the shallow donor, Si in this case.

Keep increasing the doping concentration, and the BM effect is finally able to be experimentally observed in the very heavily doped GaAs sample, as illustrated in Figure 5.3(d). According to Equations 5.1 and 5.2, the theoretical optical band gap under this doping concentration \(3 \times 10^{18} \text{ cm}^{-3}\) is \(\sim1.44 \text{ eV}\), which is very close to the observed value from the experimental data (1.458 eV).

From the above theory-experiment comparisons, the transient dispersion measurement via PPR shows strong power in reflecting the steady-state BM effect of semiconductors. Considering the ability of the time-wavelength spectrograms to map simultaneously both steady-state and dynamic BM shifts, the PPR-based transient dispersion measurement would have huge potential in future studies of optical properties of semiconductor materials and devices.

Another interpretation of the experimental data can be provided from a different perspective. As illustrated in Figure 5.5, the change of reflectivity with different wavelengths is plotted as a function of time. Here we focus on the peak region of the signals. And by employing the logarithm time scale, the difference among the sample behaviors can be emphasized. The curves in three doped samples (Figure 5.5(b)-(d)) are more discrete in the rising edge than those in the undoped sample (Figure 5.5(a)), indicating that the doping process may introduce some delay in sample response in longer wavelengths, which leads to the doping-induced wavelength-dependent response pattern. The physics behind this wavelength dependent phenomenon is not clear for now, a reasonable guess would
Figure 5.5: Transient reflectivity change over time of different wavelengths for four tested GaAs wafers.
be that it is related to the carrier-induced transient dispersion (TD). Future work of a comprehensive study of the TD will be needed to help verify and thus gain a better understanding of these observations.

5.4 Conclusion

In this chapter, by incorporating a series of wavelength filters into the home-built few-cycle PPR system, the time-wavelength resolved spectrograms of the transient reflectivity of GaAs wafers after photoexcitation by a femtosecond pulse are obtained, including the original 3D spectrograms and the projected 2D contour color maps. From these time-wavelength spectrograms, especially the 2D contour maps, both the dynamic and the steady-state Burstein-Moss (BM) shifts are observed simultaneously. The experimental observations of the doping concentration dependency of the BM shifts show good agreement with the theoretical calculations. Another wavelength-dependent shape pattern, which is possibly caused by the doping procedure, is also observed. Although further work is needed to figure out the underlying physics behind these observations, it is very delightful to show with this chapter’s study that the transient dispersion measurements feature strong abilities and potential to reveal some hidden details of semiconductor materials.
Chapter 6. Conclusions, Contributions, and Future Work

6.1 Summary of Dissertation

This dissertation reports a comprehensive study of the ultrafast photoelectron transportation inside GaAs wafers and negative electron affinity (NEA) GaAs photocathodes based on a new diffusion-drift model (theoretical) and few-cycle pump-probe reflectometry (experimental).

First, a general theoretical model is developed, upon a two-layer assumption, from the fundamental continuity equation, to describe the photoelectron behavior inside an NEA GaAs photocathode following the photoexcitation by femtosecond laser pulses. This model adds photoelectron drift into the diffusion-only model designed for the conventional uniform doping structure and therefore provides a full picture of the photoelectron transportation inside the device. The model is capable of representing both the gradient and the uniform doping structures given the corresponding parameters are set to correct values. Theoretical results show that in the gradient doping structure, a constant electric field is generated, and therefore the photoelectron transportation is enhanced by the drift-assisted photoelectron transportation along with the diffusion mechanism. The theoretical results predicted by the model have found good agreement with the experimental data measured by the few-cycle PPR, which verifies the effec-
tiveness of this theoretical model. Furthermore, through the theory-experiment comparison, a bi-exponential decay mechanism is found in all tested GaAs photocathodes. The corresponding decay times and the partition ratios along with some other key parameters are able to be determined by curve fitting, including the diffusion coefficients and the drift velocities. This time-dependent, dynamic theoretical model is complementary to the existing steady-state models and can potentially open a new avenue toward experimental characterization of key device parameters.

Next, the general theoretical model is further modified into a stepwise doping model (SDM). Limited by the current manufacturing technology, the true continuous gradient doping structure is very difficult to realize. The so-called “gradient doping structures” are actually made up of several uniformly doped sublayers with gradually varied doping concentrations. Therefore, the SDM specifically designed for this stepwise doping profile would be more accurate in representing the actual devices than the continuous gradient doping model (GDM). According to the SDM, the stepwise doping structure creates strong, constant electric fields within narrow regions across the doping boundaries between adjacent doping layers, while leaving the majority of each doping layer free of an electric field, which is apparently different from the GDM prediction. The simulation of the time evolution of photoelectron distribution based on the SDM confirms this difference – although the overall trends given by the SDM are similar to those predicted by the GDM, certain and obvious discrepancies do exist. For example, in the SDM, abrupt changes in photoelectron concentrations are observed in the
boundary regions between doping layers due to the sudden change of the built-in electric fields, which is distinct from the smooth behavior given by the SDM treatment. To evaluate the effectiveness of the SDM, theory-experiment comparisons are conducted. The results show that the theoretical predictions given by the SDM can very well match with the PPR measured experimental data. And a further comparison between the SDM and the GDM indicates that the GDM treatment leads to an overestimation in diffusion coefficients of actual devices. The SDM is a good expansion of the conventional GDM, and provides a more accurate and promising theoretical tool for analyzing photoelectron dynamics in actual semiconductor devices.

The last part of my dissertation research focuses on the study of transient dispersion in GaAs wafers with different doping concentrations. For that, I performed both time- and wavelength-resolved measurements of transient reflectivity using the home-developed few-cycle PPR system. By way of introducing proper wavelength filters into the PPR system, time-wavelength resolved experimental data of transient reflectivity of GaAs wafers is obtained. The raw data are plotted in either 3D or 2D spectrograms to provide different angles of view. From these plotted spectrograms, especially from the 2D projected color contour maps, the carrier induced optical band gap blue shifts of the tested GaAs wafers are observed. The observed shifts can very well match the theoretical values of the band gap shifts caused by the steady-state Burstein-Moss (BM) effect in heavily doped GaAs. Along with the steady-state BM shifts, the dynamic BM shifts are able to be simultaneously observed from the same spectrogram. The results show
that the extent of the dynamic BM shifts is dependent on the sample doping concentrations – higher doping concentration tends to induce a more intensive blue shift in the optical band gap. Although further investigations are required to confirm the underlying physics behind these observations, it is hoped that the time-wavelength resolved PPR measurements discussed in this dissertation would provide a potential method for future studies in the transient dispersion of semiconductor materials or devices.

6.2 Contributions to the Field

Here is a summary of the main contributions of my dissertation work to the field:

- Established the first theoretical model to describe dynamic photoelectron transportation in semiconductor photocathodes with both diffusion and directional drift incorporated (previous models are either steady-state models or dynamic models including only carrier diffusion). As such, the new model is able to analyze a much wider variety of devices, including those with non-uniform doping profiles.

- Reported the first analysis (both theoretical and experimental) of stepwise-doped semiconductor photocathodes. Quantified the difference between realistic stepwise-doped devices and idealized gradient-doping models, which provides key metrics for assessing the suitability of gradient-doping models in describing real devices.
• Provided the first quantitative evaluation of the impact of the generalized Einstein relation in a drift-diffusion model for semiconductor photocathodes.

• Reported the first experimental observation of both steady-state and dynamic Burstein-Moss effects in GaAs by using wavelength-resolved few-cycle pump-probe reflectometry.

6.3 Future Work

In this dissertation research, especially the diffusion-drift theoretical model presented in Chapters 3 and 4, has proven the great effectiveness and huge potential in studying ultrafast optical properties of GaAs devices. With the successful experience from these cases, it is reasonable to expect an extension of this research into other important photonic materials and/or devices, for example some novel two-dimensional (2D) materials and metamaterials, where the current theoretical and experimental methods can offer similar comprehensive analysis of various ultrafast processes happening inside the materials.

Meanwhile, the transient dispersion study presented in Chapter 5 is so far a preliminary-stage work, and future works are expected to be carried out. For instance, $p$-type semiconductor samples can be involved into the Burstein-Moss effect investigation; more samples with even higher doping concentrations can be tested to reveal the band gap narrowing effect, and the interplay between the BM shift and the band gap narrowing.
Over all, it is hoped that the theoretical and experimental approaches outlined in this dissertation will act as a foundation for a wide range of future study and applications.
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Appendix A: MATLAB Codes for Gradient Doping Model

A.1 Numerical Solution to Photoelectron Concentration \(n(x,t)\) in the AL

```matlab
% This code numerically calculates e concentration in AL and e injection from AL into BBR (e.g. Fig 3.2 & 3.3)
clear; clc;
%% device parameters (for simulation only)
d = 2;  % thickness of AL
alpha = 0.8553;  % absorption coeff. in AL (per um)
D = 0.2e10;  % diffusion coeff. in AL (um^2 per second)
A = 5;  % gradient doping coeff. (per um)
n0 = alpha/(1-exp(-alpha*d));

% e concentration in AL n(x,t) and e population in AL N_AL(t)
% set proper step sizes for t and x to guarantee stable solutions achievable
step_t = 0.02e-12;  % in unit of s
step_x = 0.01;  % in unit of um

t = 0:step_t:200e-12;  % range of t
x = 0:step_x:2+step_x;  % range of x, including one imaginary point after the boundary @x=2um

n = zeros(length(x),length(t));  % e concentration in AL
N_AL = zeros(1,length(t));  % e population in AL
n(:,1) = n0*exp(-alpha.*x);  % initial condition
n(1,:) = 0;  % BC @x=0
```
for j = 1:length(t)-1 % loop of time
    for i = 2:length(x)-1 % loop of x
        n(i,j+1) = n(i,j) + D*step_t/step_x^2*(n(i+1,j) -2*n(i,j)+n(i-1,j)) +...
        A*D*step_t/step_x*(n(i+1,j)-n(i,j));
    end
    n(i+1,j+1) = n(i-1,j+1); % imaginary point after boundary to guarantee the BC @x=2
    N_AL(j) = trapz(x,n(:,j));
end
N_AL(end) = trapz(x,n(:,end));

%% plot
% plot n(x,t)-- e concentration in AL with several selected time delays
fplot(@(x) n0*exp(-alpha*x),'-k','LineWidth',1) % initial curve when t=0
hold on;
k = [51 501 2501 10001]; % when t=1 10 50 200 respectively
p1 = plot(x,n(:,k),'LineWidth',1.2,'MarkerSize',5,'MarkerIndices',1:10:length(x));
xlim([0 2]);
ylim([0 1.06]);
xlabel('x (\mum)');
ylabel('n(x,t) (\mum^{-1})');
legend('t=0','','t=1 ps','t=10 ps','t=50 ps','t=200 ps');
legend('FontSize',20,'Location','northeast');
legend('boxoff');
set(gca,'YTick',(0:0.2:1.06))
set(gca,'XTick',(0:0.5:2))
set(gca,'FontSize',22)
p1(1).Color = [0.8500 0.3250 0.0980];
p1(2).Color = [0.3010 0.7450 0.9330];
p1(3).Color = [1.00,0.07,0.65];
p1(4).Color = [0.9290 0.6940 0.1250];

% plot N_I(t)-- e injection of AL into BBR
A.2 Impact of the Gradient Doping Coefficient $A$ on Photoelectron Population $N(t)$ in the BBR

```matlab
figure;
plot(t*1e12,1-N_AL)
```

%% This code shows the impact of the gradient doping coeff. $A$ on $e$ population accumulated in BBR (e.g. Fig 3.4)
clear; clc;

%% Adjustable parameters
$A = [0\ 1.15\ 3\ 5]$; % gradient doping coeff.
$D = 0.2e10$; % diffusion coeff. in AL
$c1 = 1$; % weight of fast decay, single decay mechanism is used
$\tau_1 = 200e-12$; % lifetime of fast decay (s)

%% $e$ concentration in AL $n(x,t)$ & $e$ population in AL $N_{AL}(t)$
d = 2; % thickness of AL
$\alpha = 0.8553$; % absorption coeff. in AL
$n0 = \alpha/(1-exp(-\alpha*d))$;

step_t = 0.002e-12; % step size of $t$
step_x = 0.01; % step size of $x$

t = 0:step_t:1500*1e-12; % range of $t$
x = 0:step_x:2+step_x; % range of $x$, including one imaginary point after the boundary @x=2

$n = zeros(length(x),length(t))$; % $e$ concentration in AL
$N_{AL} = zeros(length(A),length(t))$; % $e$ population in AL

$n(:,1) = n0*exp(-\alpha.*x)$; % initial condition
$n(1,:) = 0$; % BC @x=0
for m = 1:length(A) % loop for A
    for j = 1:length(t)-1 % loop of time
        for i = 2:length(x)-1 % loop of x
            n(i,j+1) = n(i,j) + D*step_t/step_x^2*(n(i+1,j)-2*n(i,j)+n(i-1,j)) + ... 
            A(m)*D*step_t/step_x*(n(i+1,j)-n(i,j));
        end
        n(length(x),j+1) = n(length(x)-2,j+1); % imaginary point after boundary to guarantee 
        the derivative BC @x=2
        N_AL(m,j) = trapz(x,n(:,j));
    end
    N_AL(m,j+1) = trapz(x,n(:,j+1));
end

%% e population in BBR N(t)
gamma1 = 1/tau1; % decay rates
N = zeros(length(A),length(t)); % e population in BBR
for m = 1:length(A)
    for k = 2:length(t)
        N(m,k) = N(m,k-1) + N_AL(m,k-1) - N_AL(m,k) - gamma1*step_t*N(m,k-1);
    end
    p2(m) = plot(t*1e12,N(m,:), 'LineWidth',1.2, 
        'MarkerSize',5,'MarkerIndices',10000:25000:length(t));
    hold on;
end
p2(1).Color = 'black';
p2(2).Color = 'red';
p2(3).Color = [0.4660 0.6740 0.1880];
p2(4).Color = [0 0.4470 0.7410];
xlim([-5 t(end)*1e12]);
xlabel(‘t (ps)’);
ylabel(‘N(t)’);
set(p2(1),’LineWidth’,1.5,’LineStyle’,’--’,’Color’,[0 0 0]);
set(p2(2),’Marker’,’o’,’Color’,[1 0 0]);
set(p2(3),’Marker’,’+’,’Color’,[0.466 0.674 0.188]);
set(p2(4),’Marker’,’diamond’,’Color’,[0 0.447 0.741]);

A.3 Theory-Experiment Comparison and Curve Fitting

% This code provides theory-experiment comparisons and curve fitting (e.g. Fig 3.5)
clear; clc;

% Load experimental data
x = readmatrix(’gradientoverallexpdata.xls’, ’Range’, ’D1:D5689’); % gradient sample MOCVD
y = readmatrix(’gradientoverallexpdata.xls’, ’Range’, ’E1:E5689’);

x_adj = x*2; % convert time scale

p1 = plot(x_adj,y/max(y),’-r’,’LineWidth’,1); % plot the experimental data
hold on;

% Adjustable parameters for curve fitting
A = 1.15; % gradient doping coeff.
D = 1.6e10; % diffusion coeff. in AL
c1 = 0.942; % weight of fast decay
c2 = 1-c1; % weight of slow decay
tau1 = 1.3e-12; % lifetime of fast decay
tau2 = 80e-12; % lifetime of slow decay
%% e concentration in AL \( n(x,t) \) & e population in AL \( N_{AL}(t) \)
d = 2; % thickness of AL
alpha = 0.8553; % absorption coeff. in AL
n0 = alpha/(1-exp(-alpha*d));

step_t = 0.002e-12; % step size of t
step_x = 0.01; % step size of x

t = 0:step_t:x_adj(end)*1e-12; % range of t
x = 0:step_x:2+step_x; % range of x, including the imaginary point after the boundary @x=2

n = zeros(length(x),length(t)); % e concentration in AL
N_AL = zeros(1,length(t)); % e population in AL
n(:,1) = n0*exp(-alpha.*x); % initial condition
n(1,:) = 0; % BC @x=0

for j = 1:length(t)-1 % loop of time
    for i = 2:length(x)-1 % loop of x
        n(i,j+1) = n(i,j) + D*step_t/(step_x^2)*(n(i+1,j) -2*n(i,j)+n(i-1,j)) + ...
        A*D*step_t/step_x*(n(i+1,j)-n(i,j));
    end

    n(length(x),j+1) = n(length(x)-2,j+1); % imaginary point after boundary to guarantee the derivative BC @x=2
    N_AL(j) = trapz(x,n(:,j));
end
N_AL(end) = trapz(x,n(:,end));

%% e population in BBR \( N(t) \)
% bi-exponential decay mechanism is used
gamma1 = 1/tau1; % decay rates
\[
\begin{align*}
gamma_2 &= \frac{1}{\tau_2}; \\
N &= \text{zeros}(1, \text{length}(t)); & \text{total e population in BBR} \\
N_1 &= \text{zeros}(1, \text{length}(t)); & \text{the group of e with fast decay rate} \\
N_2 &= \text{zeros}(1, \text{length}(t)); & \text{the group of e with slow decay rate} \\
\text{for } k = 2: \text{length}(t) & \\
N_1(k) &= N_1(k-1) + N_{\text{AL}}(k-1) - N_{\text{AL}}(k) - \gamma_1 \cdot \text{step}_t \times N_1(k-1); \\
N_2(k) &= N_2(k-1) + N_{\text{AL}}(k-1) - N_{\text{AL}}(k) - \gamma_2 \cdot \text{step}_t \times N_2(k-1); \\
N(k) &= c_1 \times N_1(k) + c_2 \times N_2(k); \\
\text{end} \\
p2 &= \text{plot}(t \times 1e12, N/\max(N), \'-\', \text{LineWidth'}, 2); & \text{plot simulation result of } N(t) \\
p2.\text{Color} = [0 \ 0.4470 \ 0.7410]; \\
xlim([-18 \ t(\text{end}) \times 1e12]); \\
ylim([-0.1 \ 1.02]); \\
xlabel(\text{'t (ps)'}) \\
ylabel(\text{'\Delta R(t) (arb. units)'}) \\
\text{legend(\text{'Experimental data'},'Numerical simulation'}) \\
\text{legend(\text{'FontSize'}, 12, \text{Location'}, 'northeast')} \\
\text{legend(\text{'boxoff'})} \\
\text{hold off} \\
\text{set(gca, 'FontSize', 12)} \\
\text{% insert an inset of doping profile figure} \\
\text{axes(\text{'pos'}, [.32 .42 .58 .51])} \\
\text{imshow('gradient.png')} & \text{for MOCVD2 sample}
\end{align*}
\]
A.4 Analytical Solution to Photoelectron Concentration $n(x, t)$ in the AL

This code calculates e concentration in AL & e population in BBR based on the analytical solution with the small doping coefficient assumption (e.g. marker-only curves in Fig 3.6)

clear; clc;
d = 2; % thickness of AL
alpha = 0.8553; % absorption coeff. in AL
D = 0.2e10; % diffusion coeff. in AL
A = 0.5; % gradient doping coeff.
r = A/2; % gamma coeff. defined in Eq (3.9)

n0 = alpha/(1-exp(-alpha*d));

x = 0:0.01:2;
t = [1 10 50 100]*1e-12; % several specific time delay
n_t0 = n0 * exp(-alpha*x); % n(x,t=0), the initial condition

num_term = 100; % number of terms included in the summation in Eq (3.15)
n = zeros(length(x),length(t)); % e concentration in AL -- n(x,t)

for i = 1:length(x) % loop of x
    for j = 1:length(t) % loop of t values
        for index = 1:100 % loop of terms added into the summation
            a = (2*index-1) * pi/2/d; % a_i coeff. defined in Eq (3.13)
b = (a + exp(-(alpha-r)*d)*(alpha-r)*(-1)^index)/ d / ((alpha-r)^2 + a^2); % b_i coeff. defined in Eq (3.14)

beta = A^2/4+a^2; % beta coeffi. defined in Eq (3.9)

result = 2*n0*b*sin(a*x(i)) * exp(-r*x(i)) * exp(-beta*D*t(j)); % a single term of the summation of n(x,t) according to Eq (3.8)

n(i,j) = n(i,j) + result;

end
end

plot(x,n)
xlabel('x (\mu m)', 'FontSize',14);
ylabel('n(x,t) (\mu m^{-3})', 'FontSize',14);
legend('t=1 ps','t=10 ps','t=50 ps','t=100 ps');
legend('FontSize',12,'Location','northeast');
legend('boxoff');