Ultrafast charge transfer at GaAs/P3HT as a model system for hybrid organic-inorganic heterointerfaces

Majid Panahandeh Fard

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for the degree of Doctor of Philosophy

Abstract

Polymer bulk heterojunction solar cells are being widely considered for the development of the future generation of photovoltaic devices, which aim at providing high conversion efficiencies at low cost. These promising devices have been conventionally constructed by blending an organic conjugated polymer donor and a fullerene acceptor. The polymer solar cells have demonstrated a few advantages over their inorganic counterparts: simple and easy processability, high throughput fabrication, and compatibility with low-temperature processes. However, few intrinsic factors are still limiting the overall performance of polymer solar cells, particularly the low carrier mobility, the weak absorbance of thin films and the poor chemical stability. To overcome some of these issues while retaining low production costs and scalability, research in polymer photovoltaics is about to converge towards organic-inorganic hybrid architectures where heterojunction is formed between inorganic acceptors from group IV, III-V, IV-VI and organic compounds (small molecules, oligomers, polymers).

Most recently, hybrid photovoltaic based on Group III-V and organic compounds were reported in the literature, which seem rather promising for the achievement of high power conversion efficiencies in a near future. The mainstream III-V compounds have demonstrated several advantages for photovoltaic application. The main advantage in the use of such “traditional” semiconductors lies in their high carrier mobility, optimal staggered band alignment relative to the most common conjugated polymers, and the possibility to finely engineer their band structure and density of states through the conventional methods of alloying, doping, and heterostructure formation.

Despite substantial progress in hybrid polymer/III-V photovoltaic devices, the primary processes of exciton dissociation and charge transfer at the heterointerface of these unconventional systems, and the coupling between the excitonic species of the polymer and

the extended states of the inorganic semiconductor are completely unknown. The understanding of these fundamental issues in polymer/III-V composites will provide a general tool for the engineering of hybrid architectures, with high potential to impact the entire organic photovoltaic research field.

In this thesis, we address some of the above issues in a prototype hybrid system based on *n*-type GaAs and a typical hole transporting conjugated polymer regioregular Poly(3-hexylthiophene-2,5-diyl) (rr-P3HT). Hybrid GaAs/P3HT heterointerface is a very interesting localized/delocalized system where conjugated polymer with discrete and localized orbitals meets inorganic semiconductor with continuous bands of delocalized quantum states. We investigate the interactions of the polymer with GaAs surfaces using model systems, P3HT/GaAs (111B and 110). We approach this problem from both theoretical and experimental points of view by using density functional theory (DFT) calculations and combining various spectroscopy measurements.

Our goal is to address some issues of fundamental scientific interest regarding charge transfer processes in organic-inorganic heterointerfaces. In this dissertation, addition to charge photogeneration and charge transfer study of hybrid GaAs/P3HT heterointerfaces, long-lived photoexcitations in pristine P3HT film, transient reflectance spectra of GaAs, the effect of polarity of GaAs surface on charge transfer, and correlation between transient absorption and reflectance spectroscopy are also studied. Our ultrafast spectroscopy provides strong evidence of ambipolar charge transfer of electrons and holes across the GaAs/P3HT heterointerface, where signatures of charge transfer are manifested by presence of long-lived photoinduced absorption and photobleaching by exciting either above or below the polymer optical gap. We demonstrate that ambipolar charge transfer can be regarded as an interesting new concept to optimize photovoltaic power conversion efficiency of hybrid organic-inorganic devices.

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Chapter 1

General Introduction

1.1 Introduction

First and second generation solar cells are based on cells made of inorganic semiconductors such as crystalline and amorphous silicon (Si), III-V compounds, Cadmium Telluride (CdTe), and copper indium gallium selenide (CIGS). The polymer solar cells are also being widely considered for the development of the future (third) generation solar cells, which aim at providing high power conversion efficiency (PCE) at low fabrication cost.¹⁻⁸ The active region of polymer solar cells typically comprises of a conjugated polymer donor intimately blended with a fullerene electron acceptor at the nanometer scale.

Nowadays energy has become a crucial issue all over the world. Scientists are trying to increase the efficiency of the solar cells so that they can be considered as serious alternative to the fossil fuels. In recent years significant efforts have been made towards commercializing polymer solar cells with the creation of start-up companies such as Solaronix, Heliotech, and Mitsubishi Chemicals. Due to the extensive research in solar cell architectures and the development of a new class of low bandgap polymers with better spectral overlap with the solar irradiance, polymer solar cells are now crossed the 10% fence of PCE.⁹⁻¹² Although, PCE of dye-sensitized and polymer solar cells are still lower than conventional semiconducting PVs, on contrary both can be produced at low-cost.¹³⁻¹⁴ However, few intrinsic factors are still limiting the overall

performance of polymer solar cells, particularly the low carrier mobility, the weak absorbance of thin films and the poor chemical stability.¹⁵

To overcome some of these issues while retaining low cost fabrication of devices on large-area substrates, research in polymer PV has turned to organic-inorganic hybrid solar cells (HSCs), where conjugated polymer donor are mixed with nanostructured inorganic acceptors such as ZnO¹⁶, TiO₂¹⁷, PbS¹⁸, and CdSe.¹⁹⁻²¹ More recently, replacement of fullerene acceptor with nanostructure inorganic semiconductors (e.g. Metal oxide nanowires or nanotubes) have been widely investigated to improve charge carrier transport/collection, in view of reducing the cost of acceptor materials and increasing device stability in self-encapsulating “inverted” device architectures.²²⁻²³

Within this context, it appears that the optimal strategies for organic PVs, are about to converge towards organic/inorganic hybrid architectures in which low-dimensional, nanostructured inorganic materials are blended or somehow integrated with organic semiconductors to improve the key limiting factors of device performance, *i.e.* light absorption, charge generation and charge transport while preserving the advantages of low-cost and scalability of fabrication. A variety of inorganic quantum dot sensitizers have been studied over the past two decades, to increase light absorption in the thin active layer.²⁴⁻²⁵ In particular electron acceptor nanocrystals with suitable energetics for charge transfer such as CdS²⁶, CdSe²⁷⁻²⁷, PbS²⁹, PbSe³⁰ and metal oxides (ZnO^{23, 31} and TiO₂³² etc.) have been considered, while more choices are available for the conducting polymers. Moreover, by introducing several strategies for the large-scale, low production costs of inorganic nanowires and quantum dots, hybrid photovoltaic aims at providing low production cost solar cells in a near future. Nevertheless, unimpressive PCEs were demonstrated so far in such systems, mainly limited by the reduced intermixing of the donor-acceptor components and by the low efficiency of charge transfer and charge

dissociation at the organic-inorganic interfaces. Figure 1-1 classified the different types of hybrid organic-inorganic PVs.²¹

Figure 1-1. Hybrid organic-inorganic heterojunction based on groups IV, III-V, metal oxide, and group IV-VI and organic semiconductors including small molecules and conjugated polymers (from Ref. [21]).²¹

1.2 Hybrid organic-inorganic flat heterojunction photovoltaics

Hybrid organic-inorganic solar cell follows second generation inorganic solar cells, such as CdTe³⁸ and amorphous silicon (a-Si)³⁹ and first generation crystalline semiconductor⁴⁰⁻⁴¹ solar cells. The optical properties of the first hybrid organic-inorganic heterojunction have been investigated by the MacDiarmid group⁴² in 1978. By measuring the quantum efficiency of the grown *p*-type polyacetylene polymer on *n*-type ZnS substrate, they demonstrated its contribution to the photoconversion process. One of the pioneer studies on the organic-inorganic solar cell demonstrated very promising PCE between 1 and 5% for Si/poly-(CH₃)Si-cyclooctatetraene bilayer.⁴³ In these devices, polymer layer plays a dual role of charge separation interface and hole-collecting layer. The a-Si has been widely considered for PV applications because it is inexpensive and can be deposited as a thin film over flexible metal substrates. The first heterojunction between conjugated polymers and a-Si was reported by

McGehee et al.⁴⁴ They interestingly found that excitonic effects of polymers show a significant contribution in photoconversion processes. Therefore, they proposed two mechanisms of charge generation at the a-Si/polymer interface, (i) exciton diffusion through polymer film towards a-Si/polymer interface and subsequently excitons dissociation at the a-Si/polymer interface followed by an electron injection to the a-Si and (ii) Förster like energy transfer from polymer to a-Si followed by backward hole transfer in the polymer.^{21, 43}

Nevertheless, thin film hybrid a-Si/polymer PVs show very low PCE. Later considerable enhancement in PCE was attained by the replacement of a-Si with crystalline *n*-Si, which resulted in a significant increase in PCE. The PCE up to 2.46% were reported for *n*-Si/polymer PVs.⁴⁵ This enhancement was attributed to the photon absorption in the near infrared solar spectrum, the higher carrier mobility of crystalline *n*-Si, and the reduction of interfacial recombination in the crystalline Si.^{21, 46-47}

Organic small molecules are also widely used to form the heterojunctions with inorganic semiconductors. Small molecules demonstrated several advantages as compared to the polymer counterparts such as better environmental stability and high molecular ordering. In addition, charge carrier mobility in the crystal phase is comparable or even higher than polythiophene-based polymers.⁴⁸ Among the organic small molecules, phthalocyanines (Pc), porphyrins, and their derivatives have been widely used to form the heterojunction with inorganic semiconductors, in particular with Si. Several studies have been demonstrated that phthalocyanines and porphyrins have excellent photoconductivity that allows using them in photodetectors and hybrid PVs. So far, *p*-type Si/copper(II) phthalocyanine (CuPc)³² Si/zinc (II) phthalocyanine (ZnPc),³³⁻³⁴ *n*-type Si/magnesium phthalocyanine (MgPc),³⁵ *p*-type Si/nickel phthalocyanine (NiPc),³⁶ *n*-type GaAs/CuPc,³⁷ and *n*-type Si/tetraphenyl porphyrin (TTP) hybrid solar cells with promising PCE in the range of 1-3.5% have been reported in the

literature.^{21, 33} The other advantage of phthalocyanines is their excellent chemical stability. However, the film deposition of phthalocyanines and its compounds requires vacuum sublimation due to their low solubility in organic solvents and water. This is the major bottleneck to utilize them for the low production cost HSCs technology.

1.3 Background and motivation

More recently, organic-inorganic hybrid solar cells based on III-V compounds and thiophene, oligomers polymers were reported in the literature, which seems rather promising for the achievement of high PCE in near future.⁴⁹⁻⁵² The main advantage of using III-V compounds lies in their high carrier mobility, optimal staggered band alignment relative to the most common conjugated polymers, and the possibility to engineer their band structure and density of states through the conventional methods of alloying, doping, heterostructure formation, and the availability of III-V low-dimensional structures at low production costs.^{15, 53-55} Together, these properties of III-V compounds make them an ideal candidate for hybrid PVs application and pay a way towards realizing high PCE devices in a near future.

Horowitz and Garnier for the first time reported poly(2-methylthiophene) (PMeT)/GaAs bilayer heterojunction in 1986.⁵² In 2002, Garnier et al.⁵¹ reported an almost identical result for *n*-type GaAs/quaterthiophene/Au flat heterojunction solar cell with ~1% PCE. In this bilayer, obtained experimental results were difficult to explain because *n*-type GaAs/Au heterojunction is already a typical Schottky barrier solar cell. In 2004, this group reported 4.2% PCE for the similar device by replacing polythiophene with thermally evaporated octylthiophene (8T).⁵⁰ In this study, they prepared two types of 8T films, microcrystalline 8T films with a grain size of 1-2 μm and nanocrystalline 8T film with a grain size of 0.1 μm . The device fabricated with microcrystalline 8T exhibited much higher PCE than nanocrystalline 8T films. The PCE

enhancement was attributed to the precise alignment of micro grains in the microcrystalline film, which improves the exciton diffusion length.

More recently, Liang Yan and co-workers⁵⁶ studied flat heterojunction of polymer/*n*-type GaAs hybrid solar cells. They used the model conjugated polymer systems (poly (9,9-dioctyl-fluorene-alt-benzothiadiazole) (F8BT), poly(benzodithiophene-dithienyldifluoro-benzothiadiazole) (PBnDTDTffBT), poly(naphthalenedithiophene, dithienyldifluoro-benzothiadiazole) (PNDT-DTffBT) and regioregular Poly (3-hexylthiophene-2,5-diyl) (rr-P3HT)) for this purpose, and established the correlation between energetics and photovoltaic properties (for the chemical structures of organic compounds mentioned in this thesis, see appendix A). They interestingly found that polymer/GaAs flat heterojunction is not a typical type II heterojunction. Their results show that GaAs forms a Schottky barrier with anode electrode while the conducting polymer acts as a hole-transporting layer. They reported PCE as high as 2.31% for GaAs/P3HT flat heterojunction.⁵⁶ In another work, this group showed that the PCE of GaAs/polymer solar cells are noticeably affected by the surface orientation of GaAs; they reported PCE as high as 4.2% for rr-P3HT/GaAs (111)B bilayer solar cell.⁵⁷

Thanks to the advances in the high-yield fabrication of low-dimensional structures of conventional group III-V semiconductors, a few demonstrations of hybrid organic-inorganic PV devices with appreciable PCE have recently appeared in the literature.^{26, 58-60} These nanostructures are used to create largest interfacial areas in contact with the polymer materials and, at the same time, a high mobility electron transport pathway. Due to the excitonic character of organic counterparts and charge separation at the interface, application of nanostructures in hybrid PV devices increases the interfacial interface with polymer and subsequently improves the photocurrent.

The quantum confinement character of nanostructured semiconductor allows tunable bandgap and lead to the enhancement of the light absorption.²⁵ Given the flexibility offered by III-V compound semiconductors for bandgap and density of state engineering through the synthesis of hetero- or low-dimensional structures, this opens up an unprecedented opportunity for the design and characterization of organic-inorganic interfaces for a better understanding of charge transfer and carrier dynamics in hybrid systems. Few demonstrations of hybrid organic/III-V nanowires/nanopillars photovoltaic devices with appreciable PCE have recently appeared in the literature. The earliest attempts to incorporate InP nanowires in hybrid solar cells yielded typical PCE approaches 1%.⁶³ New types of GaAs/P3HT bulk heterojunctions in which GaAs nanowires blended with the polymer demonstrated efficiency up to 2.36% (the TiO_x shell reduces interfacial recombination by the passivating nanowire surface states and further improving photovoltaic performance).⁵³ Recently, a remarkable 5.8%⁶¹ and 9.2%⁶² PCE were demonstrated for GaAs NW/PEDOT:PSS HSCs in which vertically aligned *n*-type GaAs nanowire arrays provide large interfacial area in contact with polymer and form a highly interpenetrating heterojunctions.

Nevertheless, PCE has demonstrated this far in such hybrid organic-mainstream III-V systems remain lower than conventional organic bulk heterojunctions with fullerene acceptors, mainly limited by the reduced intermixing of the donor-acceptor components and by the low efficiency of charge transfer and charge dissociation at the organic-inorganic interfaces. In order to optimize the performance of hybrid organic-inorganic photovoltaic devices, the detailed understanding of the primary charge generation and charge transfer at the organic-inorganic interface and the subsequent charge transport and recombination processes are required. The actual viability of this approach will depend on developing a general theoretical and experimental framework to rationally design and characterize the fundamental photoexcitation

in these hybrid systems and optimize device performance. Moreover, some technological challenges such as developing scalable methods to produce III-V functional nanostructures in large quantities with relatively low-cost will be thus essential to validate this approach. Therefore, these recent works on hybrid polymer/III-V photovoltaic devices with high PCE opens up new opportunities for tailoring the optoelectronic properties of PV materials and subsequently raises fundamental questions related to the carrier photogeneration mechanisms, and ultrafast dynamics, relaxation paths, and charge transfer states at organic-inorganic heterointerfaces with different degrees of charge delocalization.

1.4 Objectives

The performance of hybrid photovoltaic devices depends on the charge transfer and recombination at the interface of organic and inorganic semiconductors. Therefore, controlling interfacial charge separation and recombination are the most crucial factors for boosting the photocurrents in hybrid photovoltaic devices.⁵³ Despite the demonstration of relatively high performance hybrid polymer/III-V photovoltaic devices, the primary processes of the charge transfer and the charge separation at the heterointerfaces of these unconventional systems, and the coupling between the excitonic species of the polymer and the extended states of the inorganic semiconductor are completely unexplored. The current charge transfer studies of GaAs/polymer-oligomers provide useful insights into the interfacial processes of these composites and highlight the effectiveness of the use of organic/III-V bulk heterojunctions for hybrid photovoltaic devices. However, the current understanding of primary processes of the interfacial charge transfer and charge separation at the interface of these unconventional systems like GaAs/P3HT is relatively limited.⁶⁴⁻⁶⁸ Based on above perspectives, a proper theoretical description of the charge distribution and its dynamics at such interfaces will be the Holy Grail to improve the PCE of these unconventional hybrid solar cells from the fundamental

perspective. Here we conduct fundamental studies of the processes of charge carrier generation and transfer in the prototype rr-P3HT/GaAs organic-inorganic interfaces, as a model system for engineering of hybrid organic-inorganic heterointerfaces. This study will offer a completely novel and highly configurable toolbox to understand and control the critical factors for boosting the photocurrents in hybrid photovoltaic devices by investigating elementary processes at ultrashort time scales (~ 100 fs) after photoexcitation. For this purpose, the photophysical properties of hybrid GaAs/P3HT heterointerface have been investigated using a combination of steady state and ultrafast spectroscopy techniques, including photoluminescence, transient absorption (reflectance) spectroscopy and steady state photoinduced absorption (PIA) measurement. In addition to the properties of GaAs/P3HT heterointerface, we also address the most important properties of the two components, GaAs and P3HT.

1.5 Organization of this thesis

This thesis will tackle fundamental issues such as charge generation and charge transfer in hybrid GaAs/P3HT organic-inorganic heterointerfaces. We have studied charge transfer at the interface of a prototypical photovoltaic *n*-type GaAs (111)B/P3HT flat heterojunction using DFT calculations and ultrafast spectroscopy. We have provided clear evidence that both electron and hole transfer processes take place in GaAs/P3HT heterointerface, leading to generation of long-lived mobile polaron and photoinduced absorption upon creation of hybrid interfacial states.

In addition to photoinduced transient absorption measurements, we have investigated the formation of polaron band in GaAs/P3HT heterointerfaces using steady state PIA spectroscopy. The PIA spectrum of GaAs/P3HT bilayer exhibits clear signatures of polarons formation, which provides further evidence of charge transfer at GaAs/P3HT heterointerfaces.

Our works extend to find the effect of polarity of the GaAs surface on charge redistribution in *n*-type GaAs/P3HT organic-inorganic hybrid systems. We have demonstrated that surface orientation of GaAs affects the electronic orbital and charge redistribution properties: electrons are efficiently transferred to GaAs substrates, implying the formation of hybrid delocalized states at the interface.

This dissertation is organized into seven chapters. It consists of two introductory chapters; one review chapter on the emerging class of hybrid solar cells based on organic compounds and inorganic semiconductors from Group IV and III-V, and the other one is a review of principles of photoinduced absorption spectroscopy, characterization techniques, and modelling principle, four chapters on the research result, and one summary chapter.

Chapter 1 provides a general introduction to organic and hybrid organic-inorganic PV devices. Particular attention has been given to the recent advances of hybrid solar cells based on the flat heterojunction between GaAs and conjugated polymers as well as nanostructures semiconductors and organic compounds.

Chapter 2 describes the experimental setup. In addition, the mathematical formalism of transient absorption (reflectance) is also discussed

Chapter 3 provides a general review to π -conjugated polymers including absorption and fluorescence in π -conjugated polymers. Following the general introduction, we will investigate photophysical properties of pristine rr-P3HT. We will also study the long-lived photoexcitation in rr-P3HT/phenyl-C61-butyric acid methyl ester (PCBM) bulk heterojunction by steady state PIA spectroscopy. Polymer solar cells based on rr-P3HT/PCBM is one of the well-known donor-acceptor systems that has received much attention from PV community and has demonstrated PCE as high as 5%. This well-known donor-acceptor system continues to attract a large interest because it can be used as a model for both device performance optimization and

fundamentals studies of charge photogeneration. Therefore, the fundamental study of photoexcitation of P3HT/PCBM as a reference system will help to calibrate the interpretation of our experiments. This background information is given to lay the groundwork for understanding the experimental data that will be presented in later chapters 5 and 6.

Chapter 4 describes the fundamental properties of GaAs, including the energy band structure and a general description of the carrier relaxation in bulk GaAs. The various nonlinear carrier induced changes of the index refractive (absorption) are also presented. Subsequently, the experimental transient reflectance of GaAs is discussed. After studying photoinduced reflectance of GaAs and photoinduced absorption of P3HT, we turn our attention to the hybrid GaAs/P3HT heterointerfaces in the next chapters, which is the main objective of this dissertation.

Chapter 5 investigates photoinduced interfacial charge transfer dynamics between *n*-type GaAs (111)B substrate and P3HT by combining ultrafast spectroscopy measurements and DFT calculations. Transient absorption data were collected at various excitation energies clearly indicates the coexistence of electron and hole transfer taking place at the GaAs/P3HT interface. The signatures of interfacial charge transfer are manifested in transient absorption measurements by the formation of long-lived polaron and appearance of a new band that can be attributed to PIA of P3HT.

Chapter 6 presents an experimental study of energy band alignment and charge photogeneration at GaAs/P3HT heterointerfaces with different orientation and polarity of the GaAs surface. We show that both GaAs (110)/P3HT and GaAs (111)B/P3HT foster electron transfer from P3HT to GaAs. However, selective excitation of GaAs elucidated that hole injection from GaAs (111)B to P3HT induces long-lived ($\sim$ ns) PB and PIA, which is indeed absent in the case of GaAs (110).

Chapter 7 provides a summary of this research as well as an outlook for the future research works.

Chapter 2

Experimental Methods

We investigated interfacial charge transfer and exciton/polaron dynamics in pristine P3HT film, bulk GaAs, and hybrid GaAs/P3HT heterojunction, using a variety of techniques including linear absorption measurement, photoluminescence measurement, transient absorption (reflectance) measurement and steady state photoinduced absorption (PIA) spectroscopic techniques. Specifically, steady state PIA measurements will provide a complementary information compared to that of transient absorption measurement, such as the photogenerated polaron signal at hybrid GaAs/P3HT interfaces. Moreover, photoluminescence measurements will provide evidence of charge transfer through the yield and the rate of radiative emission.

2.1 Principle of photoinduced absorption spectroscopy

Ultrafast transient absorption (reflectance) spectroscopy is a technique developed to study dynamics and evolution of excited states on the sub-picosecond timescales in different materials (i.e. inorganic semiconductors, organic compounds, and biological systems). This technique is a non-contact measurement for carriers that can be generated in the absence of an external electric field.⁶⁹⁻⁷² Moreover; this technique has widely been used for studying the highly resistive materials since it is difficult to inject carriers from metal contacts into the materials.

In this technique, an ultra-short (~ 100 fs) pump pulse is used to photoexcite the material and a low-intensity, ultra-short white probe pulse is used to monitor absorption changes in the material, specifically kinetics of excited states after excitations. By delaying probe pulse respected to pump pulse we can measure the evolution of photogenerated carriers within different delay times from a few femtoseconds (fs) to a few nanoseconds (see Figure 2-1).⁷³ Typically, photoexcited carriers can go through different relaxation pathways before returning to the initial thermal equilibrium states. In inorganic semiconductors, the timescales for transient processes such as carrier-carrier scattering, intervalley scattering, and carrier-optical phonon scattering are usually in the order of few to hundreds of femtoseconds, whereas the slower optical processes such as carrier diffusion and inter-sub-band scattering take place within one picosecond or less. Other transient processes such as carrier-acoustic phonon scattering, hot carrier-phonon interaction and carrier recombination, typically takes place at longer timescale, 10 to 100 ps or even more.⁷⁴⁻⁷⁵ However, due to the typical strong electron-phonon coupling in the conjugated polymer, photon absorption in these systems will lead to the formation of self-trapped charges (polaron). The appearance of polaron initiates new sub-

gap electronic states that give rise to photoinduced transition with redistribution of the oscillator strength.

Charged photoexcitations in conjugated polymers can be investigated by pump-probe techniques, either by femtosecond transient absorption or by steady state PIA spectroscopy. The principles of photoinduced measurements can be illustrated by a simplified two excited-level system in Figure 2-1. Level 2 is the electronic state formed upon photoexcitation of the transition from the ground state (level 1) to level 3, with a characteristic time τ . By monitoring the transmittance of such system following photoexcitation, one would observe the emergence of a new absorption feature (2 $\rightarrow$ 3), the PIA within characteristic time τ . The normalized transmission change is proportional to the population of nonlinear photoexcitations and defined as:

$$\frac{\Delta T}{T} = -\frac{T^{on} - T^{off}}{T^{off}} = \Delta\alpha \quad (2-1)$$

where T^{on} is the transmittance of the probe light when the pump pulse is on and T^{off} is the transmittance of the probe light when the pump is off. As shown in Figure 2-1, the negative transient absorption signals indicate a decrease in the transmitted probe light originating from ground-state bleaching, while positive signals indicate an increase in the transmitted probe and originating from polaron absorption or exciton absorption from the first excited states towards higher excited states.⁷⁶

Figure 2-1. Schematic of the photoinduced absorption (PIA) process in a simplified two excited-level system. Ultrafast short pulse laser hits the sample and creates the excited states instantaneously. Subsequently, a weaker probe beam with the certain delay time (Δt) probes the excited states. The appearance of a sub-gap level (2) upon photoexcitation ($1 \rightarrow 3$) results in a PIA signal ($2 \rightarrow 3$) and in the bleaching of the ($1 \rightarrow 3$) transition. In the case of PIA, new states are created and absorption increase ($\Delta\alpha > 0$) whereas in the case of photobleaching decrease the ground-state optical transition ($\Delta\alpha < 0$).

Transient absorption measurements either in the transmission or reflection geometry can provide information on the dynamics of the nonlinear photoexcitation, which is fundamental to understanding the basic events taking place in the excited state. However, transient reflectance spectroscopy is more sensitive to the surface inhomogeneity.⁷⁷⁻⁷⁸ In addition, due to a limited penetration depth of the probe beam in the absorbing medium, the changes in the reflection signal due to the absorption modulation by the pump pulse are much smaller as compared to the change in transmission signal.⁷⁹⁻⁸⁰

2.2 Mathematical formalisms

When light hits an object, different phenomena may happen, resulting in some ratio of incident light is reflected, refracted, absorbed, or transmitted. If we assume that scattering is negligible, the total incident intensity is conserved as:

$$I_0 = I_r + I_t + I_a \quad (2-2)$$

where, I_0 , I_r , I_t , and I_a are incoming, reflected, transmitted and absorbed light intensity, respectively. In general, the transmission coefficient of a thin film with thickness d , refractive index of n , absorption coefficient α , and reflection coefficient R , is given by:

$$T = \frac{(1 - R^2) e^{-\alpha d}}{1 + R^2 e^{-2\alpha d} - 2R \cos 2\delta} \quad (2-3)$$

where $\delta = 2\pi n d / \lambda$ is the optical phase shifting per pass.

Similarly, the reflection coefficient R for an incident electromagnetic plane beam through a film with a thickness d and absorption coefficient α , may be described by

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (2-4)$$

where n and k are the real and imaginary parts of the complex refractive index ($\tilde{n} = n + ik$). k can be directly related to the absorption coefficient through:

$$k = \frac{\lambda}{4\pi} \alpha \quad (2-5)$$

In equation 2-3, we can safely neglect the interference effects since we assume that the thickness of the spin-cast film is much lower than the incident wavelength ($d \ll \lambda$). In addition, due to the roughness of the spin-cast film, the interference effects are expected to cancel out. Therefore, according to Lambert-Beer law the transmission of the probe light can be rewritten as:

$$I_T = I_0(1 - R)^2 e^{-\alpha d} \quad (2-6)$$

As a first approximation, we assume $R \ll 1$ then $(1-R)^2 \approx 1$, therefore, the transmitted probe light through the sample can be simplified as:

$$T = I_0 e^{-\alpha d} \quad (2-7)$$

Upon absorption of light, contributions of absorption bands due to the photoexcitation will alter absorption coefficient. Therefore,

$$\Delta T = I_0 e^{-\alpha d} (-\Delta \alpha d) \equiv T(-\Delta \alpha d) \quad (2-8)$$

The absorption coefficient is defined as product of the population of photoexcitations and a cross section of those photoexcitation as:

$$\alpha(\omega) = n_e(\omega) \times \sigma(\omega) \quad (2-9)$$

The normalized differential change in transmission can be expressed as density of photoexcitation and their optical cross section:

$$\frac{\Delta T}{T} = -\Delta \alpha d \equiv \sigma n_e d \quad (2-10)$$

where σ is the optical cross section of the photoexcited species, and n_e is the density of photoexcitation. Equation 2-10 implies that in the case of very weak reflectance, modulation transmittance is dominated by the change in absorption coefficient.

In the above-mentioned derivation, we assumed there is a very weak reflection on the surface of the film that can be neglected. In addition, we assumed that the reflection coefficient is the same for the back and front sides of the sample. Now we consider that reflection on the surface of the film cannot be neglected. By neglecting the multiple reflections, the derivation of equation 2-6 with respect to modulation field F can be written as:

$$\frac{\partial I_T}{\partial F} = -I_0 e^{-\alpha d} \left[d(1 - R)^2 \frac{\partial \alpha}{\partial F} + 2(1 - R) \frac{\partial R}{\partial F} \right] \quad (2-11)$$

Dividing by the unperturbed intensity, we obtain

$$\frac{\Delta I_r}{I_r} = -\frac{\Delta T}{T} = d\Delta\alpha + \frac{2}{1-R}\Delta R \quad (2-12)$$

For normal incidence yields

$$-\frac{\Delta T}{T} = \left[2(n\Delta n + k\Delta k) - \left[\frac{k^2 + 1}{n} \right] \Delta n \right] + \frac{4\pi d}{\lambda} \Delta k \quad (2-13)$$

Therefore, the modulated of transmittance of a film can be expressed as:

$$-\frac{\Delta T}{T} = \left[\frac{2R}{(1-R)} \right] \left(\frac{\Delta R}{R} \right) + \frac{2d\omega}{c} \Delta k \quad (2-14)$$

If we assume there is a very weak reflection on the surface of the film, the first term can be neglected and equation (2-14) can be simplified as: ⁸¹

$$-\frac{\Delta T}{T} \approx \frac{2d\omega}{c} \Delta k \quad (2-15)$$

Carrier-induced optical effects cause small changes in reflection coefficient R . Therefore, modulated reflectance, ΔR , can be expressed in terms of the complex index of refraction. Since ΔR is very small, it can be linearly approximated in terms of Δn and Δk as:

$$\Delta R = \frac{\partial R}{\partial n} \Delta n + \frac{\partial R}{\partial k} \Delta k \quad (2-16)$$

By using the Fresnel equation for reflectance at normal incidence, the differential reflectivity is given by

$$\frac{\Delta R}{R} = A(n, k) \Delta n + B(n, k) \Delta k \quad (2-17)$$

where,

$$\begin{aligned}
 A(n, k) &= \frac{4(n^2 - k^2 - 1)}{\left[(n+1)^2 + k^2 \right] \left[(n-1)^2 + k^2 \right]} \\
 B(n, k) &= \frac{8nk}{\left[(n+1)^2 + k^2 \right] \left[(n-1)^2 + k^2 \right]}
 \end{aligned} \tag{2-18}$$

In general, the real and imaginary parts of the refractive index, Δn and Δk are connected through Kramers-Kronig relations.⁸²

$$\Delta n(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\omega' \Delta k(\omega')}{\omega'^2 - \omega^2} d\omega' \tag{2-19}$$

Since the extinction coefficient is directly proportional to the absorption coefficient, the change in the index of refraction, as a function of frequency, $\Delta n(\omega)$, can also be expressed in terms of the change in absorption, $\Delta \alpha(\omega)$:

$$\Delta n(\omega) = \frac{c}{\pi} \int_0^\infty \frac{\Delta \alpha(\omega')}{\omega'^2 - \omega^2} d\omega' \tag{2-20}$$

By using the Kramers-Kronig relations (2-18), one can obtain the change in reflectivity as a function of frequency in terms of the absorption as:

$$\frac{\Delta R(\omega)}{R} = A_R \frac{c}{\pi} \int_0^\infty \frac{\Delta \alpha(\omega')}{\omega'^2 - \omega^2} d\omega' + B_R \frac{c}{\omega} \Delta \alpha(\omega) \tag{2-21}$$

The relation between Δn and the $\Delta \alpha$ is very important for the interpretation of the differential reflectivity signal. If we assume the magnitude of n is much larger than k , in this case, $A(n, k) \gg B(n, k)$. In such instances, the photoinduced reflectance response is dominated by Δn rather than Δk , unlike photoinduced absorption which is dominated by Δk .^{81, 83} Therefore, in this case the modulated reflectance $\Delta R/R$ can be simplified as:

$$\frac{\Delta R(\omega)}{R} = \frac{4\Delta n}{n^2 - 1} \tag{2-22}$$

2.3 Materials and sample preparation

2.3.1 Sample preparation for photoinduced absorption spectroscopy

The commercial medium weight rr-P3HT (>95%) and PCBM were purchased from Rieke Metals and Nano-C respectively and both were used without any further purification. For the control experiments, rr-P3HT films were spun cast at 1500 rpm from chlorobenzene solution (4 mg/ml) in inert Argon atmosphere on the quartz substrate. The resulting thickness was 30 nm, as measured by atomic force microscopy (AFM). Solutions of P3HT/PCBM (1:1, 4 mg/mL) were prepared in chlorobenzene.

A single crystal *n*-type (Si-doping $\sim 2 \times 10^{18} \text{ cm}^{-3}$) GaAs(111)B substrate was cleaned by vacuum UV ozone plasma for 20 minutes and then chemically etched for 10 seconds with a diluted H_2SO_4 : H_2O (1:10) solution to expose the GaAs surface. In order to monitor the contribution of interfacial layer to the formation of differential reflectivity signal, we need to deposit a very thin and uniform film over the GaAs surface. To fabricate GaAs/P3HT bilayer samples, we spun cast rr-P3HT films at 1500 rpm on chemically etched, GaAs (111)B substrates in an inert Argon atmosphere. The resulting P3HT film thickness was 30 nm, as measured by atomic force microscopy. All the samples were annealed for 10 minutes at 150 °C in an inert atmosphere to remove residual solvent and enhance polymer crystallinity.

2.3.2 Sample preparation for ultraviolet photoelectron spectroscopy (UPS)

Ultraviolet photoelectron spectroscopy (UPS) technique was used to investigate the energy level alignments in GaAs/P3HT interfaces. In order to prepare samples for UPS measurement, *n*-type GaAs (111)B and (110) substrates were cleaned by UV vacuum ozone for 20 minutes and then chemically etched for 10 seconds with a diluted $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ (1:10) solution. To fabricate GaAs/P3HT bilayer samples, P3HT films were spun cast at 3000 rpm from chlorobenzene solution (4 mg/ml) in inert Argon atmosphere. The resulting polymer thickness

was measured 5-7 nm using AFM. The GaAs/P3HT bilayer samples were annealed for 10 minutes at elevated temperature (up to 150 °C) in an inert atmosphere to remove residual solvent and enhance polymer crystallinity. UPS measurements were performed under high vacuum with Al K α ($h\nu = 1486.7$ eV) and He I ($h\nu = 21.2$ eV) excitations.

2.4 Spectroscopic measurements

2.4.1 Linear absorption and morphology measurement

The absorption and reflectance spectra were recorded using a UV-VIS absorption spectrometer. The AFM image was collected in tapping mode under ambient condition using a commercial AFM (D3100V, Veeco Digital Instruments).

2.4.2 Photoluminescence measurement

Photoluminescence (PL) measurement provides information about yield and the rate of radiative emission. In particular, time-resolved photoluminescence (TR-PL) spectroscopy is a powerful technique to characterize exciton recombination and their relaxation pathways in semiconductor nanostructures and organic semiconductor. Measurements of the absolute PL intensity at steady state and its time dependence at ultra-short timescales are used to assess exciton dynamics at the hybrid heterointerfaces. We employed an OPA as the excitation source. The OPA was seeded by a Ti: sapphire regenerative amplifier (1 kHz; 800 nm fundamental wavelength; average power: 1W; pulse width: ~ 100 fs). The steady state PL was recorded by using a CCD (Acton Princeton Instrument PIXIS 400) coupled with a monochromator (Acton Research Corporation SpectaPro 2500i). Subsequently, TR-PL was measured by employing fast triggered streak camera (Optronis FTSU-1) coupled to a monochromator (Spectral Products RS-232) and a CCD (Pro Sensicam). To prevent bimolecular processes, the excitation

fluence was kept to a minimum below $80 \mu\text{J}/\text{cm}^2$ per pulse.⁸⁴⁻⁸⁶ The entire measurements were performed on samples which were placed in a cryostat under pressures down to $<10^{-3}$ Pa.

2.4.3 Steady state photoinduced absorption spectroscopy

The steady state PIA is a unique experimental technique that can provide information about the long-lived photoexcited species, such as localized and delocalized polarons. The PIA experimental setup is shown in Figure 2-2. PIA measurements were performed at low temperature (78 K) in a vacuum FTIR spectrometer (Bruker Vertex 80v) equipped with a liquid nitrogen cooled MCT detector and cryostat. A visible pump (green CW laser, $\lambda=532$ nm, $I=30$ mW/cm²) was used for photoexcitation. The pump beam is deflected by acousto-optic modulator synchronizing with FTIR to have the light on and light off scans. First, both the pump and probe beam overlap directly on the sample. Then, the pump-beam is blocked and probe beam pass through the sample and was detected using a suitable detector, *i.e.* Silicon detector (visible to Near-IR range), MCT detector (Mid-IR range), and InGaAs (near-IR range) detector. The 8000 “on” and “off” scans were averaged to achieve the desired signal-to-noise ratio. Transmittance spectra were recorded under photoexcitation T_{on} and without laser excitation T_{off} , alternately. The PIA spectra were then derived as $(\frac{\Delta T}{T} = \frac{T_{\text{pump}}^{\text{off}} - T_{\text{pump}}^{\text{on}}}{T_{\text{pump}}^{\text{off}}})$.

Figure 2-2. Broadband steady state photoinduced absorption setup.

2.4.4 Femtosecond pump-probe transient absorption spectroscopy

A home-built, femtosecond pump-probe transient absorption spectrometer was used for the characterization of polymer and inorganic semiconductors, where dynamics and evolution of excited states were monitored. Since excited state species are typically, short-lived we need short (~ 100 fs) duration pump and probe pulses to get the temporal evolution of excited-states. The schematic diagram of our home-built femtosecond pump-probe transient absorption spectrometer is shown in Figure 2-3. The setup is comprised of four main parts, which are (1) a white light generator, (2) optical parametric amplifier (OPA), (3) delay-stage, and (4) processing software. The optical parametric amplifier is a frequency converter, where the parametric amplification is a three waves mixing process in nonlinear crystals. In this process, high-energy optical wave (ω_p) exchanges energy between two lower energy waves with smaller frequencies ω_s and ω_i , called signal and idler, respectively. This process follows the energy conservation rule $\omega_p = \omega_s + \omega_i$. In this set-up, white light is generated first, and then a selected wavelength (according to our requirement) is amplified in the second stages.

The optical delay between the pump and probe pulses were controlled by a delay-stage, which allow us to monitor the temporal dynamics of our system.

We control our setup by LabVIEW program where, normalized transient reflectance or transmission is measured by monitoring the change in time-resolved differential transmission

$$\left(\frac{\Delta T}{T} = \frac{T_{\text{pump}}^{\text{on}} - T_{\text{pump}}^{\text{off}}}{T_{\text{pump}}^{\text{off}}}\right) \text{ or reflectivity } \left(\frac{\Delta R}{R} = \frac{R_{\text{pump}}^{\text{on}} - R_{\text{pump}}^{\text{off}}}{R_{\text{pump}}^{\text{off}}}\right) \text{ of weaker probe beam induced by the}$$

stronger pump beam. Here, $R_{\text{pump}}^{\text{on}}$ is the reflection of probe beam when the pump is on while,

$R_{\text{pump}}^{\text{off}}$ is the reflection of probe beam when the pump pulse is blocked. Similarly, $T_{\text{pump}}^{\text{on}}$ and

$T_{\text{pump}}^{\text{off}}$ are transmissions of probe beam when the pump pulse is on and off, respectively.

Transient absorption measurements were carried out in both transmission and reflection geometries. We employed an OPA (Palitra, Quantronix) as an excitation source. The Palitra was seeded by a 1 kHz Ti: sapphire regenerative amplifier (800 nm fundamental wavelength; average power: 1W; pulse width: ~ 100 fs). The pump beam is chopped at 83 Hz and referenced to the lock-in amplifier. Optical nonlinearities effects (*i.e.* bimolecular processes) will be minimized by setting the pump power density to a value well below $80 \mu\text{J}/\text{cm}^2$ per pulse.⁸⁴⁻⁸⁷

The entire measurements were performed on samples which were placed in a cryostat under pressures down to $<10^{-3}$ Pa.

Figure 2-3. Schematics of pump-probe transient reflectance/absorption experimental setup.

Since GaAs substrate is opaque, we have to run transient absorption measurements in the reflection geometry. Pump-probe transient reflectance measurements were performed in the double-pass, backscattering configuration in which probe light passes through the P3HT film and is reflected off at the GaAs/P3HT interface, then collected and monitored using a monochromator/PMT configuration with lock-in detection. In GaAs/P3HT bilayers, the probe beam passes twice through the thin P3HT film after being reflected by the GaAs substrate. Within this experimental configuration, the differential signal obtained by amplitude modulation of the pump beam effectively gauges the photoinduced transient absorption of the P3HT film, together with photoinduced contributions from the interfacial layer.

In pump-probe measurements, we keep the pump fluence below $80 \mu\text{J}/\text{cm}^2$ in order to prevent bimolecular processes. This fluence was the minimum possible to achieve acceptable signal to noise ratio in the reflection configuration. Figure A.1 shows power dependence of transient reflectance for GaAs/P3HT; the entire signal was collected at 510 nm probe wavelength and 1.6 ps delay time.

Figure 2-4. Power dependence of transient reflectance for GaAs/P3HT. Signals were collected at 510 nm for 1.6 ps delay time.

2.5 Density functional theory

The DFT with local density approximation (LDA)¹⁶⁰ functional calculations were carried out for studying interfacial structures and electronic properties using Quantum-ESPRESSO software package.¹⁶¹ Ultrasoft (C, S and H atoms) and norm-conserving of (Ga and As) atoms pseudopotentials were used to describe the electron-ion interactions. The electronic wavefunctions and charge density were expanded with an energy cut-off of 40 Ry and 320 Ry, respectively. All the surface and interface geometries were optimized with the direct energy minimization method of Broyden-Fletcher-Goldfarb-Shanno, until forces on all atoms became lower than 0.02 eV/Å and total energy difference between two optimization steps of the minimization procedures was less than 10^{-4} eV.

Chapter 3

Photophysics of P3HT as a Prototype π -conjugated Polymer

The first part of this chapter serves as a general introduction to fundamentals of π -conjugated polymers, including the structures of conjugated polymers, electronic properties and their elementary photoexcitation. The second part of this chapter runs on the photophysics of rr-P3HT film. The rr-P3HT is a prototype polymer, which has been widely studied over the past decades as a model polymer for both device performance optimization and fundamental studies of charge photogeneration and charge transport. In order to interpret PIA signal of GaAs/P3HT, a comprehensive understanding of charge photogeneration processes and subsequent charge recombination in the pristine rr-P3HT film are required. We will study the mechanism of charge generation and the dynamics of photoexcitation in the pristine rr-P3HT film by steady state PIA and transient absorption spectroscopy techniques. This data also will be used in chapters 5 and 6 to investigate charge transfer at the GaAs/P3HT heterointerfaces. In particular, the photophysics of model system rr-P3HT/PCBM bulk heterojunction will be of extreme interest for understanding the origin of charge generation, exciton dissociation processes, and subsequent formation of the long-lived polaron bands because of charge transfer at interface of GaAs/P3HT.

3.1 Fundamentals of π -conjugated polymers

3.1.1 Structure of conjugated polymers

Conjugated polymers have a chain-like structure, consisting of mainly carbon atoms in the polymer backbone. Carbon has $1s^2 2s^2 2p^2$ electronic configuration. From molecular orbital theory s , p_x , and p_y orbital of carbon form sp^2 hybridization, allowing carbon to form σ bond with the neighbouring atoms due to 'head-to-head' overlap. The unhybridized p_z orbital of adjacent carbon atoms overlap in a 'side-way' manner, forming a π -orbital (bonding orbital when the overlap is in phase) and π^* (anti-bonding orbital when the overlap is out of phase). The bonding in polymer backbone is then an alternate between σ and $\sigma + \pi$ -bond. The bonding π orbital and anti-bonding π^* orbital are known as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively. These un-hybridized p_z orbitals form the ground and excited state wavefunctions that are delocalized over two or more polymeric chains, and subsequently this delocalization allows electron to hop from one carbon atom to another carbon, giving conjugated polymer's unique ability to conduct charges.^{8, 88}

Figure 3-1 shows the backbone of several common π -conjugated polymers.

Figure 3-1. Backbone structures of several π -conjugated polymers.

The linear polyenes are poly-unsaturated organic compounds that contain linear chains of CH units which are bonded in a sequence of alternating double and single carbon-carbon bonds and joined by sp^2 hybridized orbitals.⁸⁹

Two of the sp^2 hybridized orbitals per carbon atom forms σ -bond with the neighbouring atoms, while the third hybridized sp^2 orbital forms a σ -bond with $1s$ orbital of hydrogen. The remaining valence electron per carbon atom is delocalized on the π -orbital orthogonal to the plane formed by three sp^2 orbitals. The wavefunction of the individual π -electrons is described by the linear combination of the $2p_z$ orbitals.

The chemical structures of rr-P3HT and PCBM are shown in Figure 3-2. In the molecular structure of rr-P3HT, the hexyl side chains are attached in a regular fashion (interdigitated with each other) with the main thiophene rings to form interchain π -stacking. As shown in Figure 3-2, the regular head to tail attachment of the side group with the main chain cause to form lamellae folding on the substrate. Therefore, domains with crystalline structure can be found in rr-P3HT films. Within the microcrystalline domain, rr-P3HT has a lamellar structure that is a two-dimensional conjugated planar structure with interchain π -stacking. The planar order leads to polymer chains with longer conjugation lengths. The conjugation length can be interrupted by chemical defects, such as dopant molecules, or by physical defects such as twists and radicals on the chains. The Enhancement of the conjugation leads to an overlap of more π -electrons, thus lowering the HOMO-LUMO transitions. As shown in Figure 3-2, typical rr-P3HT lamellar structure has interplane distance around 0.38 nm, and interchain distance in the plane around 1.6 nm.

Figure 3-2. Left: molecular structure of P3HT, PCBM. Right: a schematic diagram of rr-P3HT lamellae folding on the substrate.¹⁰⁵

3.2 Absorption and emission properties

Figure 3-2 exhibits the Jablonski energy diagram of electronic and vibrational energy levels of a molecule for the quantum mechanical processes of fluorescence and phosphorescence.⁹⁸⁻⁹⁹ Absorption of light promotes electrons from the ground state, S_0 , to the first excited state, S_1 , or even higher excited states S_n , depending on the enough oscillator strength with respect to the ground-state, appropriate parity, and angular momentum.⁹³ Based on the Frank-Condon principle, the strength of allowed transitions depends on the overlap of wavefunction of the upper and lower energy states.⁹⁴⁻⁹⁵

A molecule in an excited state may return to the ground state via radiative or non-radiative transitions. The non-radiative vibrational relaxation takes place within the 100 fs after excitation. The non-radiative relaxation or internal conversion from S_1 to S_0 and from S_2 to S_1 via vibrational levels (in the form of heat) is shown in figure 3-2. Fluorescence takes place from the lowest vibrational level of first excited singlet state S_1 to any vibrational level in ground-state S_0 and phosphorescence occurs from the lowest vibrational level of the excited triplet states T_1 , to ground-state.⁹⁶⁻⁹⁷

Figure 3-3. Electronic and vibrational potential energy levels of a molecule, (Jablonski energy diagram).

Another possibility is intersystem crossing, where excited S_1 state depopulates to the excited triplet states. The photoluminescence efficiency is defined as the number of emitted photons to the number of absorbed photons and it is independent of the pump intensity. Transferring to T_1 reduces the photoluminescence efficiency because transition from T_1 to ground state is optically forbidden.

The π -conjugated polymers can be either luminescent (as in the case of polythiophene) or non-luminescent. According to Kasha's rule, photoluminescence occurs from the lowest excited singlet state. Applying this rule, π -conjugated polymer is luminescent if the lowest exciton state is of odd parity (also known as $1B_u$ state) and it is non-luminescent if the lowest exciton state is of even parity (also known as $2A_g$ state, while the ground state is $1A_g$). The $2A_g$ state may be viewed as a bound state of two triplet states. The ordering of $1B_u$ and $2A_g$, therefore

determines by the strength of the exchange interaction in the polymers (favours triplets) which has to be compared to the strength of the electron-phonon interaction.⁹⁰ In the π -conjugated polymers with A_g ground state character, all the π -orbitals are doubly occupied while promoting an electron from the HOMO to the LUMO level results in an excited state with B_u character. Figure 3-3 shows ordering of the first excited states in polyenes, where an excited state with A_g character can be formed either by promoting of one electron by an even number of orbitals or promoting of two electrons by an odd number of orbitals.⁹¹

Figure 3-4. Symmetry of the first excited states in polyenes.

The optical properties of conjugated polymers are then determined by ordering of the first excited states. As depicted in Figure 3-4, the transitions $1^1A_g \rightarrow 1^1B_u$ (absorption) and $1^1B_u \rightarrow 1^1A_g$ (fluorescence) are dipole-allowed whiles, the transition $1^1A_g \rightarrow 2^1A_g$ is dipole-forbidden. If the 1^1B_u state places at lower energy with respect to 2^1A_g state, then polymer is expected to fluoresce, while if the 1^1B_u state places at higher energy than the 2^1A_g then the polymer is not expected to fluoresce. In the luminescent polymers, $E(1B_u) < E(2A_g)$, and the optical gap E_g is equal to $E(1B_u)$.^{90, 92}

Figure 3-5. Effects of the ordering of the first excited state on the optical properties of conjugated polymers.

3.3 Primary charged photoexcitation in π -conjugated polymers

Due to the strong electron-phonon interaction, the excited states of conjugated polymers are more localized than that in conventional three-dimensional semiconductors. In general, polymers are categorized into the degenerate and non-degenerate ground state. The major difference between these two types of polymers lies in the nature of their charged excitations. The charged excitation for the degenerate ground state polymer is usually solitons, while polarons and bipolarons are charged excitations in non-degenerate ground-state polymers.¹⁰⁰⁻

¹⁰² The net charge, together with the local lattice distortion is referred as a 'polaron'. Polaron carries spin and unit charge. Upon adding or removing a charge, the polymer chain relaxes, i.e. reoptimizes the bond lengths via strong electron-phonon interaction. As a consequence of the lattice relaxation, the optical gap will be locally reduced, leading to the formation of two sub gap levels, one coming from the valence band and the other one coming from the conduction band (see Figure 3-5). Consequently, two optically allowed transitions, namely P_1 and P_2 , are present in all experimental spectra (see Figure 3-10).^{101, 103-104}

Figure 3-6. Long-lived photoexcitation in π -conjugated polymers.

A general photophysical picture of transition in π -conjugated polymers upon photoexcitation is shown in the simplified Jablonski energy diagram of single molecules. Excitation from neutral singlet ground state to neutral excited states instantaneously forms electron-hole pairs. This bound electron-hole pair has spin 0 and it is known as singlet exciton. The 0-0, 0-1 and 0-2 absorption transitions, stem from the Franck-Condon Principle by which transitions occur between the lowest level in the ground-state and different (0, 1, 2, 3) vibrational levels in the excited state, which are determined by the degree of electron wavefunction overlap. The photogenerated singlet exciton may undergo several decay processes: singlet exciton may radiatively decay to the ground state by emitting a photon in the form of fluorescence or non-radiatively recombine. Singlet exciton can undergo intersystem crossing into the triplet manifold. Another decay channel is exciton dissociation into a polaron pair either on the different segments of the same chain or on two different chains (interchain exciton). Among the above by-products of exciton, only trapped singlet, triplet exciton and polaron pairs are long-lived. These species have a wide distribution of lifetimes ranging from a few ms to a few seconds. There are two allowed transitions associated with singlet: both are in the IR range.¹⁰⁴⁻

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The process of polaron photogeneration is enhanced by addition of electron acceptor molecules, such as PCBM (see chemical structures in Figure 3-2). P3HT:PCBM blends are

commonly referred as “bulk heterojunction”, where donor and acceptor molecules are blended intimately in a nanometre length scales. The photogeneration of triplets is possible only via intersystem crossing from the singlet manifold to the triplet manifold, through singlet fission (dipole interaction between polymer chains), or resonant intersystem crossing (transfer via the upper excited state). For triplet, so far only a single absorption band in the visible range was observed. The excited triplet states transition is usually not observed in rr-P3HT and P3HT:PCBM bulk heterojunction films. In these systems, high yield formation of polaron in the excited state competes with the intersystem crossing of singlet excitons. Therefore, triplet exciton formation is negligible due to the small intersystem crossing rate. However, photoinduced absorption measurements of regiorandom P3HT film revealed the formation of excited triplet states. Therefore, triplet formation is in competition with the polaron states formation.¹⁰⁴

Figure 3-7. A simplified Jablonski diagram of single molecules. (a) Photon absorption, (b) interband transitions, (c) fluorescence (radiative quenching of excitons), (d) dissociation process singlet excitons into different excited states, (e) Photoinduced absorption of excitons (exciton

absorption from excited state to the higher excited states) and (f) Photoinduced absorption (PIA) of charged states.

3.4 Our experimental studies of P3HT and P3HT:PCBM blends

3.4.1 Linear absorption and photoluminescence measurements

The absorption and photoluminescence measurements will provide important information on the structure, energetics, and dynamics of electronic excited states of conjugated polymers. Figure 3-8a shows the linear absorption and the PL spectrum of the pristine rr-P3HT film. The absorption and PL spectra of rr-P3HT film show pronounced structures due to phonon replica, indicating that the polymer chains in this film are homogeneous. The absorption spectrum of pristine rr-P3HT exhibits well-resolved, typical vibronic replicas at 600 (0–0), 550 (0–1), and 520 nm (0–2). The vibronic peaks have been previously attributed to the π - π^* interchain-interlayer interaction.¹⁰⁶ The PL spectra of P3HT (left panel in Figure 3-8a) shows vibronic replica peaks at 660 nm and 722 nm with a shoulder at ~800 nm. Figure 3-8a shows that the absorption and PL spectra of a P3HT are almost mirror images of one another. The 50 nm wavelength difference between positions of (0-0) transition of the absorption and PL spectra is due the Stokes shift. The absorption spectra of P3HT/PCBM (left panel in Figure 3-8b) show an additional peak of PCBM at 313 nm.

The PL spectrum of P3HT/PCBM displays similar feature that originates from P3HT. However, PL spectrum exhibits a pronounced quenching in comparison with pristine P3HT film. Strong steady state photoluminescence quenching indicates effective charge transfer from P3HT to the PCBM.¹⁰⁶⁻¹⁰⁷

Figure 3-8 Absorption (left panel) and photoluminescence spectra (right panel) of (a) pristine P3HT film and (b) P3HT/PCBM bulk heterojunction films, consisting of contributions from different conjugation lengths and vibrational modes. Both absorption and PL spectra were measured at 300 K.

3.4.2 Transient absorption spectroscopy of pristine P3HT film

Transient absorption measurements were carried out at several delay times with respect to the photoexcitation at 500 nm. Figure 3-9 shows transient absorption spectra of 100 nm pristine P3HT film. Transient absorption spectra exhibit two prominent features: (1) a strong negative feature in the spectral region of 500 to 620 nm with two minima centred at 600 and 550 (corresponding to the 0-0 and 0-1 transitions) and (2) a very small PIA band in the spectral

region of 640 to 720 nm. The negative feature results from photobleaching of the absorption band of the pristine polymer. The photobleaching arises due to state filling of both ground excitonic and polaronic states. In the absence of acceptor molecules (e.g. PCBM), charge pairs may be generated as a result of strong interchain interaction between adjacent polymer chains or neighbouring chain segments.¹⁰⁶ These charges are generated in the lamellae and thus they are more mobile and have faster decay dynamics. Therefore, the appearance of PIA band with a peak centered at ~ 660 nm can be attributed to the absorption of photogenerated charges. According to literature in the spectral region between 650 and 730 nm, there are a number of charged species (*i.e.* polaron pairs, delocalized polarons), as well as stimulated emission from singlet excitons which all overlap spectrally.¹⁰⁸⁻¹⁰⁹ Since we were not able to distinguish between them, we simply assign them to PIA of “photogenerated charged species”.

Figure 3-10 shows transient dynamics of PB at 550 nm. The decay dynamics are characterized by the multi-exponential function. The magnitude of PB signal reflects the population of photoexcited species in the P3HT film. The PB decay also reflects the recombination of these photoexcited species. The PB signal exhibits a very fast rise, slightly longer than the duration of pump-probe pulses, followed by multi-exponential decays.

Figure 3-9. Transient absorption spectra of the pristine P3HT film (left panel) and OD spectrum of the same film (right panel). Note that positive ΔA signal above ~ 620 nm is due to photoinduced absorption (PIA) of photogenerated charges.

The decay times obtained from the fitting are listed in Table 3-1. The PB signal consists of an initial fast decay with the time constant of 500 fs, followed by a slow component that extends to nanosecond time scale. The fast decay dynamic of the PB band within 5 ps can be attributed to the radiative recombination of P3HT singlet excitons.⁸⁴ The prolonged PB has previously been attributed to long-lived hole polaron states.¹⁰⁶ The corresponding magnitude of PB signal at longer delay times indicates that a small fraction of P3HT molecules remains in the excited state.¹¹⁰⁻¹¹²

Table 2.1. Fitted decay times extracted from transient absorption measurement of P3HT, probed at 550 nm, corresponding weights are shown in parenthesis

t_1	t_2	t_3
0.46 (76%)	5.5 (17%)	1050 (7%)

Figure 3-10. Normalized dynamics of P3HT probed at 550 nm (black squares) and multi-exponential fitting (red line).

3.4.3 Steady state photoinduced absorption spectroscopy

We implemented the spatial mapping of photocarriers in pristine P3HT and P3HT/PCBM films, in a very wide spectral range from visible to mid-infrared by steady state PIA spectroscopy. Figure 3-11 shows PIA spectrum of pristine P3HT film. Two PIA bands at ~ 0.2 eV (DP_1) and at ~ 1.8 eV (DP_2) have previously been attributed to the formation of 2-dimensional delocalized polarons in the lamellae structures, while PIA bands centred at ~ 0.4 eV (P_1) and at ~ 1.4 eV (P_2) are due to formation of localized inter-chain polarons in the disordered portion of the film.^{105, 109} The peak at ~ 1.5 eV is due to triplet excitons absorption and the negative PIA feature below 1.9 eV is associated to GSB of the P3HT.¹⁰⁵ The PIA spectrum also shows sharp peaks which spectrally overlap with DP_1 below 0.2 eV and attributed to IRAVs modes that would arise from the induced charges on the P3HT chain.¹¹³ The PIA spectrum of P3HT also shows a very sharp PIA peak at ~ 1.7 eV. At the present, we are unable to assign this band. In this measurement, we used the low molecular weight of P3HT. Interestingly, this peak has almost disappeared in another PIA measurement with the higher

molecular weight of P3HT. Therefore, we speculate that the formation of this peak is due to low molecular weight of P3HT that was used for this measurement.

Figure 3-11. Steady state photoinduced absorption spectrum of pristine P3HT film. The various transitions are denoted as ground-state bleaching (GSB), localized polaron (P), delocalized polarons (DP), and exciton transitions (EX) ($S_1 \rightarrow S_n$), and triplet absorption (T). The inset shows IRAVs mode of P3HT. The intensity of spectrum below 0.8 eV was multiplied by a factor of 2 for the sake of clarity.

Figure 3-12 shows steady state PIA of the P3HT/PCBM bulk heterojunction film.

The PIA spectrum of P3HT/PCBM is dominated by the optical transition of species in P3HT. However, the overall strength of polaron bands and associated IRAV modes are significantly enhanced by almost one order of magnitude over those observed in the P3HT alone. Ultrafast electron transfer from photoexcited P3HT to PCBM enhances the quantum efficiency of photogeneration of free carriers and suppresses the charge carrier recombination. As a result, charged species (*i.e.* polaron pairs, delocalized polarons) have a longer lifetime and thereby enhance the strength of PIA signal.

Moreover, the sharp peak of triplet and singlet exciton transitions is almost undetectable in the PIA spectrum. This is explained by competition between the high yield formation of long-lived mobile polarons with the intersystem crossing of singlet excitons and the population of triplet excitons.

Figure 3-12. Steady state photoinduced absorption spectrum of P3HT/PCBM bulk heterojunction film. The ground state bleaching (GSB), localized polarons (P) and delocalized polarons (DP) transitions are denoted.

3.4.5 Carrier density probed by photoinduced IRAV modes

Figure 3-13 shows a series of P3HT IRAV modes. In conjugated polymers, nonlinear excitation such as polaron breaks the local symmetry and generates IRAV modes. In order to distinguish the photogeneration effects, one has to rely on complementary ultrafast measurements such as, for example, PIA measurements probing the IRAV. The presence of IRAV modes in the low-frequency region of the PIA spectrum is associated with charge formation on the polymer chains. Therefore, a high fraction of photogenerated charges with longer lifetime on the P3HT backbone strongly enhances the IRAV modes.

Figure 3-13. A series of IRAV modes in the pristine P3HT film.

Xin Yu and co-workers¹¹³ have assigned the corresponding IRAV modes by using density function theory. For P3HT, six characteristic photoinduced IR modes are found at 721 cm^{-1} (asymmetric deformation of methylene group of the hexyl chain), 822 cm^{-1} (Cb-H out-of-plane vibration), 1002 cm^{-1} (Cb-Calkyl stretching), 1084 cm^{-1} (Ca-H and Cb-H bending), 1377 cm^{-1} (Cb-Cb symmetric stretching), and 1462 cm^{-1} (Ca5Cb symmetric stretching), 1512 cm^{-1} (Ca5Cb asymmetric stretching).

3.5 Summary

In this chapter, charge photogeneration and long-lived photoexcitation were studied in the pristine P3HT film by transient absorption and steady state PIA spectroscopy techniques. P3HT is an rr-polymer, which self-organizes into a two-dimensional lamellae sheet with short interchain interlayer distance perpendicular to the film substrate. Our PIA measurements show that strong interchain interaction facilitates photoinduced electron transfer on the adjacent chain or neighbouring chain segments of the P3HT, leading to the formation of delocalized polaron. The steady state PIA spectrum also shows GSB of the P3HT well below 1.9 eV and

two PIA bands P_1 and P_2 at 0.4 eV and 1.4 eV, respectively. These PIA bands attributed to the formation of localized inter-chain polarons in pristine P3HT film. The steady state PIA spectra exhibit a series of photoinduced IRAVs modes well below 0.2 eV, which spectrally overlap with DP_1 . The photoinduced IRAVs modes arise from the induced charges on the P3HT chain. The PIA spectrum of P3HT/PCBM blends film shows similar optical transitions, which are originated from species of P3HT. However, charged species formation (*i.e.* polaron and delocalized polaron) are enhanced in the P3HT/PCBM blend film due to the presence of the charge transfer channel.

Chapter 4

Photophysics of GaAs as a Prototype III-V Semiconductor

In this chapter, we address the following key areas: a short review on ultrafast optical processes in GaAs and transient reflectance spectroscopy of GaAs. Before presenting the experimental steady state and transient reflectance of GaAs, we explicitly examine the energy band structure of GaAs and various allowed transitions from the valence bands to the conduction bands. In addition, we discuss the changes in reflection (ΔR) are being associated with carrier-induced changes in absorption coefficient ($\Delta\alpha$) and refractive index (Δn). Subsequently, we show the contribution of different optical processes such as free carrier absorption, band gap renormalization and interband absorption to the formation of differential reflectivity (ΔR) signal. A detailed description of each part is given in this chapter.

4.1 Introduction

Gallium arsenide (GaAs) has been attracting strong interest due to its wide-ranging applications in the consumer electronics.¹¹⁴⁻¹¹⁶ GaAs devices have already shown their unique performance in some areas of consumer electronics, as it has been employed for the fabrication of optoelectronics devices such as laser diodes¹¹⁷ and infrared light-emitting diodes. GaAs has also been utilized as a mid-infrared optical parametric oscillator¹¹⁸ and THz radiation source.¹¹⁹⁻¹²⁰ GaAs can also be used for the harvesting sunlight in photovoltaic devices.¹²¹

Figure 4-1 shows the energy band structure of GaAs. GaAs is a direct bandgap semiconductor, where bandgap is located at the centre of its Brillouin zone. The top of valence band degenerates at $k=0$, whereas, for $k>0$ valence band splits into a light hole and the heavy hole bands, where the light hole band is slightly lower than the heavy hole band. For the photon energy greater than the bandgap, direct interband transitions from Γ_{15} to Γ_1 (1.43 eV) is a predominate absorption. The conduction band of GaAs has three energetic minima, which are Γ valley at $(k = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}])$, L valley at $(k = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}])$, and X valley at $(k = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}])$. The spin-orbit interaction between electrons causes valence band maximum degeneracy splits into a slightly lower energy band, which is known as “spin-orbit split-off” band with spin-orbit splitting energy (E_{so}) of 0.34 eV. The transition from the split-off band can occur only for energies greater than $E_{so} + E_g$ (see $E_0 + \Delta$ arrow in Figure 4-1), while transitions from the light and heavy hole bands are available for energies greater than the energy gap. Indirect energy gap transition from Γ_{15} to X_1 (1.804 eV) and from Γ_{15} to L_1 (1.84 eV) are optically allowed. There is another critical point along the ΓL direction, which is due to the singularity in the joint density of states. As shown in Figure 4-1, it splits into points as labeled E_1 ($\Lambda_{3V}-\Lambda_{1C}$ transition) and $E_1 + \Delta$ ($\Lambda_{4V}-\Lambda_{1C}$ transitions) with corresponding energies of 2.97 eV and 3.17 eV, respectively.¹²²⁻¹²³

The mobility and mass of the electron strongly depend on which valley electron has been confined. An electron can be confined to one of these three energy valleys of Γ , L, and X points. For example, for the Γ minima there are three valence band maxima which are the heavy hole, light hole and split off bands. The electrons in these three bands are bounded and they are able to move freely throughout the crystal. Due to direct bandgap character of GaAs, photoexcitation of electrons from the valence band to the conduction band conserve both momentum and energy without the requirement of any additional momentum transfer. In addition, GaAs can also emit a photon following photoexcitation.

Pump-probe transient reflectance techniques are perfectly suited for the study of the carrier scattering and relaxation dynamics in sub-picoseconds timescales. In this technique, the generation of highly non-equilibrium conditions allows to observe all of the transient processes, taking place in semiconductors.

Figure 4-1. Band structures of GaAs (from Ref. [124]).¹²⁴

The objective of this chapter is to study transient reflectance spectrum of bulk GaAs. As we have already discussed in chapter 2, the changes in reflection (ΔR) are associated with carrier-induced changes in absorption coefficient ($\Delta\alpha$) and refractive index (Δn). Changes in the absorption coefficient and refractive index can be induced by different optical processes such as free carrier absorption, band gap renormalization, interband absorption, lattice temperature, and nonlinear effects.^{122, 125} Herein, we compare transient reflectance measurements with transient absorption measurements to find out the correlation between photoinduced transient spectrum measured in both transmission and reflection geometries. In the following complete description of the experimental techniques, as well as the theoretical modelling, are presented.

4.2 Carrier induced change in refractive index of GaAs

4.2.1 Free carrier absorption

The simpler version of carrier-induced non-linearity is intraband free-carrier absorption. In this mechanism, a free carrier absorbs a photon and moves to a higher energy state within the band. The free carrier absorption can be easily modelled by the Drude model. Free carrier absorption can induce changes in the absorption coefficient as well as in the refractive index. Therefore, in the case of a realistic semiconductor like GaAs with heavy and light hole bands, the corresponding change in the absorption coefficient is purely induced by photoexcited electrons and hole plasma, is given by

$$\Delta\alpha = \frac{e^3 \lambda^2}{4\pi^2 c^3 \epsilon_0 n} \left(\frac{N}{m_e^2 \mu_e} + \frac{P}{(m_h^*)^2 \mu_h} \right) \quad (4-1)$$

where n is the refractive index of a sample, e is the electron charge, λ is the photon wavelength, N and P refer to electron and hole density, m_e is the effective mass of electron, m_h^* is the effective mass contributed by both heavy and light holes, ϵ_0 is the dielectric constant, μ_e and μ_h are the effective mass of electrons and holes, respectively.¹²⁶

The change in refractive index induced by free carrier absorption can be calculated using the Kramers-Kronig integral.¹²² It is given by

$$\Delta n = -\frac{e^2 \lambda^2}{8\pi^2 c^2 \epsilon_0 n} \left(\frac{N}{m_e} + \frac{P}{m_h^*} \right) \quad (4-2)$$

The key factor to take into consideration is that free carrier absorption induces a negative change in the refractive index while, absorption coefficient change due to this effect is always positive value. In addition, it only relies on the absolute energy and not on the energy relative to the band. Equation 4-2 shows that Δn linearly changes with the density of conduction band electrons. By using this equation, one can estimate the order of magnitude of this effect. The change in the refractive index due to intraband free carrier absorption of GaAs with carrier

density of $1.0 \times 10^{18} \text{ cm}^{-3}$ has been reported $\Delta n \leq 0.002$ for photon energies above the bandage of GaAs (see Figure 4-2).¹²²

Figure 4-2. Predicted change in the refractive index of GaAs due to free career absorption for carrier density of $1.0 \times 10^{18} \text{ cm}^{-3}$ (from Ref. [122]).¹²²

4.2.2 Band filling

The second important carriers induced non-linearity is the band-filling or interband absorption, which is filling up the allowed states in the bands by injection of carriers. In particular, the absorption coefficient of highly doped semiconductors is slightly lower than un-doped ones, the decrease in the absorption coefficient is known as Burstein-Moss effect and it has been explained by band filling. Due to the Pauli Exclusion Principle, a decrease in the absorption coefficient is anticipated for energies slightly above the normal band gap. In III-V semiconductors with direct bandgap and smaller effective mass, this phenomenon is more obvious. In the *n*-type semiconductors, the low-lying states in the conduction band are occupied by a certain concentration of electrons. Since the density of states in the conduction band is not large, electrons easily fill the bottom of the conduction band. Therefore, it is obvious that electrons require larger photon energies than the nominal bandgap to be excited from the

valence band into the conduction band, as the bottom conduction band is already occupied. However, in *p*-type semiconductors with a much larger density of states in the valence band this phenomenon is not very significant.

In GaAs, transition from the heavy-hole and light-hole to the conduction band due to this effect has a two-third and one-third contribution to $\Delta\alpha$, respectively. Figure 4-3 shows theoretical predicted spectra of $\Delta\alpha$ and Δn as a function of energy for GaAs for the injected carrier density of $1.0 \times 10^{18} \text{ cm}^{-3}$. Here, the main point to consider, while analysing experimental data is that band-filling always causes decrease in the absorption, hence, $\Delta\alpha$ is always a negative quantity.¹²⁷

Figure 4-3. Change in absorption coefficient (left panel) and change in refractive index (right panel) as a function of energy due to band-filling effect for *n*-type GaAs for an injected carriers density of $1.0 \times 10^{18} \text{ cm}^{-3}$ (from Ref. [122]).¹²²

4.2.3 Bandgap renormalization

The third significant carrier induced non-linearity is bandgap shrinkage or bandgap renormalization. This effect arises due to the large concentration of carriers, which present in the bandedge of semiconductors. In general, injected electrons occupy the states at the bottom

of the conduction band. For the large concentration of injected carriers, their wavefunctions start to overlap to some degree of extent, thus creating a gas of particles that interact with each other. The carrier with same spin tries to repel each other due to the Pauli Exclusion Principle. As a result, the electrons tend to screen each other and thus decrease their energy in the conduction band while the energy of holes increases in the valence band. This is equivalent to say that band gap of the semiconductor is shrunk because of large concentration of carrier in both the valence and conduction bands.

It should be taken into account that this effect is directly related to inter-distance between carriers. If the inter-distance between carriers is larger than effective Bohr radius of the carrier, Coulomb coupling significantly drops. Therefore, $\Delta\alpha$ due to bandgap renormalization has always a positive value. Figure 4-4 shows carrier induced change in the refractive index and absorption coefficient of GaAs due to the contribution of band gap shrinking. As it is shown in Figure 4-4, $\Delta\alpha$ and Δn reaches own maximum value near the bandedge.

Figure 4-4. Change in absorption coefficient (left panel) and change in refractive index (right panel) as a function of energy due to band-gap shrinkage for *n*-type GaAs for an injected carriers density of 10^{18} cm^{-3} (from Ref. ¹²²).

The above-mentioned nonlinearity effects are considered to have an independent contribution to the $\Delta\alpha$ and Δn of GaAs. The net result of band filling and bandgap renormalization strongly depends on photon energy of probe light. Among these three carriers induce nonlinearities, the band filling has a significant contribution to the total carriers induce changes of refractive index for the $E > E_g$. The contribution of interband free carrier absorption to total carrier induced change can be safely neglected as compared to band filling and bandgap renormalization. Hence, for $E > E_g$, Δn is always a positive value due to band filling while in the case of bandgap shrinking $\Delta n < 0$. Figure 4-5 shows the total contribution of carrier induced non-linearity (i.e. contribution of band-filling, free carrier, and bandgap renormalization) in Δn of GaAs for the carrier density of 10^{18} cm^{-3} .

Figure 4-5. The predicted total carrier induced change in refractive index of GaAs (from Ref. [122]).¹²²

Figure 4-6 shows the extinction coefficient and refractive index of GaAs at room temperature. In the spectral range $\lambda < 500 \text{ nm}$, $|k|^2$ is comparable to $|n|^2$, thus the contribution of extinction coefficient cannot be neglected in differential reflectivity signal in this spectral range (equation 2-16). However, for the below band gap of GaAs, the extinction coefficient will satisfy the

condition $|k|^2 \ll |n|^2$. Therefore, for the below bandgap of GaAs, Δn is the dominant term in differential reflectivity signal in agreement with mathematical formalism, indicating the change in reflectivity signal is mainly dominated by the change in the refractive index and not change in the absorption coefficient. However, in the spectral range $\lambda < 500$ nm we need to take into account the contribution of both components Δn and $\Delta \alpha$ in the reflectivity signal.

Figure 4-6. (a) Refractive index and (b) extinction coefficient spectra of GaAs (provided from Ref. [128]).¹²⁸

4.3 Our experimental studies of GaAs

4.3.1 Steady State photoinduced reflectance spectroscopy of GaAs

Steady state photoinduced reflectance of GaAs was obtained by measuring the change in specular reflectance ΔR at near-normal incidence over a wide spectral range, from visible to NIR region. The average applied pump power was 5 mW, excitation wavelength $\lambda=532$ nm, and pump beam was focused to a 20 μm -spot on the GaAs sample. By considering the absorption coefficient of GaAs at 532 nm, the initial photoinjected carrier density at the surface of GaAs is order of $\sim 10^{18} \text{ cm}^{-3}$. Thus, this process may induces absorption nonlinearities through free-carrier absorption, band filling, and bandgap renormalization. Figure 4-7a shows photoinduced reflectance spectrum of *n*-type GaAs (111)B at 77K for the spectral range between 0.80 and 2.00 eV. The photoinduced reflectance spectrum exhibit a positive feature above the bandedge of GaAs with three distinct peaks at 1.95, 1.80 and 1.59 eV, and a negative feature near the bandedge of GaAs. The broad positive feature above about 1.55 eV and negative band near the bandedge are similar to change in refractive index of GaAs, indicating the change in reflectivity signal is mainly dominated by the change in the refractive index. For the photon energies $E > E_g$ for a typical *n*-type GaAs with 10^{18} cm^{-3} carrier densities, interband absorption and plasma screening of Coulomb enhancement of continuum states have a major contribution to the carrier induced change of refractive index, and hence Δn is expected to be positive. At room temperature, donor impurities are mostly ionized, thus creating a large concentration of free carriers, which occupy states in the lower energy states of the conduction band. The occupation of these states by donor electrons reduces the number of low energy interband transitions that are nominally available for absorption at the lower photon energy.

Figure 4-7. (a) Steady state photoinduced reflectance spectrum of *n*-type GaAs (111)B following photoexcitation at 532 nm, the signal is taken at reflection geometry (b) steady state PIA of *n*-type GaAs (111)B. PIA signal was obtained in the transmission geometry.

As mentioned in the previous section, due to the Pauli Exclusion Principle, interband absorption reduces the transition probability from the valence-band to conduction-band. In addition, screening reduces the exciton binding energy, Coulomb enhancement of the continuum states, and thus the band gap of the semiconductor.

Therefore, the band at 1.51 eV arises from the band filling of states near the bandedge, and screening of the continuum state Coulomb enhancement in good agreement with theoretical predictions. We assign the negative band to the direct interband transition from the valence

band maximum of available states in the bottom of the conduction band at Γ region. The tail of photoinduced reflectance signal well below the bandgap is due to band filling whereas the screening has mainly been responsible for the sharp peak near the bandgap. However, free carrier absorption also has a dominant contribution to the observed signal well below of bandedge.

In order to confirm the sign of the spectrum, steady state PIA measurement was carried out in the transmission geometry below the bandedge of GaAs since GaAs is transparent in this spectral region. The PIA spectrum was obtained by measuring the spectral change ΔT in the near-IR region between 1.45 to 0.80 eV are shown in Figure 4-7b. The PIA measurement of *n*-type GaAs (111)B in transmission geometry reveals a negative feature at 1.48 eV, which is good agreement with the reflection geometry measurement. However, the PIA spectrum is slightly red-shifted as compared to the reflection geometry. Therefore, the measured spectra in both the transmission and reflection confirm the theoretical prediction of carrier induced change in refractive index and absorption coefficient of GaAs.

Electron population dominates the photoinduced reflectance signal between 1.85 to 2.00 eV. The photoinduced peak at about 1.95 eV is associated with the electron population, which are photoexcited from the LH and HH bands in Γ .⁷⁸ According to minimum required transition energy from split-off band to the conduction band, the presence of peak at around 1.80 eV may be attributed to transition from split off band to conduction band; even though, indirect transitions might have some contribution to the formation of this band. The nature of the positive peak at 1.59 eV cannot be easily explained.

4.3.2. Transient reflectance spectroscopy

Figure 4-8 shows transient reflectance spectra of polar *n*-type GaAs (111)B with respect to photoexcitation at 500 nm. Transient reflectance spectra show similar features as obtained by

steady state PIA: a negative band at 1.49 eV and two positive bands at 1.70 and 2.00 eV. Since photoexcitation of carriers occurs far from the bandedge of GaAs, the initial photoexcited carriers have large excess energy. Therefore, intraband carrier scattering and relaxation on the sub-picosecond timescales play a significant roles in differential reflectance signal. Photoinduced reflectance spectra shows two bands at 2.87 and 3.12 eV, which assigned to the $\Lambda_{3V}-\Lambda_{1C}$ and $\Lambda_{4V}-\Lambda_{1C}$ transitions, respectively (see E_1 and $E_1+\Delta$ arrows in Figure 4-1). The formation of these bands is not due to direct photoexcitation from Λ_{3V} and Λ_{4V} region to Λ_{1C} because pump photon energy (2.42 eV) is less than these transitions. Therefore, we consider that pump pulse first promotes electrons to Γ valley and then photoexcited carriers with large excess energy in the Γ -valley interact with a phonon and scatters to the L-valley.

The amplitude of transient reflectance drastically increases for the probe photon energies >1.70 eV because at this probe energy photoinduced reflectance signal involves transition from both top of the valence band and spine split-off valence band to the conduction bands.

Figure 4-8. Transient reflectance spectra of *n*-type GaAs (111)B at the indicated delay time following photoexcitation at 495 nm.

4.4 Results and discussion

Both carriers and phonons are the primary excitations in semiconductors. A phonon is quanta of optical and acoustic modes in a periodic, elastic arrangement of atoms or molecules in the lattice, while carriers are conduction-band electrons or valence band holes. Photon absorption excites electron-hole pairs across the bandgap and creates excess (nonequilibrium) carrier distributions. The dynamics of phonons and nonequilibrium carriers depends on the interactions among these excitations. Eventually, electrons with extra energy can either relax to a conduction band minimum by emitting optical phonons or scatter to the neighbouring valleys, which compromise the conduction band by intervalley scattering. Depending on the various relaxation processes, the photoexcited carriers can undergo different temporal spatial evolution with characteristic times of few fs to several ns. Shah and co-workers classified the relaxation process of excited carriers into four different regimes, which comprise different processes, as well as different timescales.^{78, 129}

In the coherent regime (the first 10's to 100 fs after excitation), scattering proceeds both by intravalley and intervalley processes. Depending on the excess energy of the carrier, interaction of highly energetic electrons in the Γ valley with a large wave vector phonon causes carrier being scattering to either L- or X-valleys.¹³⁰⁻¹³¹ This intervalley scattering may occur in timescales less than 50 fs. In our experiment, we are unable to resolve the scattering of photoinjected carriers since the time reference of our setup is ~ 0.1 ps. The carrier-carrier scattering results in quasi-thermal distribution. After scattering, a number of processes may occur:¹³²⁻¹³⁴

- i- Carrier relaxation within the same valley by the emission of LO-phonons.
- ii- Carriers scattering to the neighbouring satellite valleys (known as “intervalley carriers scattering”).

iii- Carrier recombination or trapping at deep levels.

Hence, on the picosecond timescale the side valleys are depopulated and the carriers attain thermalization in the Γ -valley. The scattering rate from the L to Γ -valley is order of $3 \times 10^{12} \text{ s}^{-1}$ while, scattering rate from the Γ -valley to the L-valley is one order of magnitude larger than scattering rate from the L to Γ -valley. This difference rate has already been attributed to the available density of states to scattered. Figure 4-9 schematically demonstrates intervalley electron-phonon scattering. As shown in Figure 4-9, photoexcited carriers with large excess energy in the Γ -valley can interact with a phonon and scatter to the L-valley. Then, the scattered electron relaxes within the L-valley and scatters back into the Γ -valley.

In the isothermal or recombination regime, the excess electron-hole pairs recombine and semiconductor reaches the thermodynamic equilibrium.

Figure 4-9. Intervalley electron-phonon scattering in GaAs. (a) Photoexcitation of hot carrier with large amount of energy in Γ -valley, (b) interaction of hot carrier with a phonon and scattering to the L-valley, (c) relaxation of electron within the L-valley, and (d) scattering back into the Γ -valley.

However, the effective carrier temperature is still different from the lattice temperature; this process is known as carrier thermalization and it is governed by the Boltzmann transport equation. Interaction of carriers with various phonons equilibrates the carriers and lattice temperatures. On the other hand, band filling is said to occur. When the carrier's energy relaxes and all of the lowest states in the conduction band are being occupied. In the final stage, the electrons and holes recombine, returning the semiconductor to the initial equilibrium state. Figure 4-10 shows the kinetics of $\Delta R/R$ at 429 nm for *n*-type GaAs (111)B. The rise and decay times extracted from the multi-exponential fitting are listed in Table 4-1. Upon photoexcitation, the transient reflectance signal shows an almost instantaneous decrease in reflectivity within $t=200$ fs. Then, reflectivity signal crossing the zero axis and rises within 4 ps. After 10-12 ps after excitation, reflectivity signal starts to decay.

Figure 4-10. Kinetics of $(\Delta R/R)$ at 429 nm for *n*-type GaAs (111)B following photoexcitation at 495 nm. Two different features are observed in the reflectivity signal. Transient reflectance signal shows the initial decrease in reflectivity and a subsequent rise within 4 ps, and then crossing the zero axes and a subsequent slow recovery of the signal which extend to nanosecond timescale regime.

Two different decay components are observed: fast decays within 27 ps and other subsequent slow decay with a characteristic longer lifetime ($t > 1\text{ ns}$). The initial decrease in reflectivity is due to injection of carriers followed by fast interband relaxation. The subsequent rise of $\Delta R/R$ is due to filling of conduction and valence bands. Later decrease of $\Delta R/R$ within $t=27\text{ ps}$ is due to thermalization and relaxation of carriers towards the band edge, as well as intervalley transfer. The slower transient reflectance decay has previously been attributed to recombination and trapping of carriers at deep trap level of GaAs.¹³⁵⁻¹³⁷ In our experiment, carriers (electron and holes) are generated by photoexcitation predominantly at the edge of L-valley. Therefore, photoexcitation at 500 nm is able to effectively create a highly nonequilibrium condition. The contribution of non-linearity change in refractive index and thus photoinduced reflectance mainly depends on carrier density and it is not very sensitive to interband carrier distributions. Increasing density of states enhances the reflectance. Thus, bandgap renormalization predominates over the reduction of the Coulomb enhancement that reduces the reflectance. The subsequent rise of photoinduced signal mainly arises from filling of heavy hole states as the initially cold distribution heats up and thermalizes. The filling of low energy states by ionized donor electrons also may slow the relaxation of the electrons.¹²⁷

Table 4.1 Decay constant probed at 429 nm.

t_1 (ps)	t_2 (ps)	t_3 (ps)
3.6	26.9	$>1\text{ ns}$

4.5 Summary and conclusions

In this chapter, we discussed ultrafast carrier dynamics of the *n*-type GaAs (111)B. Absorption of laser pulse excites electron-hole pairs across the bandgap and create excess (nonequilibrium) carrier distributions through interband absorption. Change in the population of the initially injected carrier density will also cause a similar time variation in the induced absorption or

refractive index change. Depending on the incident photon energy, several transitions can occur from different regions of the valence band to the conduction band.

We show that transient reflectance measurements directly give the evolution of carrier density in a particular band. In order to validate the theory prediction of carrier-induced changes in refractive index, steady state PIA was carried out on *n*-type GaAs (111)B. The photoinduced reflectance signal displays a good agreement with theory prediction. In addition, we extracted information about the carrier photogeneration mechanisms, carrier relaxation, and relaxation paths in bulk GaAs.

Chapter 5

Ambipolar Charge Generation and Transfer at Hybrid GaAs/P3HT Heterointerfaces

Recent work on hybrid III-V compound and polymer photovoltaic devices with promising PCE opens up new opportunities for tailoring the optoelectronic properties of photovoltaic materials and subsequently arises fundamental questions related to the carrier photogeneration mechanisms and ultrafast dynamics and photoinduced charge transfer at organic-inorganic heterointerfaces with different degrees of charge delocalization. In this chapter, we investigate the photophysical properties of *n*-type GaAs (111)B and rr-P3HT heterointerface by using a combination of steady state and ultrafast spectroscopy techniques, and density functional theory (DFT) calculations to understand the fundamental mechanisms underlying device operation. Transient absorption data collected at various excitation energies clearly indicate the coexistence of electron and hole transfer taking place between the GaAs and P3HT. The signatures of interfacial charge transfer are manifested in transient reflectance measurements by the formation of long-lived polarons. This is consistent with DFT predictions for polar

(111)B GaAs surfaces, for which calculations suggest that P3HT acts as an acceptor for hole transfer from the GaAs valence band state to the HOMO of P3HT.

5.1 Introduction

Integration of organic semiconductors with inorganic electron donors or acceptors, such as metal-oxide or II-VI semiconductors, has been proven an attractive strategy to increase the PCE of low-cost photovoltaic devices.^{17, 53, 138-142} Typically, in this type of hybrid solar cells, photogenerated excitons dissociate at the inorganic/polymer interfaces, transferring an electron to the semiconductor nanocrystals and leaving behind a positive polaron on the polymer chain. Charge carriers can then escape recombination and be extracted from opposite electrodes so that the competition between charge dissociation and charge recombination becomes the primary factor affecting the overall photocurrent.¹⁴³⁻¹⁴⁴ One way to improve the PCE of polymer solar cells is to replace the commonly used fullerene-based acceptors with high electron mobility inorganic counterparts such as silicon (Si)¹⁴⁵ and germanium (Ge)¹⁴⁶, lead sulfide (PbS)¹⁴⁷ and lead selenide (PbSe)¹⁴⁸⁻¹⁴⁹, cadmium selenide (CdSe)^{43, 150} and cadmium sulfide (CdS)⁴² or metal oxide titanium oxide (TiO₂)¹⁷ and zinc oxide (ZnO).^{16, 151} Recently, hybrid organic/inorganic PVs based on III-V compounds (e.g. GaAs and InP) and conjugated polymers demonstrated promising performance. GaAs is one of the promising materials for fabrication of efficient organic/inorganic hybrid solar cell, thanks to the strong near-infrared absorption, the high carrier mobility, and the optimal staggered band alignment to common conducting polymers of III-V materials.^{15, 53-55} These properties of III-V semiconductors make them as an ideal candidate for application in the field of hybrid PVs for the achievement of high PCE in a near future.

The earliest attempts to incorporate InP nanowires in hybrid solar cell yielded PCEs approaching 1%.²⁵ PCEs as high as ~4.2% was obtained in GaAs/octithiophene bilayers

heterojunction⁵⁰ and ~2.31% in GaAs/polymer bilayers.¹⁵² New types of GaAs/P3HT bulk-heterojunction in which GaAs nanowires are coated with TiO_x and blended with the polymer demonstrated efficiency ~2.37%.⁵³ Despite the demonstration of relatively high performance hybrid polymer/III-V compounds PV devices (e.g. GaAs/P3HT), the current understanding of primary charge generation and charge transfer process at inorganic/polymer interfaces and specifically the coupling between localized excitonic species in the polymer with fully extended states in the inorganic semiconductor are rather limited. Thus, a better understanding of the nature of hybrid photoexcitation and their physical origin at III-V/polymer heterointerfaces is of primary importance and impacts from both experimental and theoretical standpoints. The recent studies on charge transfer in hybrid III-V/organic compounds (small molecules, oligomers, and polymers) provided useful insights into interfacial processes upon photoexcitation, as well as some guidelines for the design of efficient PV devices.^{64-68, 135, 153-155} Blackburn et al.¹⁵⁶ investigated ultrafast hole-transfer from colloidal InP quantum dots to organic hole transfer material by photoluminescence and transient absorption spectroscopy. Lanzani et al.^{155, 157} observed charge transfer induced exciton dissociation at the hybrid GaAs/oligothiophene bilayer interface. Subsequently, this group reported photoinduced electron transfer from CuPcF16 to GaAs and from GaAs to C60 in hybrid CuPcF16/GaAs¹⁵⁵ and C60/GaAs¹⁵⁷ bilayers, respectively. Employing electric field induced second harmonic generation, Zhu, and co-workers¹⁵⁴ reported photoinduced charge transfer from photoexcited GaAs to localized CuPc molecular orbital. This was attributed to charge carrier separation in GaAs by the space charge field following ultrafast hole injection to CuPc.¹⁵⁴ More recently, Giustino and co-workers performed DFT modelling on GaAs/polythiophene heterojunction. They showed that the resulting interfacial dipole can lower the HOMO of the polythiophene until the whole system attains equilibrium.¹⁵³ Our group also investigated the effect of surface orientation of GaAs on the charge redistribution at the GaAs/P3HT heterointerface using DFT

modelling. We show that polar GaAs(111)B facilitates hole injection from the valence band states to the HOMO of P3HT as compared to non-polar surface GaAs(110).¹⁵⁸ While all these studies demonstrate effectiveness of either electron or hole transfer at III-V/organic heterointerfaces, “ambipolar” charge transfer is expected to occur in GaAs/P3HT, whereby both electron transfer from the HOMO of P3HT to the conduction band of GaAs and hole transfer from excited states of GaAs to the LUMO of P3HT can occur simultaneously. This interesting new paradigm may improve charge photogeneration efficiency in hybrid photovoltaic devices.¹⁵⁹ In this chapter, we focus on charge carrier photogeneration and photoinduced interfacial charge transfer between the polar GaAs (111)B and P3HT by several steady state and ultrafast investigation techniques and theoretical modelling by DFT calculations.

5.2 Results and analysis

5.2.1 Energy alignment of GaAs/P3HT

Figure 5-1 shows surface topography of P3HT films deposited over GaAs substrate. The film clearly reveals fibre like network and high crystallinity. Therefore, the high crystallinity of film gives rise to polymer aggregates.

Figure 5-1 Tapping mode AFM topography of $4\ \mu\text{m} \times 4\ \mu\text{m}$ image of the annealed P3HT film deposited over GaAs substrate.

UPS technique was used to investigate the energy level alignment in GaAs/P3HT interfaces. Figure 5-2 shows a schematic of the energy diagrams of GaAs (111)B/P3HT. The valence band maximum (VBM) and conduction band minimum (CBM) of GaAs are respectively deeper than the HOMO and LUMO of P3HT which makes it an attractive candidate as an electron acceptor in combination with P3HT. Moreover, as its band energy diagram suggests, GaAs has one of the most favourable energetics for hole transfer to P3HT so that ambipolar charge transfer could indeed be achieved in GaAs/polymer solar cells with proper design engineering. Therefore, type II heterojunction is anticipated to form at the hybrid interface. Due to the staggered band alignment with P3HT, GaAs is expected to serve as both electron acceptor and hole donor. Therefore, from the optimal type-II energy alignment of GaAs(111)B versus P3HT, electron transfer from P3HT to GaAs is indeed expected to yield positive polarons in P3HT; while at the same time, hole injection from GaAs to P3HT is also favourable.¹⁶²

Figure 5-2. Energy level diagram of GaAs (111)B/P3HT. Due to the staggered band alignment with P3HT, GaAs serves as an electron acceptor and hole donors. Δ : interfacial dipole energy, Φ_{SUB} : work function of substrate, E_F : Fermi energy, VBM: valence band maximum, CBM: conduction band minimum.

5.2.2 Absorption and reflectance measurements

Figure 5-3 shows the reflectance spectra of a typical GaAs/P3HT bilayer, a bare GaAs substrate, and the absorption spectrum of the pristine P3HT film deposited on the quartz substrate, where the replica vibronic features are indicated. GaAs substrate shows a broad reflectance band covering the entire visible region, while the absorption spectrum of pristine P3HT exhibits well-resolved, typical vibronic replicas at 605 (0-0), 560 (0-1), and 520 nm (0-2). There is a one-to-one correspondence between replica vibronic peaks in the two curves, except for the feature around 640 nm, which is due to the superposition of GaAs reflectivity with the onsets of P3HT absorption at the HOMO-LUMO energy. The reflectance spectra of both GaAs and GaAs/P3HT samples show additional two peaks at 395 and 425 nm where assigned to $\Lambda_{3V}-\Lambda_{1C}$ and $\Lambda_{4V}-\Lambda_{1C}$ transitions, respectively.

Figure 5-3. (a) Reflectance spectrum of a bare GaAs, (b) reflectance spectrum of GaAs/P3HT bilayer heterointerface, and (c) absorption spectrum of P3HT.

5.2.3 Steady state and time resolved photoluminescence

Figure 5-4 shows the corresponding steady state photoluminescence (PL) spectra of P3HT, GaAs/P3HT bilayer, and bare GaAs. The GaAs/P3HT system shows main peaks originating from both P3HT, with emission peaks centred at 650 and 720 nm, and from the GaAs substrate, with an emission peak centred at ~ 860 nm. However, the intensity of photoluminescence transitions corresponding to P3HT is reduced in the bilayer compared to the pristine P3HT film. The quenching of steady state photoluminescence in P3HT is a first indication of the

excitons population reduction upon charge transfer across the heterointerface, similar to the well-known case of P3HT/PCBM blends, where radiative emission is completely quenched upon ultrafast (<50 fs) electron transfer to the fullerene acceptor.¹⁶³⁻¹⁶⁴

Figure 5-4. Steady state photoluminescence spectra of P3HT (blue line), GaAs/P3HT bilayer (red line), and GaAs substrate (black line).

Both emission and reflectance spectra of the GaAs/P3HT bilayer, therefore, suggest that GaAs acts as the effective electron acceptor and light absorber in the combined hybrid system. We take it into account that the PL from GaAs is not reduced in the bilayer. One reason, why we do not observe a significant change of GaAs PL intensity, may be the reduction of effective pump intensity exciting GaAs directly due to the absorption of P3HT in the bilayer. Energy transfer could indeed happen in this hybrid system due to the overlap of the emission spectrum of P3HT and the absorption spectrum of GaAs. However, energy transfer would happen prior to electron injection from P3HT to GaAs, on time scales faster or comparable to our actual time resolution. Therefore, in first approximation, we neglected energy transfer and focused on the charge transfer processes that we can time-resolve.

Figure 5-5 shows a comparison between the photoluminescence transient dynamics of pristine P3HT, P3HT on GaAs and a P3HT/PCBM bulk heterojunction (1:1 wt%). The photoluminescence lifetime of P3HT deposited over GaAs substrate is found to be significantly reduced compared to the pristine P3HT sample, in agreement with the observed quenching of steady state photoluminescence. Assuming that effective exciton dissociation takes place at the GaAs/P3HT interface, followed by photoinduced charge transfer between the two components, the charge transfer efficiency can be estimated from the exciton lifetimes extracted from Figure 5-5.¹⁶³

The charge transfer efficiency is calculated from exciton lifetime (TR-PL measurements) using the formula, $k = (1/t - 1/t_{\text{ref}})$, where t_{ref} is the average exciton lifetime in the pristine P3HT control sample and t is the average lifetime in the P3HT spun onto GaAs. The relative charge transfers efficiency of the combined system is obtained from the ratio $k_{\text{GaAs/P3HT}}/k_{\text{PCBM/P3HT}}$ where $k_{\text{GaAs/P3HT}}$ is the fast component of the radiative decay of GaAs/P3HT and $k_{\text{PCBM/P3HT}}$ is that of the P3HT/PCBM blend (where charge transfer efficiency is expected 100%)⁸⁶ is on the order of 3%. This indicates that the GaAs/P3HT interface facilitates dissociation of photogenerated excitons, although charge-transfer efficiency is significantly lower than that in the P3HT/PCBM bulk heterojunction system, which offers larger interfacial area compared with the simple bilayer thanks to the interpenetrating morphology of the nanometer-scale donor-acceptor network.

Figure 5-5. Time-resolved photoluminescence of pristine P3HT film (black squares), P3HT/PCBM blend film (green triangles), and GaAs/P3HT bilayer (red circles). The time-resolved photoluminescence spectra was recorded at 660 nm with photoexcitation at 500 nm. The photoluminescence decay dynamics were fitted to a bi-exponential function (solid lines), where t_1 and t_2 are the extracted lifetimes.

5.2.4 Femtosecond transient reflectance spectroscopy

Pump-probe spectroscopy was carried out with an excitation wavelength of 500 nm and probe wavelengths in the range of 350-850 nm, collecting relative differential signals ($\Delta R/R$) in backscattering configuration. In GaAs/P3HT bilayer, the probe beam passes twice through the thin P3HT film after being reflected by the GaAs substrate. Within this experimental configuration, the differential signal obtained by amplitude modulation of the pump beam effectively gauges the photoinduced transient absorption of the P3HT film, together with photoinduced contributions from the interfacial layer. Negative signal correspond to the decrease in the reflected probe light, originates from ground state bleaching (GBS) or stimulated emission (SE), while positive signals are due to an increase of reflected light intensity, and originate from polaron absorption. The fluence was used to obtain the data was

80 $\mu\text{J}/\text{cm}^2$. This fluence was the minimum possible to achieve acceptable signal to noise ratio in our measurements in the reflection configuration.

Figures 5-6a and 5-6b show transient reflectance spectra of *n*-type GaAs (111)B and transient absorption of the pristine P3HT film at different delay times: respect to $\lambda_{\text{exc}} = 500$ nm. The transient absorption spectra of pristine P3HT film (Figure 5-6b) exhibit negative features with 2 distinct vibronic peaks, 550 nm (0–1), and 600 nm (0-0), assigned to ground state bleaching (GSB); a weak positive band at 650 nm arising from the PIA of photogenerated charged species.¹⁶⁵⁻¹⁶⁶ The spectra of *n*-type GaAs (Figure 5-6a) consist of five main features, four of which are positive bands centred at 395, 410, 650 and 770 nm, and the fifth is a negative band centred at 850 nm. At early times after excitation, the negative band at 850 nm is broad due to hot carrier cooling towards the band edge of GaAs.¹⁶⁷ Figures 5-6c shows transient reflectance spectra of *n*-type GaAs (111)B/P3HT at the indicated delay times. Even at a short delay time after photoexcitation the transient reflectance spectra of GaAs/P3HT are significantly different than those of control GaAs and P3HT samples.

In the transient reflectance spectra of the GaAs/P3HT bilayer, five main features are evident: (1) Two positive bands at 390 and 410 nm, (2) a PIA band between 570 and 770 nm, (3) a negative photobleaching (PB) band below about ~ 570 nm, (4) and a negative band at longer above > 800 nm. The positive bands at 390 and 410 nm could result from excitation from the excited state of the GaAs. The negative PB band shows characteristic peaks at about 510, and 550 nm, which are attributed to the GSB of P3HT due to state filling of the ground excitonic and polaronic states. Conversely, the 0-0 vibronic feature at 600 nm appears as a positive signal, most likely due to the spectral overlap of the PB with the tail of the PIA band. The PIA band at about 650 nm persists beyond the 250 ps temporal window of our measurements. Several factors may contribute to the observed long-lived PIA signal. According to the staggered band

alignment of GaAs and P3HT, the GaAs/P3HT bilayer interface is expected to facilitate dissociation of photogenerated excitons.

This results in the conversion of P3HT excitons into positive P3HT polarons, which is reflected in the transient reflectance signatures of the GaAs/P3HT bilayer. On the other hand, the appearance of strong PIA band could be due to the enhancement of polaron formation in P3HT as a result of charge transfer induced excitons dissociating at the heterointerface: this would inhibit recombination of hole polarons in P3HT, thus increasing the lifetime. The assignment of the PIA band to positive P3HT polarons is indeed supported by our steady state PIA (see chapter 3) as well as charge-modulation spectroscopy measurements performed on P3HT diodes P3HT/PCBM bulk heterojunction films.⁸⁴ In the GaAs/P3HT bilayer, the PB and PIA bands exhibit a significantly longer lifetime of >1 ns, ($\sim 20\%$) of the initial amplitude in comparison to pristine P3HT film. The long-lived PIA dynamics show enhancement of polaron formation in P3HT due to the electron transfer to GaAs.¹⁶⁸ The rise time of PIA correlates well with the fast decay time of PB signal due to the depletion of the ground state (see Figure 5-7).

Figure 5-6. (a) Transient reflectance spectra of *n*-type GaAs(111)B, (b) transient absorption of pristine P3HT film, and (c) transient reflectance spectra of hybrid *n*-type GaAs(111)B/P3HT bilayer at the indicated different delay times following photoexcitation at 500 nm.

The second positive band between 700-770 nm could result from the excitation of both GaAs and P3HT. Therefore, we suggest that both, GaAs and P3HT contribute to the formation of this band. The dynamics of PB at 550 nm for pristine P3HT and GaAs/P3HT heterointerface are shown in Figure 5-7. The decay dynamics are characterized by the multi-exponential function. The decay times obtained from the fitting are listed in Table 6-1.

Figure 5-7. Photoexcitation dynamics of the (a) pristine P3HT film and (b) n-type GaAs/P3HT bilayer at 550 nm probe.

The PB signal is proportional to the population of the exciton and polaron in photoexcited P3HT film. The PB decay also reflects the recombination of all the photoexcited species. The PB signal of the pristine P3HT film (Figure 5-7a) consists of an initial fast decay with the time constant of 460 fs. The initial fast PB decay followed by two different decay components with lifetime of $\tau \sim 50$ ps and 1050 ps. The decay of the PB with the lifetime $\tau \sim 50$ ps corresponds to the radiative recombination of P3HT singlet excitons. This prolonged PB is attributed to the long-lived hole polaron states, indicating that a small fraction of P3HT molecules remain in the excited state. Similar to P3HT film, GaAs/P3HT sample exhibits initial

fast decay with the lifetime of $\tau \sim 660$ fs. However, the PB signal of GaAs/P3HT bilayer is almost invariant between 10 ps and 1 ns. The PB signal also exhibits significantly longer lifetimes (with $\tau > 5$ ns) compared to pristine P3HT film. Therefore, the prolonged PB is attributed to long-lived hole polaron states, indicating small re-population of excited states following charge transfer. The long-lived PB signal provides clear evidence of formation of mobile polarons upon charge transfer induced exciton dissociation at the GaAs/P3HT heterointerface.^{84, 110-112} The dynamics of transient reflectance peaks corresponding to PB confirms the generation of long-lived species and PIA upon interfacial charge transfer across the heterointerface. In addition, exciton dissociation and charge transfer across the GaAs/P3HT bilayer interface happen on a sub-picosecond time scale.

Table 5-1 Decay constants of PB dynamics (probe wavelength at 550 nm) for pristine P3HT film and GaAs/P3HT heterojunction bilayer, the corresponding weights are shown in parenthesis.

Samples	t_1 (ps)	t_2 (ps)	t_3 (ps)
P3HT	0.46 (76%)	5.5 (17%)	1050 (7%)
GaAs/P3HT	0.62 (52%)	2.7 (25%)	>5 ns (23%)

Figure 5-8 shows PIA and PB dynamics of GaAs (111)B/P3HT. The PB and PIA dynamics exhibit significantly longer lifetime compared with pristine P3HT film, indicating an enhancement of delocalized polaron formation due to the presence of the inorganic interface. The rise time of PIA band correlates well with the decay time of PB signal due the depletion of the excitonic ground state.

Figure 5-8. PIA (positive signal) and PB (negative signal) dynamics of *n*-type GaAs (111)B/P3HT bilayer probed at 650 nm and 550 nm, respectively.

5.2.5 Steady state photoinduced reflectance spectroscopy

In order to confirm the assignment of transient reflectance and provide further evidence of the formation PIA band upon photoexcitation, steady state PIA was carried out on of GaAs(111)B. Figure 5-9 shows photoinduced reflectance spectra of GaAs (111)B, GaAs (111)B/P3HT, and P3HT/PCBM bulk heterojunctions. The photoinduced reflectance spectrum of GaAs (111)B shows positive band in the entire visible region which tails off to lower wavelength region with a peak centred at 840 nm. The PIA spectrum of GaAs (111)B/P3HT shows different features than the bare GaAs, consistent with photoinduced charge transfer taking place in this hybrid system. The photoinduced spectrum clearly shows the formation of GSB below 630 nm and new PIA band above 650 nm with the peak entered at 660 nm. Similar to P3HT/PCBM (Figure 5-9c), the positive band can be safely attributed to the formation of delocalized polaron in the P3HT film. Similar to transient reflectance spectra of GaAs (111)B/P3HT, both photoexcited species of GaAs and polaron of P3HT have a contribution to the photoinduced spectrum above

700 nm. Therefore, the tail of photoinduced reflectance band between 700 and 770 nm could result from the excitation of both GaAs and P3HT.

Figure 5-9. Steady state PIA of (a) p-GaAs (111)B, hybrid p-type GaAs (111)B/P3HT bilayer (b), and P3HT/PCBM bulk heterojunction control sample.

5.2.6 Density functional theory (DFT) calculation

DFT calculations were performed on the ground state of idealized Si-doped GaAs (111)B/P3HT bilayer model by replacing one As atom by Si atom on the GaAs top layer. Charge transfer is usually determined by the electronic coupling strength, reorganization energy, the energetics of the organic adsorbate and semiconductor, and their density of states

(DOS). Figures 5-10(a) show that the total DOS of the GaAs and P3HT combined system (black lines) is largely dominated by the projected DOS of GaAs (shaded grey area) while the projected DOS of P3HT (blue line) only slightly perturbs the top of the valence band (VB) of GaAs. DOS of the P3HT extend over a broad energy range, and there is a small overlap between the LUMO level of P3HT and the conduction band (CB) of GaAs compared to the relatively large overlap of the HOMO of P3HT and the GaAs VB. While the CB of GaAs gains overlaps with the HOMO of P3HT, easing hole injection from GaAs to P3HT. The electronic charge rearrangement upon formation of GaAs/P3HT interfaces is also shown in Figure 5-10(b). The charge transfer from P3HT to the GaAs substrate was calculated as charge density difference $\Delta\rho(r) = \rho_{\text{GaAs/P3HT}} - [\rho_{\text{GaAs}} + \rho_{\text{P3HT}}]$ where r is the position vector within the computational cell, ρ_{GaAs} is the charge density of the GaAs (111)B slab, ρ_{P3HT} is the charge density of the P3HT layer without substrate, and $\rho_{\text{GaAs/P3HT}}$ is the electronic charge density of the GaAs/P3HT interface. The in-plane average of $\Delta\rho$ along the z -direction shown in Figures 5-10(b) provides quantitative estimates of the electron ($\Delta\rho < 0$) and hole ($\Delta\rho > 0$) accumulation, indicating a large charge redistribution (up to $\sim 5.38 \times 10^3 \text{ e}/\text{\AA}^3$). Upon charge redistribution with adsorbed P3HT, the intrinsic surface dipole moment of GaAs surfaces is enhanced by induced charge displacement. To understand the origin of the interfacial dipole moment, a Löwdin charge analysis of the charge density was conducted for these hybrid systems.¹⁶⁹ By comparing the sum of the Löwdin charge on the GaAs and P3HT molecule before and after formation of the interface a total charge (ΔQ) of $0.223e$ for GaAs(111)B/P3HT is found to be transferred between P3HT and GaAs, which is slightly larger than the intrinsic GaAs(111)B/P3HT system ($\Delta Q = 0.209e$).¹⁵⁸ This implies an efficient charge transfer compared to other hybrid systems, such as Cu (110)/petencene, ZnO/P3HT and ZnO/Graphene and etc.¹⁵⁸

Figure 5-10. (a) Density of states and electronic orbital distribution of electronic orbitals of GaAs (111)B/P3HT hybrid system. The dashed line indicates the position of the Fermi energy. The insets show the electronic distribution of HOMO and LUMO of P3HT; (b) Charge redistribution in one-dimensional plane-averaged charge density difference, $\Delta\rho(z)$, upon P3HT adsorption. The inset shows a three-dimensional representation of the charge density difference with an isovalue of $\pm 0.005 \text{ e}/\text{\AA}^3$. The solid lines indicate the average positions of the GaAs surface and the P3HT plane while the horizontal dashed line shows the interfacial distance at which charge depletion converts into charge accumulation.

5.3 Carrier lifetime enhancement in GaAs

The GaAs and P3HT both have a contribution to the transient reflectance signal above 500 nm. However, below 450 nm, the contribution of P3HT to the transient reflectance spectra of GaAs/P3HT (Figure 5-6b) is almost negligible and transient reflectance spectra at this spectral region are mainly dominated by photoexcited species of GaAs. Therefore, probing carrier dynamics below 450 nm would enable us to monitor the evolution of carriers in GaAs in the presence of the P3HT film. Figure 5-11 compares the kinetics of $\Lambda_{3V}-\Lambda_{1C}$ transition in GaAs and GaAs/P3HT. Monitoring transient reflectance signal of these two samples would allow us to get insight on the carrier lifetime of GaAs. The $\Delta R/R$ transient shows that decay dynamics of photoexcited species of GaAs are significantly changed in the presence of polymer film. It

is remarkable that initial fast decay component in GaAs/P3HT signal is absent and subsequent trapping/recombination of the carrier at the long delay times is significantly reduced. Therefore, due to the presence of P3HT film carrier lifetime in GaAs is enhanced. Our DFT calculations on a GaAs/P3HT heterojunction demonstrate that both electron and hole transfer take place at the GaAs/P3HT interface and P3HT film can provide a channel for hole injection from GaAs.

Figure 5-11. Photoexcitation dynamics of (a) *n*-type GaAs (111)B/P3HT bilayer and (b) *n*-type GaAs (111)B probed at 429 nm. The solid lines are fitting of the data with multi-exponential functions.

Therefore, the hole injection to P3HT, may prevent recombination and thus enhance the yield of charge carriers. Chaw Keong Yong and co-workers¹⁷⁰ have previously demonstrated that carrier lifetimes of GaAs nanowires were enhanced in the presence of the P3HT film. They attributed this enhancement to the electron transfer from the HOMO of P3HT into the lower energy levels of surface trap states of the GaAs nanowires. Thus, we suggest that P3HT film can act as a surface passivating layer as well as the hole acceptor in GaAs/P3HT heterojunction.

5.4 Hole injection studies

5.4.1 Time resolved photoluminescence

Figure 5-12 shows TR-PL of GaAs (111)B and hybrid GaAs/P3HT bilayer. The PL decays were detected at 860 nm following excitation at 800 nm.

Figure 5-12. Time-resolved photoluminescence of *n*-type GaAs (111)B (black squares), and *n*-type GaAs (111)B/P3HT bilayer (red circles). The photoluminescence was recorded at 860 nm after excitation at 800 nm. The PL decay was fitted to a tri-exponential function (solid lines).

Since excitation energy is far below the P3HT optical gap (HOMO-LUMO transition), there is no contribution from P3HT emission in PL spectra of GaAs/P3HT, and PL spectra is only

dominated by the emission of GaAs substrate. The PL lifetimes of GaAs are significantly reduced in the presence of P3HT film. The quenching of PL can be attributed to the hole injection from GaAs to the adjacent P3HT chain according to their relevant energy level alignment as well as DFT prediction.

5.4.2 Transient reflectance spectroscopy

Ultrafast spectroscopy data and energy considerations suggest that the rapid generation of charges at the GaAs/ P3HT heterointerfaces may be induced by either electron transfer from P3HT to GaAs or by hole injection from GaAs to P3HT. To address the nature of charge-transfer polarity, we lowered the excitation energy below the optical gap of P3HT (photoexcitation at 800 nm) to selectively excite GaAs and isolate the contribution of hole injection from GaAs to P3HT. As shown in Figure 5-13a, the transient reflectance spectra of GaAs/P3HT bilayer at $\lambda_{\text{exc}}=800$ nm shows similar features as photoexcitation at 500 nm, namely PB and PIA bands. In this case polaron, related bands are also rather long lived. The main difference between the dynamics of different excitations conditions (with energies above or below the P3HT band gap) appears in the characteristic PB signal below 560 nm. Initially, PB signal is dominated from the contribution of GaAs due to predominant excitation of GaAs. Once GaAs relaxation is almost completed, the PB signal evolves and rises within few picoseconds. Subsequently, the PB relaxes at time scales much longer than our detection window of 500 ps. The long-lived polarons corresponding to the PB and the PIA signals are a clear indication of interfacial charge generation upon hole injection from GaAs(111)B to P3HT. Therefore, when GaAs is selectively excited, holes are injected to P3HT; since the final state coincides with the electron transfer state from P3HT to GaAs (111)B, this process gives rise to similar PIA signal. Similar results were also reported by A.J. Heeger and co-workers¹⁷⁰ in PCPDBT/PCBM bulk heterojunction film, in which identical PB and PIA features of the

polymer are observed with energy-selective excitation of PCBM. This was attributed to ultrafast hole transfer from the HOMO of PCBM to the higher HOMO energies of the polymer, with identical final states following the electron transfer from PCPDBT to PCBM.^{157, 171}

Figure 5-13. (a) Transient reflectance spectra of GaAs/P3HT at various delay times following energy-selective photoexcitation of GaAs at 800 nm, (b) Transient reflectance decay profiles of photobleaching (PB) probed at 550 nm, and (c) photoinduced absorption (PIA) probed at 650 nm. The solid lines are multi-exponential functions fits.

Figure 5-14 summarizes the photophysics of the GaAs (111)B/P3HT bilayer following photoexcitation at 500 nm and selective photoexcitation of GaAs at 800 nm.

Figure 5-14. Schematic of the excitation and charge transfer pathways in GaAs (111)B/P3HT.

5.5 Summary and conclusions

In conclusion, we investigated charge photogeneration and charge transfer in a prototype hybrid *n*-type GaAs/P3HT bilayer by a combination of linear and ultrafast spectroscopy, and DFT calculations. Our ultrafast spectroscopy data provide consistent evidence for ambipolar charge transfer of electrons and holes across the heterointerface, where large populations of long-lived polarons is manifested by PIA and PB signatures with excitation either above or below the P3HT band gap.

These findings are in agreement with DFT simulations that predict a fairly large interfacial dipole moment due to electrostatic interaction of electrons accumulated at the GaAs (111)B surface and holes below the P3HT molecule adsorbed at the surface. Ambipolar charge transfer can be regarded as an interesting new concept to optimize photovoltaic power conversion efficiency of hybrid organic-inorganic devices. This work shows that efficient ambipolar transfer can be achieved at the interface between organic semiconductors and III-V compounds, and may be further optimized by bandgap and DOS engineering.

Chapter 6

Charge Redistribution at Hybrid GaAs/P3HT Heterointerfaces with Different Surface Polarity

The surface orientation of semiconductors can affect the density of surface states, energy levels, electronic orbital, and some of their intrinsic properties. By using DFT calculations, we have already shown that both GaAs (110)/P3HT and GaAs (111)B/P3HT foster electron transfer from P3HT to GaAs substrates. However, GaAs(111)B tends to promote hole transfer to P3HT compared to GaAs(110) surfaces.¹⁶² These results, therefore, suggest that the efficiency of GaAs/polymer hybrid solar cells would highly depend on the GaAs surface orientation. In this chapter, we investigated charge photogeneration in hybrid *n*-type GaAs/P3HT with different GaAs surface orientation. For this purpose, we choose both nonpolar GaAs (110) and polar GaAs (111)B surfaces. Time-resolved photoluminescence and transient reflectance spectroscopy of GaAs (111)B/P3HT were discussed in detail in chapter 5. In this chapter, we only focus on GaAs (110)/P3HT heterointerfaces. By using time-resolved photoluminescence and transient reflectance spectroscopy, we investigated the electron and hole transfer processes. Ultraviolet photoelectron spectroscopy (UPS) was used to determine the energy level position,

which was found to be strongly dependent on the surface orientation. Moreover, UPS data supported our DFT prediction, where it was found that different polarity of the GaAs surface affects the electronic orbital, and charge redistribution properties.¹⁵⁸

6.1 Energy level alignment

According to the integer charge transfer (ICT) model¹⁷² the energy level alignment of organic/inorganic systems with weak interfacial interactions can be determined from the change in work function upon adsorption of the organic molecule. Removing charges from the conjugated polymer can induce substantial geometric and electronic relaxation effects, which leads to localized positive polaronic states.¹⁷³ If the work function of substrate (Φ_{SUB}) is larger than the energy of the polaronic states ($E_{\text{p}+}$), electrons will spontaneously be transferred from the organic layer into the inorganic substrate, creating a dipole that reduces the vacuum level, where the interfacial dipole energy (Δ) caused by charge redistribution can be obtained from the energy difference between the Φ_{SUB} and $E_{\text{p}+}$. The position of the HOMO level of P3HT is determined to be 1.10 and 0.64 eV below the Fermi energy from the Fermi-edge regions of UPS spectra of P3HT-coated GaAs (110) and GaAs (111)B substrates. Meanwhile, from the cut-off of the UPS spectra, the work function of P3HT on GaAs (100) and GaAs (111)B substrates ($\Phi_{\text{P3HT/SUB}}$) are found to be 3.78 and 4.00 eV, respectively. To determine the energetics of the bare substrates, the thin P3HT films were removed by Argon ion sputtering, until the exposure of clean GaAs surfaces. GaAs (110) and GaAs (111)B substrates show the valence band maxima (VBM) of 0.69 and 0.68 eV and work functions of 4.76 and 4.95 eV. The LUMO level of P3HT is determined by adding the optical gap energy (1.9 eV) to the HOMO; similarly, the CBM of GaAs is the sum of VBM and GaAs optical gap energy (1.42 eV).

The overall picture of the energy level alignment determined by the above measurements is sketched in Figures 6-1(a, a'). A type-I heterojunction is obtained at the *n*-type GaAs (110)/P3HT interface, whereas a type-II heterojunction is observed at the *n*-type GaAs (111)B/P3HT interface, which are in good agreement with DFT predictions.¹⁵⁸ Both configurations favour electron transfer from P3HT to GaAs substrates due to the barrier between conduction band minimum (CBM) of GaAs and LUMO of P3HT film. The higher work function of bare GaAs substrates compared to the hybrid GaAs/P3HT systems could be attributed to the build-up of interfacial dipole barrier of -0.98 and -0.95 eV, respectively, which result from the displacement of negative charge from P3HT film to GaAs substrates. On the other hand, only in the case of GaAs(111)B the valence level offset is favourable for the hole injection from the P3HT layer ($E_{\text{HOMO}}-E_{\text{VBM}}=0.04$ eV), suggesting that P3HT could act as a 'hole acceptor'; opposite behaviour is expected for the GaAs(110) surface.¹⁶²

Figure 6-1. The energy diagrams of (a) GaAs (110)/P3HT and (a') GaAs (111)B/P3HT heterointerfaces obtained from UPS measurements.¹⁶²

6.2 Time resolved photoluminescence spectroscopy

In order to investigate the possible hole injection from GaAs (110) to P3HT, the PL dynamics were recorded at 860 nm following selective photoexcitation of GaAs at 800 nm. Figure 6-2 shows time-resolved PL dynamics of GaAs (110) and GaAs (110)/P3HT bilayer heterointerface. Since excitation energy is far below the P3HT optical gap, there is no contribution of P3HT emission in PL spectra of GaAs/P3HT, and PL is only dominated by emission of the GaAs. The PL decay dynamics were fitted to a multi-exponential function. The short PL lifetime in GaAs has previously been attributed to non-radiative relaxation, originating from charge trapping at surface-defect states.¹⁶⁷ According to the energetic level alignment between P3HT and GaAs, the formation of type I heterojunctions at the interface of GaAs and P3HT as well as position of valence level offset limits hole transfer to P3HT. Therefore, following selective photoexcitation of GaAs hole injection from GaAs (110) to the P3HT film is not anticipated to reduce the PL lifetime. Surprisingly, we find that lifetime of charge carriers in GaAs in the presence of P3HT film are enhanced. Similar results have been observed by Chaw Keong Yong and co-workers¹⁷⁰ for P3HT/GaAs nanowires heterojunction. They attributed the PL lifetime enhancement to the interfacial charge transfer between P3HT and GaAs. They show that electron transfer from HOMO of P3HT to surface states of GaAs nanowire effectively reduces the density of unsaturated surface state GaAs nanowire, leading to the enhancement of carrier's lifetime. Therefore, overcoating of GaAs with P3HT can effectively induce surface state passivation and enhance the carrier lifetime in GaAs.

Figure 6-2. Time resolved photoluminescence (TR-PL) of *n*-type GaAs (110) (black square) and *n*-type GaAs (110)/P3HT bilayer (red circle). The TR-PL spectra were recorded at 860 nm with photoexcitation at 800 nm. The PL decay dynamics were fitted to a multi-exponential function (solid lines), where t_1 , t_2 , and t_3 are the extracted lifetimes.

Figure 6-3 shows PL decays of pristine P3HT film and *n*-type GaAs (110)/P3HT bilayer. The PL decays were detected at ~660 nm following photoexcitation at 500 nm. Similar to the *n*-type GaAs (111)B polar surface, quenching of the polymer singlet excitons is observed which can be attributed to ultrafast electron transfer from P3HT layer to GaAs substrate. The TR-PL measurement of GaAs/P3HT heterointerfaces with different polarity of GaAs validates UPS measurements of the energy alignment of GaAs/P3HT interfaces as well as DFT prediction.

Figure 6-3. Time resolved photoluminescence of pristine P3HT film (Black Square) and *n*-type GaAs (110)/P3HT bilayer (red circle). The time TR-PL was recorded at 660 nm with photoexcitation at 495 nm. The PL decay dynamics were fitted to a multi-exponential function (solid lines).

6.3 Transient reflectance spectroscopy

In order to provide further evidence of charge transfer, transient reflectance spectroscopy was carried out to determine the photogenerated exciton/carrier dynamics across the GaAs/P3HT heterointerface. GaAs/P3HT bilayer heterointerface samples with the different polarity of GaAs (*i.e.* 111B and 110) were prepared with coating of 30 nm P3HT over the GaAs substrate. Figure 6-4 shows transient reflectance spectra of GaAs substrates, GaAs/P3HT, and transient absorption of P3HT over the spectral range from 350 to 850 nm measured at several different time delay times following excitation at 500 nm. Transient reflectance obtained from GaAs (110)/P3HT are significantly different than the spectra obtained from the control samples (*i.e.* P3HT film and bulk GaAs) even at delay times as short as 1 ps pump-probe delay time, consistent with ultrafast photoinduced charge transfer in the donor-acceptor bulk heterojunction systems. Several features are evident in the transient reflectance spectra of GaAs

(110)/P3HT: (1) a negative signal below about 600 nm, (2) a positive signal with the maximum peaks centred at ~ 660 nm, and (3) a broad PIA band above about 700 nm. The negative signal with three maximum at 600, 550, and 519 nm result from photobleaching of the absorption band of the pristine P3HT film. However, the photobleaching signal exhibit significantly longer lifetimes compared to transient reflectance lifetimes obtained from measurements on the pristine P3HT film. We note that (0-0) vibronic peak at 600 nm slightly overlaps with the tail of PIA.

Similar to GaAs (111)B/P3HT heterojunction, the appearance of a strong photoinduced absorption band above 630 nm with the maximum peaks centred at ~ 660 indicates enhancement of delocalized polaron formation due to the presence of the inorganic interface. The rise time of this band correlates well with the fast decay time of both the photobleaching signal below 600 nm due the depletion of the excitonic ground state. The PIA band nm persists beyond 250 ps temporal window of our measurement.

The longer lifetime of the polaron band was expected because charge transfer from photoexcited polymer to the conduction band of semiconductor forms a P3HT positive polaron and an electron transfer to the GaAs. This photoinduced charge separation at the GaAs/P3HT interface inhibits recombination of the hole polarons on the P3HT film; hence the longer lifetime. Therefore, charge transfer processes take place across the GaAs (110)/P3HT heterointerface, resulting in the formation of long-lived mobile polarons upon charge transfer induced exciton dissociation at the GaAs/P3HT heterointerface. The PIA band above 700 nm could result from excitation from either the excited state of the GaAs or the excited state of P3HT.

Figure 6-4. (a) Transient reflectance spectra of *n*-type GaAs (110), (b) transient absorption spectra of pristine P3HT film, and (c) transient reflectance spectra of *n*-type GaAs (110)/P3HT at various delay times after photoexcitation at 495 nm.

6.4 Charge generation versus crystallographic orientation

Figure 6-5 and 6-6 shows the $\Delta R/R$ transients probing the PB ($\lambda=550$ nm) and PIA ($\lambda=670$ nm) for the GaAs/P3HT with different surface polarity following photoexcitation at 500 nm and 800 nm, respectively. Both Figures show a comparison between the dynamics of hybrid GaAs (110)/P3HT (left) and GaAs (111)B/P3HT (right) systems. Dynamic traces obtained with

excitation wavelength at 500 nm (Figure 6-5) are attributed based on transient reflectance spectra (Figure 6-4).

Both hybrid GaAs (110)/P3HT and GaAs (111)B/P3HT systems show similar features: PB and PIA signals are long-lived (>1000 ps), consistent with the formation of charged polaron states in P3HT. The rise time of PIA correlates well with the fast decay time of PB signal due to the depletion of the excitonic ground state. The prolonged PB signal also indicates small re-population of excited states following charge transfer. The PB signal at 550 nm nearly instantaneously decays within few hundred of fs, to the $\sim 40\%$ of its initial amplitude. However, the number of long-lived charges left in GaAs (111)B are slightly larger than those in GaAs(110)/P3HT. These observations correlate well with DFT calculation that predict electron transfer from P3HT to GaAs is expected in both hybrid systems, but its largely favoured in the case of GaAs (111)B polar surface.

Figure 6-5. Transient reflectance decays of GaAs (110)/P3HT (left) and GaAs (111)B/P3HT (right) at 550 nm (PB) and 650 nm (PIA). Excitation wavelength: 500 nm.

Ultrafast spectroscopy data and energy considerations suggest that prompt formation of charges at the GaAs/P3HT heterointerfaces may be induced by either electron transfer from the photoexcited P3HT to GaAs or by hole injection from excited GaAs to P3HT.

To address this issue, we have excited GaAs/P3HT below the optical gap of P3HT. In this case, selective excitation of GaAs allows isolating hole injection from GaAs to P3HT. Figure 6-6 shows $\Delta R/R$ transients probing the PB ($\lambda=550$ nm) and PIA ($\lambda=670$ nm) following photoexcitation at $\lambda=800$ nm.

Figure 6-6. Transient reflectance decay profiles of GaAs (110)/P3HT (left) and GaAs (111)B/P3HT (right) at 550 nm (PB) and 650 nm (PIA) probe wavelengths. Excitation wavelength: 800 nm.

One- and two-photon absorption in P3HT was ruled out at these optical fluences from the absence of any photoluminescence or SE from the polymer. The transient reflectance spectra of *n*-type GaAs(111)B/P3HT bilayers excited at 800 nm shows similar features as in

photoexcitation at 500 nm (chapter 5). Notably, even without the direct excitation of the polymer, both PB and PIA features of P3HT are clearly visible. In the case of GaAs(111)B, the long-lived (up to ns) polarons corresponding to the PB and PIA signals (650 and 550 nm) indicate interfacial charge generation upon hole injection from GaAs(111)B to P3HT, with a final state that coincides with the electron transfer state from P3HT to GaAs(111)B. Therefore, upon selective excitation of GaAs (111)B, holes are efficiently injected into P3HT with $t < 1$ ps. Conversely, PB bands are absent in GaAs (110)/P3HT and transient reflectance signal at 550 nm mostly dominated by GaAs species. This indicates that hole transfer is unfavourable compared to the case of the polar GaAs (111)B orientation. Our observations of charge transfer are consistent with the theoretical predictions and UPS measurements. Figure 6-7 summarizes the photophysics of the both GaAs (110)/P3HT and GaAs (111)B/P3HT systems.

Figure 6-7. Schematic of the excitation and charge transfer pathways in GaAs/P3HT bilayer with two interfaces, GaAs (111)B/P3HT top panel and GaAs(110)/P3HT bottom panel. Only in the case of GaAs(111)B the valence level offset is favorable for the hole injection from the P3HT layer, suggesting that P3HT could act as a “hole acceptor”; opposite behavior is expected for the GaAs(110) surface.

6.5 Summary and conclusion

We investigated charge carrier photogeneration and transfer in hybrid GaAs/P3HT bilayers with different surface orientation (polarity) of GaAs by TR-PL and transient reflectance spectroscopy measurements. Our experimental data provide clear evidence for interfacial charge transfer of both electrons and holes at the GaAs/P3HT heterointerface. Both GaAs (110)/P3HT and GaAs (111)B/P3HT favour electron transfer from P3HT to GaAs substrate. The experimental transient reflectance measurements of GaAs/P3HT bilayers show clear signatures of both electron and hole transfer through the presence of large population of long-lived polarons in PIA signal as well as by the appearance of a characteristic long-lived hybrid-state PIA signals. Selective excitation of GaAs in GaAs (111)B/P3HT bilayers shows that hole injection from GaAs(111)B to P3HT induces long-lived ($\sim$ ns) PB and PIA, which is indeed absent in the case of GaAs(110). Our experimental findings are in agreement with the theoretical predictions, and provide a robust framework to understand and design hybrid photovoltaic systems.

Chapter 7

Summary and Recommendations for Future Research Works

7.1 Summary

In this dissertation, we have studied the processes of charge carrier generation, transfer and carrier dynamics at hybrid GaAs/P3HT heterointerfaces by a variety of spectroscopic techniques including ultrafast transient absorption, photoluminescence and steady state photoinduced absorption. The combination of several investigation techniques enables us to address all major excited species and probing their spectral features in a very wide spectral range as well as their dynamics. In addition to charge transfer investigation in the hybrid GaAs/P3HT bilayer heterointerface, we addressed the most important optical properties of two components, GaAs and P3HT. The effect of polarity of GaAs surface on hole injection to adjacent polymer chains, and correlation between transient absorption and reflectance spectroscopy data have also been studied in this dissertation. The interaction of polymer with III-V surfaces and charges distribution at the interface of P3HT with GaAs were also modelled using first-principle DFT method.

This thesis provides an understanding of the critical factors that enhances the photocurrent in hybrid photovoltaic devices through investigation of elementary processes at

ultra-short timescales after photoexcitation. In this respect, this research addresses the fundamental issues in prototype hybrid GaAs/P3HT bilayer to provide a general tool for the engineering of hybrid architectures that may have an impact in the entire organic PV research area. Major results obtained in this work are summarized in the following section.

The charge transfer investigation involved a mathematical formalism of the transient absorption and reflectance spectroscopy. The relationship between photoinduced reflectance and absorption was realized using the mathematical formalism that analytically explains the experimental observation of transient reflectance spectra of GaAs, P3HT, and hybrid P3HT/GaAs. The analytical model predicts that the differential reflectivity signal, $\Delta R/R$, mainly reflects the change in the refractive index (Δn) rather than the change in absorption coefficient ($\Delta\alpha$). However, the absorption coefficient dominates the differential transmittance signal, $\Delta T/T$.

Chapter 3 describes P3HT investigation, P3HT is one of the most important polymer in the field of organic solar cell, thus it was chosen as a model material. We implemented the spatial mapping of photocarriers in pristine P3HT and P3HT/PCBM films in a very wide spectral range, from visible to mid-infrared using steady state PIA spectroscopy. Charge carrier generation in pristine P3HT was also investigated by transient absorption spectroscopy. We show that in the absence of acceptor molecules (*i.e.* PCBM) small fraction of polaron is photogenerated as a result of strong interchain interaction which facilitates photoinduced electron transfer on the adjacent chain or neighbouring chain segments of the P3HT. The PIA spectrum of P3HT shows the formation of GSB well below 1.9 eV and two PIA bands P_1 at 0.4 eV and P_2 at 1.4 eV due to the formation of localized inter-chain polarons. The PIA spectrum also exhibits a series of photoinduced IRAVs modes below 0.2 eV, which spectrally overlaps with DP_1 that arises from the induced charge on the P3HT chain. Steady state PIA measurements of P3HT/PCBM blend film show that the PIA spectra are governed by the

optical transitions of P3HT. However, the overall strength of polaron bands and associated IRAV modes are significantly enhanced by almost one order of magnitude over those observed in the P3HT because of charge transfer induced exciton dissociation at the P3HT/PCBM interface. The PIA data shows that the ultrafast electron transfer from photoexcited P3HT to PCBM improves the quantum efficiency of the photogeneration of free carriers and suppresses the charge carrier recombination. As a result, polarons have a longer lifetime and thereby enhance the strength of PIA signal.

Chapter 4 addresses ultrafast processes in GaAs. The main processes responsible for the formation of transient reflectance spectra are analysed. The correlation between photoinduced absorption and photoinduced reflectance spectra of *n*-type GaAs is found using steady state photoinduced absorption measurements in both reflection and transmission modes. Transient reflectance spectroscopy provides the time evolution of charge carriers in the conduction band such that the photoinduced reflectance spectrum of GaAs exhibits similar spectral features of photoinduced absorption. The obtained photoinduced absorption and reflectance spectra of GaAs validates the theoretical prediction where differential reflectivity signal, $\Delta R/R$, is associated with the carrier induced change of refractive index (Δn).

The relaxation mechanisms of photoexcited carriers and intervally carrier evolution in GaAs are investigated using excitation of GaAs at the edge of the L-valley at $\lambda_{\text{exc}}=500$ nm. Contribution of the nonequilibrium heavy-hole, light-hole, and the split-off hole transitions were attributed to the spectral profile of *n*-type GaAs. Photoinduced reflectance spectrum of GaAs shows a negative band at 1.51 eV which is assigned to direct interband transition from the valence band maximum of available states to the bottom of the conduction band at Γ region in accordance with theoretical predictions. Two photoinduced bands at 2.87 and 3.12 eV were also assigned to $\Lambda_{3V}-\Lambda_{1C}$ and $\Lambda_{4V}-\Lambda_{1C}$ transitions, respectively. The kinetics of $\Delta R/R$ are in good agreement with theoretical prediction, indicating that bandgap shrinkage predominates

over band-filling effects within the initial short delay time after excitation, which yields in an almost instantaneous decrease in differential reflectivity signal.

Chapter 5 investigates the electron and hole transfer processes in GaAs/P3HT heterointerfaces. Our ultrafast spectroscopy data provide consistent evidence of ambipolar charge transfer of electrons and holes across the *n*-type GaAs (111)B/P3HT heterointerface. The UPS measurement on GaAs/P3HT reveals that the GaAs presents one of the most favourable energetics for electron transfer from P3HT. Measurements on the photoluminescence intensity at steady state and its time dependence at ultra-short time scales provide a clear evidence of interfacial charge transfer through the yield and the rate of radiative emission. The photoluminescence quenching of P3HT in the presence of GaAs indicates an effective charge transfer from P3HT to the GaAs substrate. Quenching of the integrated photoluminescence intensity is consistent with the well-known behaviour of P3HT/PCBM blends and other organic-inorganic hybrid systems. The spectral emission corresponding to the GaAs interband transition also suggests that GaAs acts not only as an electron acceptor but also as a light harvester. Transient reflectance measurements provided a profound understanding of the dynamics of the nonlinear photoexcitation processes. Transient reflectance spectra of GaAs/P3HT heterointerface exhibits the formation of a new PIA band which is long-lived and persists beyond 1 ns temporal window our transient reflectance measurements. The appearance of a strong photoinduced absorption band centred at 660 nm in GaAs/P3HT heterointerface indicates an enhancement of polaron formation due to the presence of the inorganic interface. The rise time of this band correlates well with the fast decay time of photobleaching signal at 500-630 nm.

Our photoluminescence and transient reflectance data provide a clear evidence for the formation of long-lived mobile polarons upon charge transfer induced exciton dissociation at the GaAs/P3HT heterointerface. Ultrafast spectroscopic data and energy considerations

suggest that the rapid generation of charges at the GaAs/P3HT heterointerfaces can be induced by either electron transfer from P3HT to GaAs or by hole injection from GaAs to P3HT. These findings are supported by DFT simulations.

DFT calculation demonstrated a fairly large interfacial dipole moment due to the electrostatic interaction of electrons accumulated at the GaAs (111)B surface and holes below the P3HT molecule adsorbed at the surface. It was found that the carrier lifetime of GaAs is enhanced as a result of hole injection to P3HT. Through selective excitation of GaAs, a strong contribution of hole injection from GaAs to P3HT was demonstrated. The transient reflectance spectra of GaAs/P3HT bilayer followed by photoexcitation at $\lambda_{\text{exc}}=800$ nm show similar spectral feature as at photoexcitation $\lambda_{\text{exc}}=500$ nm, namely PB and PIA bands. The long-lived PIA provides a clear evidence of charge generation upon hole injection from GaAs to P3HT. We demonstrated that ambipolar injection of electrons from photoexcited P3HT and holes from excited GaAs takes place at the interface of GaAs/P3HT. The ambipolar charge transfer can be regarded as an interesting new concept to optimize photovoltaic PCE of hybrid organic-inorganic devices.

Chapter 6 describes a more detailed investigation of the energy level alignment in GaAs with different surface orientation. Subsequently charge carrier photogeneration and photoinduced interfacial charge transfer at the heterointerface of a prototype P3HT and *n*-type GaAs substrates with different orientation and polar surfaces are discussed. We found that the surface orientation of *n*-GaAs affects the electronic orbital, charge redistribution properties, and energy level alignment with P3HT. We have shown that both GaAs (110)/P3HT and GaAs (111)B/P3HT favours electron transfer from P3HT to GaAs substrates. The obtained experimental transient reflectance data of GaAs/P3HT bilayers show clear signature of both electrons and holes transfer through the presence of large populations of long-lived polarons in PIA signal as well as by the appearance of a characteristic long-lived PB signal-. Selective

excitation of GaAs in GaAs (111)B/P3HT bilayers shows that holes injection from GaAs(111)B to P3HT induces long-lived ($\sim$ ns) PB and PIA, which is absent in the case of GaAs(110). All these findings have been already supported by UPS measurement and DFT calculations, which confirm that, irrespective of the crystal orientation, P3HT acts as an efficient electron donor. In the other words, the intrinsic surface dipole moment of GaAs surfaces is enhanced by induced charge displacement, facilitating hole transfer to P3HT in the case of GaAs(111)B.

7.2 Recommendations for future research

The present research provides a solid evidence of ambipolar charge transfer of electrons and holes on hybrid GaAs/P3HT heterointerface, where large populations of long-lived polarons is manifested by PIA and PB signatures with excitation either above or below the P3HT absorption energy. Our experimental findings provide a robust framework to understand and design hybrid PV systems. Although we show that electron transfer from P3HT to GaAs can occur in P3HT/GaAs bilayer, the transfer efficiency is only 3%. The next step would be to increase charge separation and reduce recombination pathways by using large interfacial areas in contact with the organic materials in hybrid solar cells, similar to bulk heterojunctions. This can be achieved using low-dimensional crystals, for instance, nanowires, and quantum dots, as solution additives while preserving conventional organic PV fabrication techniques and architectures. Low-dimensional compounds, such as GaAs nanowires or quantum dots can be effectively incorporated in hybrid organic-inorganic devices, providing a large extent of flexibility for the surface, bandgap, and DOS engineering. We suggest studying the heterogeneous integration of conjugated polymers with III-V compounds of various compositions and dimensionality.

This work highlights efficient ambipolar transfer can be achieved at the interface between organic semiconductors and III-V compounds, and could be further optimized by bandgap and DOS engineering. Given the flexibility offered by III-V compound semiconductors for bandgap and DOS engineering through the synthesis of low-dimensional structures, present charge transfer studies open an excellent opportunity for the design and characterization of organic-inorganic interfaces for further understanding of charge transfer and carrier dynamics in hybrid systems. The understanding of this fundamental issue in polymer/III-V composites will provide a general tool for the engineering of hybrid architectures.

Moreover, recent advances in perovskite solar cells materials suggest that these hybrid organic-inorganic structures can be used in combination with commercial solar cells (Si) in tandem architecture. We suggest that similar studies that we carried out in GaAs/P3HT may be repeated in Si/CIGS/GaAs/perovskite to screen by the DFT, transient absorption, and etc. for characterization hybrid interfaces.

Author's Publication

Journal publications

1. **M. Panahandeh-Fard**, M. Kumar, J. Yin, Z. Wang, F. Scotognella, and C. Soci, "Ultrafast Photoinduced charge transfer dynamics at hybrid GaAs/P3HT interfaces", in preparation.
2. J. Yin, D. B. Migas, **M. Panahandeh-Fard**, S. Chen, Z. Wang, P. Lova, C. Soci, Charge redistribution at P3HT/GaAs heterointerfaces with different surface polarity", *J. Phys. Chem. Lett.* 4, 3303 (2013).
3. **M. Panahandeh-Fard**, J. Yin, M. Kurniawan, Z. Wang, G. Leung, T.C. Sum, C. Soci, "Ambipolar charge photogeneration and transfer at GaAs/P3HT heterointerfaces", *J. Phys. Chem. Lett.* 5, 1144 (2014).
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Book chapter

1. J. Yin, M. Kumar, **M. Panahandeh-Fard**, Z. Wang, F. Scotognella, C. Soci, "Photoinduced charge transfer dynamics at hybrid GaAs/P3HT interfaces", in: *Ultrafast Dynamics in Molecules, Nanostructures and Interfaces*, G. G. Gurzadyan, G. Lanzani, C. Soci, T. C. Sum (Eds.), 2014, World Scientific Publishing Series in Optics and Photonics – Vol. 8 (ISBN 978-981-4556-91-0).

Conference presentations

1. European Materials Research Society (E-MRS) Spring Meeting 2014: Ultrafast electron transfer from P3HT to pyridine-capped InP quantum dots, J. Yin, M. Kumar, Q. Lei, **M. Panahandeh-Fard**, D. Cortecchia, Z. Wang, R.S.S. Kumar, C. Soci.
2. Institute of Physics Singapore (IPS) Meeting 2014: Pyridine-capped InP quantum dots as electron acceptors for polymer photovoltaics, J. Yin, M. Kumar, Q. Lei, **M. Panahandeh-Fard**, D. Cortecchia, Z. Wang, S.S. Kumar Raavi, C. Soci.
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Appendix A

Molecular structures of polymers discussed in this thesis

Table D-1. Chemical structures of some polymers have been used in hybrid solar cells.

F8BT

rr-P3HT

ZnPc

CuPc

TTP

NiPc

PEDOT:PSS

MgPc

Quaterthiophene (4T)

Octylthiophene (8T)

(PNDT-DTffBT)

PBnDT-DTffBT

Appendix B

Transient reflectance spectroscopy of pristine P3HT film

In chapter 2 we demonstrated that carrier induced optical effects cause the small change in reflection coefficient R . Therefore, change in reflectivity, ΔR , can be expressed in terms of the complex refraction index.

$$\Delta R = \frac{\partial R}{\partial n} \Delta n + \frac{\partial R}{\partial k} \Delta k \quad (\text{B1})$$

By using the Fresnel equation for reflectance at normal incidence, the differential reflectivity is given by

$$\frac{\Delta R}{R} = A(n, k) \Delta n + B(n, k) \Delta k \quad (\text{B2})$$

where

$$A(n, k) = \frac{4(n^2 - k^2 - 1)}{\left[(n+1)^2 + k^2 \right] \left[(n-1)^2 + k^2 \right]} \quad (\text{B3})$$

$$B(n, k) = \frac{8nk}{\left[(n+1)^2 + k^2 \right] \left[(n-1)^2 + k^2 \right]}$$

We demonstrated that change in reflectivity could be described as a function of frequency in terms of the absorption as

$$\frac{\Delta R(\omega)}{R} = A_R \frac{c}{\pi} \int_0^\infty \frac{\Delta \alpha(\omega')}{\omega^2 - \omega'^2} d\omega' + B_R \frac{c}{\omega} \Delta \alpha(\omega) \quad (\text{B4})$$

The relation between change in absorbance and change in reflectivity is very important to interpret the pump-probe reflectivity signal.

Figure B.1 shows refractive index and extinction coefficient of 100 nm RR-P3HT film. Below the energy gap of P3HT the magnitude of extinction coefficient, $|k|$, is very small. Therefore, the contribution of extinction coefficient to the differential reflectivity signal in this spectral region can be neglected.

Figure B-1. Refractive index and extinction coefficient of 100 nm pristine P3HT film.

In the spectral range $\lambda < 600$ nm, the magnitude of extinction coefficient of P3HT is one-fifth of refractive index so that the contribution of extinction coefficient will have the small contribution to observed photoinduced reflectance signal. In this case, the change in reflectivity (2) can be simplified as

$$\frac{\Delta R(\omega)}{R} = \frac{4\Delta n}{n^2 - 1} \quad (\text{B5})$$

Figure B.2 shows transient reflectance spectra of pristine P3HT film at various delay times with respect to photoexcitation at 500 nm. The differential transient reflectance is defined as $(\frac{\Delta R}{R} = \frac{R_{\text{pump}}^{\text{on}} - R_{\text{pump}}^{\text{off}}}{R_{\text{pump}}^{\text{off}}})$, where $R_{\text{pump}}^{\text{on}}$ designate the probe reflected with pump on, and $R_{\text{pump}}^{\text{off}}$, the probe reflected with pump off. Transient reflectance spectra show almost the same feature of transient absorption, PB signal with vibronic replica below 630 nm and SE band at 730 nm.

However, transient reflectance shows opposite sign and PB feature is slightly red-shifted as compared to transient absorption spectra. Heeger and co-workers have reported similar results for P3OT film. They reported that photoinduced absorption and reflectance spectra of P3OT films show almost similar feature with opposite sign.⁸¹ The sign can be deduced from

$$-\frac{\Delta T}{T} = d\Delta\alpha + \frac{2}{1-R}\Delta R \quad (\text{B6})$$

The mathematical formalism shows that the change in reflectivity signal is mainly dominated by the change of refractive index and not the change of absorption coefficient. Therefore, the change of refractive index is the dominant term for a carrier-induced reflectivity measurement on P3HT and transient reflectance can be described by equation (B2) and (B4). As shown in Figure B.2, vibronic replica in the refractive index of P3HT slightly red-shifted as compared to extinction coefficient. Therefore, the shift of PB signal provides further evidence that signal mainly dominated by the change in refractive index and not absorption coefficient. The band at 730 nm decays within 50 ps, according to the lifetime of singlet exciton in P3HT film this band again attributed to SE which arises from P3HT singlet exciton. However, the band at 750 nm is more pronounced than transient absorption. This can be explained by the higher sensitivity of transient reflectance to refractive index rather than absorption coefficient in the spectral region below the energy gap of P3HT.

Figure B-2. fs-transient reflectance spectra of the pristine P3HT film at various delay times after 500 nm excitation.

Figure B.3 compares normalized transient kinetics at 550 nm for both transmission and reflection modes. The decay is characterized by the triple exponential function. The decay times obtained from the fit are listed in Table. B.2.

Table B-1. Decay constant probed at 550 nm for reflection and transmission geometries. (Noted in parentheses as the normalized percentage *i.e* $[A_i/(A_1+A_2+A_3)] \times 100$).

Fitted decay times (ps)			
t_1	t_2	t_3	t_4
Reflection geometry			
0.46 (72%)	5 (15%)	55 (7%)	1300 (6%)
Transmission geometry			
0.43 (74%)	4 (16%)	72 (5%)	1300 (5%)

Figure B-3. Normalized decay kinetics of PB at 550 nm. Absorbance change (blue dot) and reflectance change (red dot).

Appendix C

UPS spectra of thin P3HT film on GaAs substrates

Figure C-1 and C-2 show UPS spectra of thin P3HT film on GaAs substrates at Fermi-edge regions and cut off, respectively.¹⁶²

Figure C-1. UPS spectra of thin P3HT film on GaAs substrates at Fermi-edge regions: (a) HOMO of P3HT on GaAs(110)=1.10 eV, (b) VBM of GaAs(110)=0.69 eV, (c) HOMO of P3HT on GaAs(111)B=0.65 eV, (d) VBM of GaAs(111)B=0.68 eV.¹⁶²

Figure C-2. UPS spectra of thin P3HT film on GaAs substrates at cutoff: (a) WF of P3HT on GaAs(110)=3.78 eV, (b) WF of GaAs(110)=4.76 eV, (c) WF of P3HT on GaAs(111)B=4.00 eV, (d) WF of GaAs(111)B=4.95 eV.¹⁶²

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