Compound semiconductor nanowires based organicinorganic hybrid solar cell

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**COMPOUND SEMICONDUCTOR
NANOWIRES BASED ORGANIC-
INORGANIC HYBRID SOLAR CELL**

WU DAN

SCHOOL OF ELECTRICAL AND ELECTRONIC ENGINEERING

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Abstract

As the demand for clean and sustainable energy sources increases, extensive research attention has been directed to photovoltaics owing to its inexhaustibility, abundance and wide availability. Despite the great efforts devoted, reasonable efficiency and price reduction are still the main issues to enable the solar cells to be fully competitive with traditional energy sources. Organic photovoltaics have provided a low-cost solution but the low efficiency and reliability issues threaten their wide application. Semiconductor nanowire (NW) arrays have demonstrated great potential for solar energy harvesting and material reduction. However, the lack for optimization and fabrication cost limit their large scale implementation. To further reduce the cost and improve the performance of the photovoltaics, hybrid solar cells (HSCs) based on III-V NWs and organics have emerged as promising candidates to combine the advantages of inorganic and organic materials. In this work, we unravel the role of III-V semiconductor NWs in the inorganics-organics HSCs through theoretical modeling, numerical simulation, device fabrication and characterization. First of all, an effective and efficient algorithm was provided to guide the design of geometrical dimensions for NW arrays to achieve maximal solar energy harvesting regardless of the materials, single or multiple diameters, and the arrangements of NW arrays. Compared with time-consuming numerical simulations, the proposed method maintained a low tolerance of below 2.2% for all cases. Next, an opto-electrical model was built to fully evaluate the performance of the GaAs NWs based HSCs elaborating the light absorbing features and electrical characteristics. Validation with the published experimental results had proved the effectiveness of the above two theoretical work. Thirdly, HSCs based on vertically aligned GaAs NWs fully-

infiltrated by poly(3-hexylthiophene-2,5-diyl) (P3HT) were fabricated and characterized. Well control over the diameters and periodicities of the GaAs NW arrays was realized by combining nanospheres lithography and dry etching. The role of the geometrical parameters of the GaAs NW arrays was investigated by characterizing the performance of HSCs. The power conversion efficiency (PCE) of the HSC reached 4.6% with the optimized GaAs NW arrays dimensions. We have also demonstrated a new prototype of low-material-cost GaAs NWs HSC. Freely standing GaAs NWs were for the first time directly grown on low-cost substrate of indium tin oxide (ITO) glass using Au nanoparticles as the catalysts by metal organic chemical vapor deposition (MOCVD). The size and area density controllable Au nanoparticles deposition by droplet-only method and centrifugation technique were initially developed to control over the diameters, position and the density of the as-grown NWs. Quantitatively and qualitatively study of the growth parameter' influence was also carried out to evaluate and optimize the growth of the GaAs NWs. Freely standing GaAs NWs of various sizes and area densities with high crystal quality were obtained. Based on these results, a prototype of the GaAs NWs/P3HT HSCs was developed which provided a new pathway of low-cost HSCs.

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Chapter 1 Introduction

1.1 Background and Motivation

With the fast growth of the population (over 7.5 billion in 2017) and rapid development of the modern society, the globally huge energy demanding problem becomes more and more severe. According to a report in the International Energy Outlook, they summarize and foresee a significant growth in worldwide energy demand from 1990 till 2040 as shown in Fig. 1.1. The total world energy consumption will expand from 629 quadrillion British thermal units (Btu) in 2020 to 815 quadrillion Btu in 2040. Currently, fossil fuels, petroleum, coal, and natural gas have all been largely consumed to account for about eighty percentage of the primary energy consumption [1]. However, these nonrenewable energy will eventually be depleted in the future at the current consumption rate resulting in serious energy crisis as predicted by the mid-21st century. Moreover, these non-renewable energy sources also cause the carbon pollution that leads to climate change and threatens public health [2]. In 1880s, the carbon dioxide (CO_2) concentration in the atmosphere was measured at 280 ppm and it has increased by 45% to 407 ppm in 2016 [3]. This large emission of CO_2 accounts for seventy to eighty percentage of the main composition of the greenhouse gases [4] which results in increase in sea level, global warming, ocean acidification etc.. Therefore, to address the energy crisis and environment issues, it is important to search for alternative energy sources that are secure, clean, and renewable, so as to sustain our long-term society development [5].

Figure 1.1 Summary and prediction of the world energy demand from 1990 to 2040.

Among various types of clean energy sources such as wind, marine, solar, geothermal energy and bioenergy, photovoltaics are considered as the most promising energy source since it is environmental friendly, widespread, and inexhaustible. It is calculated that the solar power that strikes on the earth's surface in one and half hours is about 482 exajoule (EJ) which is higher than worldwide energy consumption of 426 EJ in the whole year of 2001 [6]. It is also estimated that the sun can continue to shine for another 7 billion years [7]. Therefore, world-wide leaders have proposed effective policies and plans to stimulate photovoltaic technology [8]. The summary of solar photovoltaics capacity and additions for the top 10 Countries in 2016 is provided in Fig. 1.2. China has taken the lead in the implementation of photovoltaics due to the effective low-carbon energy policies [9]. The U.S. has rapidly increased 53.6% the amount of solar power in one year from 27.6 gigawatts (GWs) in 2015 to 42.4 GWs in 2016 and is expected to nearly tripled over the next five years [10].

Besides, the solar installed capacity of Japan and Germany have over 40 GW installed [11] which are considerably higher than any other parts in the world. With the current momentum, it is projected that the solar energy will become the world's largest source of electricity by 2050 according to the International Energy Agency [12].

Figure 1.2 Solar photovoltaics capacity and additions of the top 10 Countries in 2016 [13].

However, despite its fast development, solar energy is still one of the most expensive renewable energy sources, which is the major reason that it takes up only 1.5% of the global electricity production by the end of 2016 [13]. High-performance thick mono- and multi-crystalline silicon wafer-based photovoltaic cells constitute 80–85% of current global photovoltaic market owing to the natural abundance, high reliability and excellent lifetime of crystalline silicon materials. In March 2017, a record breaking over 26.3% power conversion efficiency (PCE) was reported by Kunta Yoshikawa *et al.*. This is close to the theoretical conversion efficiency limit of 29.1% for Si solar cells [14]. However,

the widespread use of silicon photovoltaic cells has been seriously limited due to the high processing cost of high-purity crystalline silicon materials [15-17]. Thin film silicon solar cells are very attractive for photovoltaics due to significantly reducing the amount of active material [18]. Up-to-date the recorded PCE for amorphous Si based triple-junction thin-film fabricated on periodically textured substrate with a stabilized efficiency of 13.6% [19]. However, due to the weak absorption of sunlight, thin film silicon solar cells are much less efficient [20]. In addition to inorganic solar cells, organic photovoltaics (OPVs) based on polymers or small molecules have attracted lots of attentions with advantages such as low material costs [21, 22], solution processability [23-25] and mechanical flexibility [26-28]. The recorded PCE of a polymer tandem solar cell has been reported by Yang Yang's group by achieving 10.6% [29]. However, due to limitation of the inefficient carrier hopping transportation and low dissociation efficiency of the excitons, it is still challenging to boost the PCE of OPVs while maintain their reliability.

This inspires the idea of organic-inorganic hybrid solar cells (HSCs) with the expectations that they possess the advantages of both the organics and inorganics. Hybrid heterojunctions are formed at low temperatures by a solution-processable method to replace the expensive p-n junction. Most of the incoming light will be absorbed in the inorganic semiconductor materials with proper band gaps. Thus, with proper design, it is expected that the efficiency of the hybrid inorganic/organic solar cells may in principle be comparable to conventional inorganic solar cells. In 2002, a HSC fabricated using CdSe nanorods and a conjugated polymer received a PCE of 1.7% [30]. Since then, there have been remarkable progresses made in the studies of HSCs taking the unique optical and electrical properties of the inorganic semiconductor NWs. Nanowires with

subwavelength scale have excellent light coupling and trapping capability and therefore offer comparable or better solar energy harvesting than their planar counterparts. Besides, the large surface-to-volume ratio provides efficient pathways for excitons dissociation and transportation. Along with the low fabrication cost, the NWs based HSCs promise bright future for highly efficient and low-cost solar cells solution. Up-to-date, the highest PCE of a GaAs NWs/polymer HSCs received 9.2% [31].

Despite the progress made, it is challenging to achieve high performance and low-cost inorganic semiconductor NWs based HSCs. Compared with the organics, most of the incident solar energy will be harvested by the inorganic NWs of proper band gaps and large extinction coefficients. It is clear that optimization of the NW arrays to absorb higher percentage of the incident solar energy is important to improve HSCs performance. However, there are few reports that directly disclose the optimal geometrical dimensions of NW arrays for maximal solar energy harvesting. What's more, there is lacking of opto-electrical model both focusing on the light absorption and the electrical performance of the HSCs. Beyond that, fabrication and characterization over the role of the geometrical dimensions of the NW arrays inside the hybrid active layer should be carried out which is indispensable for high efficiency HSCs. Moreover, novel low-cost NWs based HSCs are greatly needed to provide an alternative solution to the current HSCs design.

1.2 Objectives

In this thesis, the roles of the geometrical dimensions of inorganic III-V semiconductor NWs in the HSCs are thoroughly investigated to improve the

performance and reduce the cost of the NWs/organics HSCs. The scope of this research includes development and application of the effective and efficient algorithm and numerical model to analyze, and optimized the inorganic NW arrays for high performance of HSCs. Moreover, fabrication and characterization for well control over GaAs NWs are also carried out for developing low-cost and efficient GaAs NWs/P3HT HSCs. The objectives of this study are summarized as follows:

1. Design of optimal geometrical dimensions of III-V NW arrays for maximal solar energy harvesting is highly demanded without relying on the time-consuming numerical simulations. We will develop an analytical algorithm which provides a fast and accurate route to find out the exact values of diameters and periodicities of NW arrays leading to maximal solar energy harvesting. This algorithm will be applied to the NW arrays regardless of the materials, various diameters combinations, and arrangement manners. The accuracy of the algorithm will be compared by both the published experimental results and widely adopted finite-difference time-domain (FDTD) simulations.
2. A numerical model that cooperatively design the light harvesting and the electrical characteristics is indispensable to guide the design of NW arrays/organics HSCs. We will propose an opto-electrical model that co-designs both the solar energy harvesting and the electrical characteristics of NWs based HSCs. The light absorption features of the fully-infiltrated NWs/organics HSCs will be analyzed and optimized. Following that, the opto-electrical model will be constructed to disclose the influence of the geometrical dimensions of the NWs on the photovoltaic performance of the HSCs. The accuracy of the model will be checked by comparison with published experimental results.

3. Although the light harvesting capability of GaAs NW arrays are seriously affected by the geometrical dimensions, most of the reported GaAs NW arrays/organics HSCs still neglect their influence. We will fabricate GaAs NW arrays/P3HT HSCs in which the geometrical dimensions of the NWs are varied, analyzed, and optimized for better photovoltaic performance. Fabrication of GaAs NW arrays will be performed and the diameter, periodicity and length of the NW arrays will be well controlled. Characterization of the performance of the device will be carried out to understand the influence of geometrical dimensions of the NWs on the HSCs.

4. The conventional design and fabrication of inorganic III-V NWs based HSCs usually compose of hundreds of micrometers underlying III-V wafers. We will design and fabricate a prototype of NWs based HSC by direct growth of GaAs NWs on transparent conductive substrate. The morphology, area density, and crystal quality of GaAs NWs will be quantitatively and qualitatively analyzed, controlled and optimized through variation of the growth parameters and characterization techniques. The influence of the as-grown GaAs NWs on the photovoltaic performance of this novel NWs based HSC will also be investigated.

1.3 Major Contribution of the Thesis

The major contributions of this thesis are summarized as follows corresponding to the respective objectives described above.

1. An effective and efficient algorithm was proposed for optimal geometrical dimensions of the vertically-aligned GaAs and InP NW arrays for maximal solar

energy harvesting. The algorithm was applied to single, two, and four diameters NW arrays arranged squarely and hexagonally to pursue the largest short-circuit current densities upon solar illumination. For single diameter NW arrays, the optimal diameters were 168 nm for GaAs and 184 nm for InP to excite two resonant modes while remain their FWHM of HE_{11} mode in the absorbing region. Compared with the experimental work, the optimal diameter was only 4 and 3 nm difference to the reported highest efficiency InP and GaAs NWs solar cells. By matching the absorption valley of the primary NWs, the optimal secondary diameters of GaAs and InP NW arrays are 114 and 119 nm. Through comparison of two diameters InP NW arrays arranged squarely and hexagonally, we demonstrated that the proposed algorithm was valid regardless of the arrangement of NWs. Moreover, broadband high absorption was achieved for four diameters NW arrays through matching their respective resonant wavelengths to the valleys of the superposition of the primary and secondary NWs' normalized absorption efficiency spectrum. Therefore, the third and fourth diameters were 92 and 140 nm for GaAs NWs whereas 92 and 148 nm for InP NWs. At the same time, the effective medium layer method combined with Fresnel reflection and transmission leading to the optimal FR of 0.22 for GaAs and 0.2 for InP NWs despite various diameters combinations. The optimal geometrical dimensions of four diameters NW arrays led to the highest short-circuit current densities of 29.88 and 33.13 mA/cm² for GaAs and InP respectively. Besides, intensive numerical three-dimensional FDTD simulations were also carried out to find the optimal geometrical dimensions of various NW arrays for maximal solar energy harvesting. Compared with the simulations, the predicted maximal short-circuit current densities from our method lied within 2.2% tolerance for all cases. Along with the high accuracy, through directly disclosing the exact geometrical dimensions of NW arrays, this algorithm provided an

effective and fast route for guiding the high performance NWs based photovoltaic design.

2. A coupled opto-electrical model for simulating the semiconductor NWs based HSCs has been developed. This model provided a thorough insight of the photovoltaic process in NWs based HSCs as a function of the diameter of NWs and periodicity. An active layer consisting of GaAs NWs as acceptor and poly(3-hexylthiophene-2,5-diyl) (P3HT) as donor were studied. Absorption features were fully explored by studying the electrical field intensity distribution around the NWs. The resonant modes were clearly identified containing the leaky modes and Fabry-Perot resonance. Focusing firstly on the GaAs/air layer before extending to GaAs/P3HT hybrid active layer gave the fundamental understanding of the influence of the organics layer on the incident energy harvesting. The highest absorption efficiency reached 39% for the hybrid active layer under AM 1.5G illumination. Combined with the optical absorption analysis, our method coupled with the electrical model to predict electrical performance of HSC considering excitons dissociation, transportation, and collection efficiencies within both inorganic NWs and a polymeric shell of 20 nm thickness. The validity of the simulation model was also proved by the well agreement of the simulation results with the published experimental work indicating an effective guidance for high performance HSC design.

3. Hybrid solar cells based on GaAs NW arrays and P3HT were fabricated and characterized. The effects of the NWs' diameters and periodicities on the HSCs performance have been investigated. The GaAs NW arrays were formed by top-down method combining nanospheres lithography and inductively coupled plasma reactive ion etching (ICP-RIE). Spin-coating technique and self-assembly

at ethanol-water interface method were investigated to form low defects density and hexagonally closely packaged polystyrene (PS) nanospheres. Monolayer of closely packed PS nanospheres of 500, 350 and 200 nm monolayer were achieved to serve as etching masks. Through optimization of the dry etching condition, uniform and hexagonally arranged GaAs NW arrays with various diameters and periodicities were obtained. The HSCs were fabricated by infiltration the P3HT into the forest of NWs. The photovoltaic performances were measured along with the numerical study of the role of NWs. In general, the rise of periodicity of NW arrays would decrease the photon harvesting when FR was fixed which was mainly due to the poor light coupling efficiency. For a fixed periodicity, the rise of FR would cause the competence of energy harvesting among adjacent of NWs which lowered the PCE. The highest PCE achieved was 4.6% for 200 nm periodicity and FR of 0.44. This study further clarified the role of geometrical dimensions of GaAs NWs in HSC which also demonstrated the potential of inorganics/organics HSC for large-scale application.

4. A prototype of low-material-cost GaAs NWs HSCs has been proposed by growing of freely standing GaAs NWs directly on indium tin oxide (ITO) using Au nanoparticles (NPs) as catalysts by metal organic chemical vapor deposition (MOCVD). An area density controllable Au nanoparticle deposition method on ITO was presented by centrifugation. The highest area densities for Au NPs were achieved as 509 NP/ μm^2 for 10 nm and 130 NP/ μm^2 for 20 nm. Freely standing GaAs NWs were grown on ITO without kinks or worm shape defects. A kinetic model was adopted to quantitatively analyze each growth parameters including the growth temperature, precursor flow rates, growth time, and the size of the Au catalysts. These investigations showed thermally activated growth of GaAs NWs with activation energy of 65 kJ/mol. The growth rate of NWs was linearly proportional to the precursor flow rates of trimethylgallium when the V/III ratio

was 9.5. Also, the growth rate decreased as the shrink of the Au catalysts due to the Gibbs-Thomson effect. The smallest Au NPs was calculated as 2.14 nm.to induce the NWs growth. Moreover, there were almost no observable crystal defects along the NWs. It was noticed that larger size of Au NPs (20 and 40 nm) induced NWs possessed zinc-blende structure whereas wurtzite structure was found for 10 nm Au NPs induced NWs. This was due to the supersaturation differences caused by the size of the catalysts. A prototype of the GaAs NWs/P3HT HSC was fabricated and characterized. It was proved that the ohmic contact had been formed among GaAs NWs and the ITO. These results provided an alternative pathway of fabrication of low-cost organic/inorganic HSCs.

1.4 Organization of the Thesis

This thesis consists of seven chapters which are organized as follows:

Chapter 1: An introduction is presented including the background, motivation, objectives, and major contributions of this research topic. The organization of this thesis is also described.

Chapter 2: The basic structures and the photovoltaic process of the NWs based HSCs are presented. Following that, the theoretical background is mainly covered focusing on the light trapping of NWs and the opto-electrical model construction for NWs based HSCs. Then, the widely used organic and inorganic materials for NWs based HSCs are summarized. Focus is put on III-V NWs based HSCs.

Chapter 3: An analytical design is presented to effectively and efficiently approach the optimal geometrical dimensions of GaAs and InP NW arrays for

maximal solar energy harvesting. Detailed description about this algorithm is described followed by its applications for single, two and multiple diameters NW arrays of various arrangements. The validity of the algorithm is verified by comparing the predicted results with those received by the intensive FDTD simulations.

Chapter 4: A coupled opto-electrical model is proposed to fully explore the performance of NWs based HSCs. Light absorbing characteristics of GaAs NWs fully-infiltrated by P3HT are systematically investigated followed by the generation of photogeneration profiles upon solar illumination. Next, an electrical analysis is presented to study the effect of the geometrical dimensions of NWs on the photovoltaic performance of HSCs. In the last part, the validity of the model is also proved by well prediction of the HSC performance of the published work.

Chapter 5: Hybrid solar cells based on fully-infiltrated GaAs NW arrays/P3HT are fabricated and characterized. Vertically aligned GaAs NW arrays are fabricated by nanospheres lithography and ICP-RIE. Formation of closely packed monolayer of the PS nanospheres as etching masks are described in details. Following that, optimal lithography condition is found for NW arrays of various diameters and periodicities. Photovoltaic performance is evaluated along with theoretical study to unravel the NW's role in HSCs.

Chapter 6: Direct growth of freely standing GaAs NWs on transparent conductive oxide substrate is presented by MOCVD followed by a prototype of low-material-cost NWs based HSC. An area density controllable Au nanoparticles deposition method is proposed serving as catalysts for NWs growth. Well control

over the morphology and crystal quality of the GaAs NWs are realized through quantitatively and qualitatively study of the growth parameters. Based on these, a prototype of low-material-cost of GaAs NWs HSC is fabricated and characterized which provides an alternative design for future HSCs.

Chapter 7: A summary of the work done and suggestions for future work are presented.

Chapter 2 Literature Review

This chapter reviews the theoretical background and the research work in current literatures on nanowires (NWs) based hybrid solar cells (HSCs). The chapter begins by elaborating the fundamentals of solar cells and the typical structures of the NWs based HSCs. Theoretical study about the NWs based HSCs are reviewed focusing on the light trapping of NWs and the opto-electrical model construction. In the last part, the most frequently used organic and inorganic materials for HSCs are reviewed and the respective advantages and disadvantages are compared.

2.1 Introduction and Fundamentals of Hybrid Solar Cells (HSCs)

2.1.1 Introduction of Solar Cells

Solar cells are devices that directly convert sunlight into electrical energy. They consist of a light absorbing material typically in the form of a semiconductor p-n junction connecting to an external circuit [32-34], as shown in Fig. 2.1. There are four main steps involved in the solar energy conversion including light absorption, charge separation, carrier transportation and collection. Upon illumination of the sunlight, the photons with energy larger than the band gap of the light absorbing material will be absorbed and electron-hole pairs (or excitons in the organics) are generated. Those electron-hole pairs are dissociated by the electric field built in the p-n junction and swept across the junction as the majority carrier without recombination. The carriers are driven to the respective contacts and pass through the external circuit to form the electricity. In this way, the solar cell creates a photovoltage at the external circuit and deliver electrical energy when it connects to a load.

Figure 2.1 Schematic for working principle of a solar cell.

Solar cells are generally classified into three generations. The first generation solar cells are single p-n junction devices. They are fabricated from the high quality single crystalline or multicrystalline semiconductor wafers. Highly efficient as they are, they suffer from high material and production cost. The second generation solar cells are semiconductor thin-film solar cells. They consume much less material but with lower efficiency. The third-generation solar cells are made from emerging technologies and new materials such as NWs, organic dyes etc.. They aim to achieve higher efficiency at lower cost.

Among the third generation solar cells, research on organic photovoltaics (OPVs) has attracted a lot of interest mainly due to their potential as an affordable energy harvesting technology [35-38]. To increase the power conversion efficiency (PCE), the most successful design is the creation of an active layer by mixing the donor poly(3-hexylthiophene-2,5-diyl) (P3HT) and acceptor Phenyl-C61-Butyric-Acid-Methyl-Ester (PCBM) polymer to form a bulk heterojunction with full interpenetrating networks [39]. However, the interpenetrating network cannot be effectively formed by the two polymers in the way to provide a continuous path for the carriers to transport through. In addition, due to the short exciton diffusion length ~ 20 nm [40] and low mobility, the polymers are not

efficient in the carrier transportation. Therefore, the PCE of a bulk heterojunction OPV is still limited by the low dissociation probability of excitons and the inefficient hopping carrier transportation.

Inorganic semiconductor NWs based HSCs are hence proposed with the purpose of achieving higher PCE by incorporating the advantages associated with both the inorganic and organic materials. Compared with the OPVs, the only difference is that the organic electron accepting material of PCBM (or other fullerene derivatives), is replaced by an inorganic NWs. The advantages of this design lie in the light harvesting, excitons dissociation and transportation, as well as device reliability. On the optical side, both components have the ability to absorb incident light energy unlike the typical polymer fullerene system where the fullerene contributes very little to the photocurrent generation [41]. Moreover, modification of size and shape of the inorganic NWs at nanometer scale results in absorption spectrum profile variation, which can improve the light absorption efficiency. On the electrical side, the high aspect ratio of the NWs can provide large interfacial area resulting in efficient exciton dissociation. Also, direct transport pathways generated by NWs will increase the carriers transport efficiency by reducing recombination loss [30]. Moreover, the inorganic semiconductor materials are more stable which can help overcome the photon induced degradation of the polymers to improve device reliability.

2.1.2 Typical Active Layer Structures for Inorganic Nanowires based HSCs

The basic structure of an inorganic semiconductor NWs based HSC consists of a photoactive layer sandwiched between the two electrodes. The photoactive layer is a mixture of the inorganic semiconductor NWs and organic polymers. Transparent conductive oxide such as indium tin oxide (ITO) is deposited on a transparent substrate serving as electrode. Light illuminates through this side of electrode. The organic material is spin coated on the ITO glass or NW arrays.

The NWs can be synthesized by bottom-up or top-down methods. The other electrode is usually deposited on the active layer by thermal evaporation [32].

Figure 2.2 Schematics of basic structures of inorganic semiconductor NWs based HSCs with (a) bulk and (b) interdigital heterojunctions.

There are two main types of heterojunctions of the NWs based HSCs including bulk heterojunctions [39] in Fig. 2.2(a) and interdigital heterojunctions in Fig. 2.2(b). For the bulk heterojunctions, the NWs are peeled off from their grown substrates and randomly mixed with the organic material. The mixture is deposited onto a substrate to make a photoactive layer. This structure is simple but the NWs in the mixture tend to aggregate which will prevent efficient donor acceptor (DA) interfaces formation. Exciton dissociation will be hindered [42]. At the same time, the vertically aligned NWs can stand on the substrates of the same inorganic material with organic material spin-coated over. Ordered heterojunctions are generally considered as an ideal configuration for efficient exciton dissociation and charge transport as shown in Fig. 2.2(b) [43]. In such a structure, the distance from exciton generation sites in the donor material to the DA interfaces can be controlled. After exciton dissociation, both holes and electrons transport along separate pathways to the respective electrodes.

2.1.3 Photovoltaic Process for HSCs

The photovoltaic process of NWs based HSCs is shown in Fig. 2.3. Organics is

donor and inorganic NW is acceptor. In the organic material, lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) should form staggered band gap alignment with conduction band (CB) and valence band (VB) of the inorganic material. Upon illumination, both the organic and the inorganic materials in the active layer absorb photons and generate excitons. Excitons diffuse to the DA interfaces and are separated into free carriers if the band gaps of the two materials are staggered. Electrons are held by the inorganic NWs which have higher electron affinity while holes are captured by the polymer with high ionization energy. The carriers are then transported to the respective electrodes through either inorganic NWs (for electrons) or polymer (for holes) and generate the photocurrent.

Figure 2.3 Schematics of the energy level arrangement and photovoltaic process for inorganic NWs based HSC (LUMO: lowest unoccupied molecular orbital; HOMO: highest occupied molecular orbital; CB: conduction band; VB: valence band; $h\nu$: incident photon energy).

2.2 Nanowires for Solar Energy Harvesting

2.2.1 Introduction of Light Interaction with Nanowires

Strong light trapping makes the inorganic semiconductor NWs especially attractive in the photovoltaic application. Compared with the organic materials,

the extinction coefficients of the inorganic materials can be orders of magnitude higher. Therefore, the inorganic materials play the major role in the hybrid active layer for solar energy harvesting. As a result, to maximize the light absorption of the NW arrays is one of the prerequisites to guarantee high performance of NWs based HSCs. The most attractive feature is that the light absorbing cross-section of NWs can be several times of their physical cross-section dimensions which enable high light absorption. This favorable property is largely dependent on the geometrical dimensions of NW arrays. Specifically, for the widely adopted cylindrical NW arrays, the diameter, periodicity, length and arrangement of NW arrays all play important roles.

Researchers focus on different aspects of the enhancement of incident energy harvesting of NWs and the theoretical basics origin largely form the Mie scattering theory and/or leaky/guided mode theory. In the following, we provide the basic description of the two theories to explain of the light interaction with NWs. Following that, we present the literature review of the represented work in the light trapping of NWs. Detailed mathematical derivations of the individual theories can be found in many textbooks such as Refs. [44, 45].

2.2.2 Description of Light Interaction with Nanowires by Mie Theory and Waveguide Theory

The interaction of light with inorganic semiconductor NWs can be analytically described in two ways. One is Mie theory which focuses on the extinction, scattering and absorption of light incident on infinitely long cylinders [44]. The other is waveguide theory, according to which the infinitely long circular cylinders support waveguide modes [46]. These modes can be bound to the peripheral of the NWs (guided modes) or radiate into the surrounding medium (leaky modes) while propagate along the axes of NWs.

Description of Light Interaction with Nanowires by Mie Theory

Upon a plane wave incidence, an infinitely long cylinder suspended in a non-absorbing and homogeneous medium will cause light scattering and absorption due to the material property with a complex refractive index for the incident spectrum. As shown in Fig. 2.4, the electric field $\vec{E}$ of the incident light oscillates in the plane containing the axis of the cylinder and the incident wave vector $\vec{k}$. A cylinder of diameter D (radius r) is illuminated by a plane wave whose direction is described by the angles θ and ϕ . The angle θ is measured from the axis of the cylinder to the direction of $\vec{k}$. Due to the cylindrical symmetry of the cylinder, the incident wave vector can only be described by θ irrespective of azimuthal angle ϕ .

Figure 2.4 Coordinate system considered in Mie theory including an infinitely long circular cylinder of diameter D illuminated with a plane wave with vector $\vec{k}$ incident from a direction described by two angles (θ, ϕ) .

By solving the Maxwell's equations in the cylindrical coordinates, we obtain the light absorption of the infinite cylinder based on the expansion of the electric and magnetic fields of the incident and scattered light into infinite series of vector cylindrical harmonics. The concept of optical cross section is used to measure the amount of energy that can be removed from an incident light which has the unit

of area. Therefore, the absorption cross section describes the amount of incident light that is absorbed by the cylinder. By taking the normalization to the geometrical cross section of the cylinder, the absorption efficiency is calculated. The detailed mathematical derivations of Mie theory can be found in the references [45, 47].

Description of Light Interaction with Nanowires by Waveguide Theory

According to the waveguide theory, light propagates in the infinitely long circular cylinders can be referred to as optical modes. These modes fall into three categories: 1) radial mode resonance, 2) near-field evanescent wave coupling, and 3) Fabry-Perot (F-P) mode along the axial direction of NWs [46]. Radial modes appear when the incident light couples effectively with NWs at a certain wavelength. These modes are the electromagnetic wave solutions to the radial boundary conditions. They are also referred to as leaky modes since their field intensity can leak out from the peripheral of the NWs in radial direction and decay as they are far from the NWs. Near-field evanescent wave coupling happens among the adjacent NWs. These modes are a component of leaky modes but extend outside of NWs. When the spacing of adjacent NWs is narrow, the same evanescent waves from neighboring NWs may significantly overlap with each other. In this case, the power can move from one NW to the other. This means the amplitude of one leaky mode decreases causing the rise of the amplitude of the other NWs leading to near-field coupling. Both modes attenuates as the modes propagate along the axis of NW. Moreover, the boundary condition at the tip and base of the NWs cause the F-P modes. They describe the longitudinal standing wave solutions along the length of NWs through constructive interferences of the guided waves. The localized peaks in the electric field amplitude along the axis of NWs are mostly caused by this F-P mode.

Leaky mode resonance is the key phenomenon that closely relates to light

trapping and coupling of the incident light since they can capture large amount of light which can be several times of their geometrical cross-section dimensions. To obtain the analytical expression of leaky modes, the expansion of the electric and magnetic fields inside and outside of the cylinder in vector cylindrical harmonics involving Bessel and Hankel functions are required. A detailed derivation of the electric and magnetic fields in a cylindrical structure can be found in reference [47].

2.2.3 Representative Work of Optimal Solar Energy Absorption in Nanowires

Since 2009, NWs have been intensively investigated as promising candidates for efficient sunlight trapping across a wide solar spectral range [48] whose theoretical background is described in the above sections [44]. Linyou Cao *et al.* demonstrated the leaky mode resonance within the separated Ge NWs [48]. In this pioneer work, they pointed out the possibility to engineer resonant modes inside the NWs to tune their spectral absorption features. Later, they also proved the diameter-dependent multicolor light scattering of individual Si NWs [49, 50]. They showed that variation of the geometrical dimensions of the NWs to change their absorbing characteristics was universal to any semiconductors [50]. Their work was focused on the selectivity of light absorption and the control over the light absorption spectrum rather than maximal light harvesting. Grzegorz Grzela *et al.* reported that the enhanced absorption of NWs was realized through tailored the leaky/guided modes [51]. They also provided the detailed mathematical derivations of Leaky/Guided mode for infinite cylinders [52].

Along with the study of separated NWs, research focus has been put on the NW arrays for photovoltaic applications. The absorbing properties of the single diameter InP NW arrays can be modified by adjusting their geometrical parameters by Nicklas Anttu *et al.* [53]. Both theoretical study and experimental

measurements were adopted to verify their conclusions [54]. The geometrical dimensions of the InP NWs were optimized as 180 nm. They successfully fabricated InP NWs solar cells reaching the recorded efficiency of 13.8% in 2013 [55]. Double or multiple diameters NW arrays also attracted great attention to achieve higher absorption of incident solar spectrum [56-58]. Harry A. Atwater *et al.* reported four diameters of III-V NW arrays to achieve near-unity of light absorption [56, 57]. Multi-diameters NW arrays of Si and GaAs [59, 60] have been studied in their later work [61].

There are also reports that focus on the influence of the arrangement of NW arrays on light absorption [48]. In 2013, Pere Roca i Cabarrocas *et al.* studied the arrangement of Si NW arrays [58]. By comparison of the squarely and hexagonal NW arrays, they drew the conclusions that it was the material filling ratio that mattered instead of the arrangement of NWs. This was because the strongest light trapping of NWs was due to the individual propagation of confined modes which relied less on the periodic arrangement.

However, most of the publications adopted time-consuming numerical simulations to achieve the localized optimal geometrical parameters of the NW arrays for maximal solar energy harvesting. Apparently, these optimal values are seriously parameter-space-determinant. Moreover, the drawbacks of the numerical simulations become more obvious for multiple diameters NW arrays. Due to the long period of time for data acquisition, only a handful of design examples can be provided. Recently, Bjorn C. P. Sturmberg *et al.* proposed the ideas that greatly narrowed down the range of the optimal geometrical dimensions of single diameter NW arrays for maximal light harvesting. This method was suitable to the most frequently used IV and III-V materials for photovoltaics [62]. Nevertheless, it is still limited to single diameter NW arrays and the optimal zones vary for hundreds of nanometers for periodicity of the NW arrays.

2.3 Theoretical Study of Inorganic Nanowires based HSCs

2.3.1 Theory for Optical and Electrical Modeling of HSCs

Theoretical study of inorganic NWs based HSC is indispensable to guide the design and evaluate the performance of the device fabrication. Upon illumination, photons will be absorbed by the hybrid active layer containing both the organics and the inorganic NWs. Excitons are generated in the organics whereas electron-hole pairs are generated in the inorganic NWs. The excitons will diffuse to the interfaces among the organics and the inorganic NWs to be dissociated into free carriers. Next, the electrons and holes will transport to respective electrodes through either NWs (for electrons) or organics (for holes) [43]. During the process, the six key efficiencies will affect the device performance: 1) light absorption efficiency (η_{abs}); 2) exciton generation efficiency (η_{gen}); 3) exciton diffusion efficiency (η_{diff}); 4) exciton dissociation efficiency (η_{disso}); 5) carrier transport efficiency (η_{trans}); 6) carrier collection efficiency ($\eta_{collect}$). To quantitatively analyze the performance of HSC, external quantum efficiency (EQE) is defined as a percentage of the number of charge carriers collected at the electrode under short-circuit condition to the number of photons incident on the device. It can be expressed as the product of the above efficiencies.

$$EQE = \eta_{abs} \times \eta_{gen} \times \eta_{diff} \times \eta_{disso} \times \eta_{trans} \times \eta_{collect} \quad (2.8)$$

To numerically simulate the performance of the NWs based HSCs, the photovoltaic process in the device under solar illumination is usually subdivided into two parts: optical absorption and the electrical performance of the photovoltaic device.

Light Absorption of Nanowires Based HSCs

To evaluate light harvesting, early work usually adopts Shockley-Queisser detailed balance calculation. This is based on geometric optics assuming of perfect light absorption and no recombination other than radiative. Therefore, each exciton contributes to the short-circuit current [63]. However, the light absorbing characteristics of NW arrays with subwavelength scale are mainly influenced by their geometrical dimensions. It is necessary to evaluate the light absorption efficiency in a way including the geometry of the NW arrays using wave optics. For NWs based HSC, the NWs are surrounded by the organics. The electric field distributions should be analyzed considering the dispersive properties of the organics.

After acquisition of the electric field distribution, the excitons and/or electron-hole pairs in three-dimensional distribution will be obtained. Next, these excitons will transport to DA interface to be dissociated. If the distance between the exciton generation location and the DA interface is larger than the diffusion length, the excitons will recombine. This gives the constraint on the exciton diffusion efficiency [64]. After dissociation the electrons and holes will transport to respective electrodes through interpolated pathways and will be collected by the cathode and anode.

Electrical Modeling of Nanowires Based HSCs

To characterize the electrical performance of HSC, the widely accepted equivalent circuit is shown in Fig. 2.5, which has been verified by the HSCs fabricated using various materials [43]. The photocurrent source J_{ph} describes the ability of converting photons into free carriers under illumination. A diode parallel to the photocurrent source generates the dark current, which represents how much the photovoltaic device behaves like a diode without illumination. The series resistance R_s origins from the resistance of active layer and the contact

resistance with electrodes whereas the shunt resistance R_{sh} accounts for the leakage current in the device [65].

Figure 2.5 Equivalent circuit of a HSC.

This equivalent circuit proposed by Petrisch for solar cells directly gives the final form of the J - V relation in Eq. 2.1 [43]. The shunt resistance is usually an order of magnitude greater than the series resistance and is neglected in the analysis. The reverse saturation current J_{sat} of the Schottky diode is given by Richardson's thermionic emission equation where A^* is the effective Richardson's constant. V_{bi} is the absolute value of built-in voltage of the anode and the inorganic NWs. k_B is Boltzmann constant and T is absolute temperature. q is elementary charge. Since the mobility of the charges in polymer is orders of magnitude lower than in the inorganic materials, we assume that all the internal resistance arises only from the polymer.

$$J = J_{sat} \left[\exp \left(q \left(\frac{V - JR_s}{k_B T} \right) \right) - 1 \right] - J_{ph}, \quad (2.1)$$

$$J_{sat} = A^* T^2 \exp \left(- \frac{V_{bi}}{k_B T} \right).$$

As shown in Fig. 2.6, the J - V curves of the HSCs are therefore calculated. The four characteristic parameters to reflect the performance of a solar cell are the

open circuit voltage V_{oc} when the current is zero; short-circuit current density J_{sc} when the biased voltage is zero. Fill factor FF and the PCE η are defined in the below Eqs. 2.2 to 2.4 [66]. $P(E)$ is the spectral irradiance of the standard solar spectrum [67].

Figure 2.6 The current voltage and power-voltage characteristics of an ideal cell.

$$J_{sc} = q \int P(E) \eta(EQE) dE \quad (2.2)$$

$$V_{oc} = \frac{kT}{q} \ln\left(\frac{J_{sc}}{J_0} + 1\right) \quad (2.3)$$

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}. \quad (2.4)$$

2.3.2 Representative Work of Optical and Electrical Simulation of Nanowires Based HSCs

Early as 2003, Balaji Kannan *et al.* gave the first systematic theoretical analysis of the operation and performance of the nanostructured interdigital

heterojunction HSCs [64]. In their work, a theoretical model was developed to analyze the performance of heterojunction HSCs composed of ordered inorganic NWs surrounded by polymers. The light absorption of the inorganics was neglected. They drew the conclusions that to obtain reasonable efficiencies, the size and spacing of the nanostructures should be on the order of the exciton diffusion length scale. Later work took into consideration of the absorption of NWs. The effect of size and periodicity of NW arrays were studied within the hybrid active layer but the diameter of NWs was limited below 50 nm [68].

In most of these investigations, light absorption in the NWs was estimated in the way of geometric optics. Nevertheless, when the diameters of NWs fall in the range comparable to the solar spectrum wavelengths, their absorption characteristics are influenced both by their geometrical dimensions and material composition [20]. Therefore, in the more recent work, researchers adopt the coupled opto-electrical design [69] to fully evaluate device performance accounting both the size effect as well as intrinsic material property [70, 71]. Wang *et al.* used coupled opto-electrical simulation to describe the conformal coating thickness of the organics on HSC performance [72, 73]. Due to the addition of organic coating, higher light absorption was obtained both at the spectrum below and the above the critical wavelength of the organics. This was because below the critical wavelength of organics, both the organics and the inorganics could harvest light. Above the critical wavelength, the organics served as nonabsorbent and dielectric shell which decreased the difference of the refractive index of the organics and air and harvested more light.

2.4 Organic and Inorganic Materials for Nanowires Based HSCs

Proper choice of organic and inorganic materials in HSC is crucial to the overall efficiency. In this part, we will summarize the major organic and inorganic semiconductor materials that are currently being used in HSC devices.

Advantages and disadvantages will be listed and different groups of materials will be compared.

2.4.1 Commonly Used Organic Donors

In semiconductor NWs based HSCs, the organics is used as donors to harvest light, generation excitons and transport holes. According to the photovoltaic process in the section 2.1.3, band gaps of the organics should be reduced to absorb a large portion of the solar spectrum. At the same time, the LUMO energy band edge should close to the CB of inorganic material to avoid energy loss by an amount of binding energy. Binding energy is provided for excitons dissociation. HOMO level of the organic material should be low enough to maximize open circuit voltage [43]. Besides, the organics should also have high hole mobility. The materials are desired to be self-assembled to an organized structure for efficient carriers transport by thermal or solvent annealing.

Poly [2-methoxy-5-(20-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) has been the focus of the early work. They have large band gap of 2.4 eV [74] leading to a low photon absorption efficiency. Also the low device performance is attributed to the small hole mobility to around $10^{-5} \text{ cm}^2/\text{Vs}$ [75]. Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) with band gap of 1.6 eV and better solubility have demonstrated better device performance [76]. P3HT with smaller band gap of 2 eV and the improved mobility are favored in later research [77]. Through thermal annealing, the hole mobility in the P3HT phase of the P3HT: PCBM is increased by more than three orders of magnitude, to reach a value of up to $\approx 2 \times 10^{-8} \text{ m}^2/\text{Vs}$ as a result of an improved crystallinity of the film [78].

Table 2.1 Summary of MEH-PPV, PTB7, and P3HT properties

Name	MEH-PPV	PTB7	P3HT
Chemical structures
HOMO (eV)	-5.1	-5.15	-5.2
LUMO (eV)	-2.7	-3.31	-3.3
Energy band gap (eV)	2.4	1.84	1.9
Reference	[32]	[79]	[80]

Chemical structures energy band gaps of the three most commonly used organic donors are listed in the Table 2.1. We also summarize an energy band diagram of commonly used organic polymer and inorganic semiconductor NWs in the Fig. 2.7. This gives the guidance to choose the appropriate polymer and inorganic acceptor material pairs with proper energy offsets. The energy levels shown are from isolated donor and acceptor materials. When they are in contact with each other and form junctions, these energy levels may shift due to interface dipoles. For simplicity these effects are not considered here.

Figure 2.7 Energy band gaps for commonly used donor and acceptor materials.

2.4.2 Commonly Used Inorganic Acceptors

According to Fig. 2.7, we can find that most of the combinations of the organic polymer and inorganic NWs satisfy staggered band alignment, but for high efficiency device there are other factors to be considered. Band gap of the materials must be minimized to absorb more portion of the solar spectrum. As open-circuit voltage is dependent on the diagonal band gap difference of inorganic CB and organic HOMO. Besides, there should be an energy offset of the CB with respect to the organic LUMO which is required to facilitate exciton dissociation [32]. What is more, available NWs synthesis method is also an important factor. For ideal ordered heterojunction structures, the vertical or freely standing NWs morphology are required [81]. We divide the commonly used acceptor materials into four groups including cadmium compound, silicon, metal oxides, III-V compound semiconductor materials [32].

Cadmium compounds such as CdTe, CdSe, CdS have attracted lots of interest in early hybrid photovoltaic applications [82-85]. Although they have appropriate energy levels to combine with organics, the reported PCE of cadmium compounds combined with organics usually below 3% and the toxicity of the material limits their application. Metal oxides have also been investigated as possible candidates for the HSCs [86-90]. The main advantage is the ability to form ordered heterojunction in large quantities. However, electronic structures of metal oxides are not desirable for acceptor material in HSC. The PCE of metal oxides NWs based HSC is usually lower than 5%.

Due to the abundance of Si compounds, non-toxicity, and low band gap~1.12 eV [91], Si NWs combined with organics have attracted lots of attentions [92-98]. The wet [99] and dry etching synthesis method enables the Si NWs to penetrate deep into the conjugated polymer matrix which are of great advantages for improving device performance. There are mainly two routes for Si NWs based HSC fabrication. One is deposition organics on the surface of ITO and then the Si NWs are pressed onto the organics shown in Fig. 2.8(a). The other method is drop-casting the organics onto the surface of the Si NWs and then attaching the transparent conductive electrodes over the organics illustrated in Fig. 2.8(b). The highest PCE reported is 13% by Peichen Yu *et al.* in National Chiao-Tung University. They used wet etching method to fabricate Si NWs and then deposited TAPC and PEDOT:PSS on top of Si NWs [99]. In order to form proper DA interface, 2,2',7,7'-tetrakis(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD) small molecule has also been introduced by Rusli *et al.* [100]. It was found that the Si NWs/Spiro cells exhibited a PCE of 10.3%, which was higher than the Si NWs/PEDOT cells with the same architecture. The reasons were mainly attributed to organics infiltration ability to fill the gaps between the Si NWs leading to increase in the junction area, better surface passivation, and decrease in the reflectance.

Figure 2.8 Process flow schematics for Si NWs based HSC.

2.4.3 III-V Nanowires based HSCs

III-V materials such as InP and GaAs NWs based HSC are also widely investigated [31, 101-108]. These materials are suitable for photovoltaic device fabrication since they possess excellent optical and electrical properties including direct band gap and high electron mobility. Due to desirable band gap of 1.43 eV for GaAs and 1.34 eV for InP, they can make use of a great portion of AM 1.5 G incident spectrum.

Ordered III-V NWs have been synthesized by both top-down and bottom-up methods. The top-down method for synthesis III-V NW arrays are favorable for photovoltaic device fabrication. In most of the cases, the NWs are formed by dry or wet etching [31, 102, 109-111]. For dry etching in Fig. 2.9, in the first step, the nanospheres form a closely packed monolayer on top of the III-V wafers as the etching mask where the diameter of the nanospheres can be tuned by plasma etching. The periodicity of the nanospheres arrays can be controlled by choosing

different diameters of the nanospheres. Inductively coupled plasma reactive ion etching (ICP-RIE) system is usually adopted to form vertically NW arrays [110, 111]. The remaining nanospheres will be removed before the fabrication of the HSCs. For wet etching, a famous metal-assisted chemical etching method was firstly introduced for GaAs in 2011[109]. The aim was to form high aspect ratio NWs with low damage to the crystal structure and lower cost compared with the reactive ion etching method involving the high-energy ions. However, despite the great advantages associated with this methods, to obtain high morphology of NW arrays the experimental window was rather narrow as stated in the patents filed by the same group [112].

Figure 2.9 Schematic of nanosphere lithography combining with ICP-RIE forming vertically aligned III-V NW arrays.

For bottom-up approach, the NWs grow from a vapor phase precursors to from the supersaturated liquid alloys inside foreign metal nanoparticles (such as Au) at elevated temperatures which is described by the vapor-liquid-solid (VLS) mechanism in 1964, as shown in Fig. 2.10 [113]. The chemical potential difference at the surface of the metal particle drives the continuous precipitation of semiconductor material to the liquid-solid interface. By continuous supply of the growth material, the eutectic alloys crystallize and form the NWs. Nanowires growth use Au nanoparticles as catalysts via VLS mechanism by metal organic

chemical vapor deposition (MOCVD) is one of the most common and promising techniques for III-V NWs growth because of the precise control over complex axial structures and large scale commercialization capability.

Figure 2.10 Schematic of vapour-liquid-solid growth mechanism.

There are various reports on study, analyze, and optimize the bottom-up growth of III-V NWs since control over the morphology and crystal quality are vital to the device performance [114-129]. Systematic study was carried out about the growth parameters influence on the growth rate of III-V NWs on the same substrates including the temperature, precursor flow rates, time, and the size of the catalysts [114, 121, 122, 125, 129, 130]. Kinetics analysis is also reported to have a fundamental understanding of the growth rate and crystal quality as a function of those parameters [116, 120, 128]. Besides, there are reports focusing on the direct growth of III-V NWs on low cost substrates such as glass [131] and transparent conductive oxide [125, 127, 132] for photovoltaics fabrication [133].

The highest PCE reported for GaAs NWs HSC was 9.2% by Chao *et al.*[31]. Organic material of P3HT and PEDOT:PSS were infiltrated into the GaAs NW arrays as shown in Fig. 2.11. By tuning the dry etching time, various morphologies of GaAs NW arrays were obtained. There are also reports that focusing on NWs grown directly on low-cost substrate coating transparent

conductive oxide (TCO). Clint J *et al.* reported MOCVD growth of InP NWs on ITO and fabricated the HSC. They proved that the ohmic contact formed between InP NWs and ITO. According to their results, the free-standing InP NWs acted as acceptor and P3HT was used as donor. The reasons for low short-circuit current density of $2.2 \times 10^{-6} \text{ A/cm}^2$ included the non-uniformity of the thickness of the active layer across the sample, and the leakage source at the interface between the NWs and the polymer. GaAs NWs had also been grown by MBE on ITO and HSC were fabricated with full infiltration structure with P3HT achieving PCE of 1.04% [101].

Figure 2.11 The cross-sectional SEM images of GaAs NW arrays after being dry-etched for 1 min and the contact morphology between organic materials and GaAs NW arrays [31].

2.5 Conclusion

In this chapter, the development of inorganic NWs based HSCs is introduced focusing on the numerical analysis of solar energy harvesting of the NWs, opto-electrical model construction, organic/inorganic materials for HSCs, and the performance analysis. To begin with, bulk and ordered heterojunctions are presented as two typical NWs/organics hybrid active layers followed by the photovoltaic process description. Next, Mie theory and Waveguide theory are

briefly introduced to explain the theoretical background of the light trapping of NW arrays for photovoltaic applications. Following that, the literature review of solar energy harvesting of NW arrays is presented. Besides, the opto-electrical models of the NWs based HSCs are introduced emphasizing on coupled design of both the light absorption and the electrical characteristics of the hybrid active layer. Basic concepts such as EQE, open-circuit voltage, short-circuit current, and PCE are elaborated. A brief review is followed to cover the represented literatures in the opto-electrical numerical study of the NWs based HSCs. In the last part, the most commonly used organics and the inorganic NWs in the current literatures are summarized. Inorganic III-V NWs are the research focus of this thesis and both top-down and bottom-up synthesis methods of NWs are introduced followed by the literature review of fabrication process and device performance of III-V NWs based HSCs.

Chapter 3 An Efficient and Effective Design of the Optimal III-V Nanowire Arrays for Maximal Solar Energy Harvesting

Semiconductor nanowire (NW) arrays based solar cells promise comparable or better performance than their planar counterparts taking the advantages of strong light coupling and light trapping. In Chapter 3, we present an accurate and time-saving analytical design of the optimal geometrical dimensions of vertically aligned GaAs and InP NWs for maximal solar radiation absorption. Followed by the development of this algorithm, it was applied to single and multiple diameters of NW arrays with different arrangement manners. The geometrical dimensions were quantitatively calculated for maximal solar energy harvesting. Short-circuit current densities of the NW arrays with the optimal geometrical dimensions was computed to evaluate their light harvesting capability. In the meantime, the largest short-circuit current densities for GaAs and InP NW arrays were also obtained by the widely-adopted but time-consuming finite-difference time-domain (FDTD) numerical simulations. Compared with the two results, the small difference demonstrated that our analytical method provided a fast and accurate route to guide maximal solar energy harvesting for III-V NW arrays.

3.1 Introduction and Motivation

Semiconductor III-V NWs are attracting intense interests in photovoltaic application due to their unique optical and electrical properties [134, 135]. Firstly, because of the leaky mode resonance (LMR) supported in the NWs, they can concentrate and absorb light more efficiently [48, 52]. Besides, vertically-aligned NW arrays can form heterojunctions in the radial directions which decouple the requirements for light absorption and carrier collection into orthogonal spatial directions. The NWs can be long in the direction of the incident light, allowing

for optimal light absorption, and thin in the radial direction allowing for effective carrier collection [16]. GaAs and InP NWs are considered as the promising candidates to achieve excellent photovoltaic performance. This is because they hold high absorption coefficients, ideal band gaps and are capable of incorporation core-shell or axial multi-junction structures [107, 136]. Lots of efforts have been devoted to the geometrical design of NW arrays to maximize solar energy harvesting. This is because their light absorption properties are both determined by the geometrical dimensions and the material properties. Geometrical parameters of the NW arrays, such as the diameter [56, 57, 137-140], the length of NWs [58], periodicity [53, 140, 141], and the arrangement [58, 142, 143], are numerically studied for maximal light absorption. Specifically, it is reported that tuning the diameter of the NW will change the optical modes existed within the NW. This will lead to localized light absorption maxima for those incident wavelengths corresponding to the respective resonant modes [50, 52, 138, 140]. Also, NW arrays with optimized periodicity or filling ratio (FR) can suppress the reflection and transmission while enhance the scattering to the incident light resulting in the prolonged optical path and thus the enhanced light absorption [141, 144, 145]. Besides, Martin Foldyna et al. have concluded that the dependence of the light absorption on the arrangement of the NW arrays is rather small since the light trapping effect of NWs is based on the individual wave-guiding when the light coupling among neighboring NWs is neglected [58]. However, most of the obtained optimal values are parameter-space-determinant let alone the time-consuming process. To solve this problem, Sturmberg *et al.* proposed a semi-analytic method to rationally narrow down the range of the optimal geometrical dimensions of the NW arrays which was applicable to various materials [146]. Nevertheless, the confined range was still among hundreds of nanometers for periodicity and the algorithm was limited to single diameter NW arrays. Hence, an effective and efficient design is greatly desired to directly find out the exact optimal geometrical parameters for maximal solar

energy absorption regardless of diameters, arrangement manners, and the materials of III-V NW arrays for photovoltaic application.

In this chapter, we propose an analytic algorithm to calculate the optimal geometrical dimensions of the GaAs and InP NW arrays in order to achieve the highest solar energy harvesting. Diameters of the NWs were computed based on the LMR and Mie theory mentioned in Chapter 2. The optimal periodicity of the NW arrays was determined according to the effective medium layer to minimize light reflection and transmission. The proposed algorithm was then applied to single, two, and four diameters of NW arrays arranged squarely and hexagonally to calculate the optimized geometrical parameters. The short-circuit current densities were obtained for each optimized NW arrays. Meanwhile, intensive FDTD numerical simulations were carried out to find out the optimal geometrical dimensions of the NW arrays for highest solar energy absorption. The well matching of the short-circuit current densities calculated from our optimized NW arrays and the largest short-circuit current densities obtained from numerical simulations proved the effectiveness of the proposed method.

3.2 An Analytical Design of III-V Nanowire Arrays for Maximal Solar Energy Harvesting

3.2.1 Algorithm Description of Optimal Geometrical Dimensions for Nanowire Arrays

Most of the semiconductor NWs based core-shell or hybrid solar cells have the NWs vertically aligned [43, 68]. As shown in Fig. 3.1, the NWs are squarely arranged with the smallest repeatable unit cell as identified in the inset. Each unit cell consists of four NWs standing on SiO₂ substrate with the same or different diameters, D_i . In this chapter, our method is fully explored in the single, two and four different diameters of NW arrays. In the single diameter case, all four diameters of NWs in the unit cell have the same value. In the two diameters case,

the diameters of the diagonal NWs such as D_1 and D_3 or D_2 and D_4 have the same value whereas the NWs in the same column and row have different values. All of the four NWs in the unit cell have different diameters in the case of the four diameters NW arrays. The four NWs are named according to the sequence in our analytical method to obtain each value and are therefore named as primary, secondary, third and fourth NWs. Besides, periodicity p is defined as the center to center distance of a pair of adjacent NWs which has the same value for squarely arranged NWs as shown in the Fig. 3.1 inset. Accordingly, the filling ratio (FR)

of the squarely arranged NW arrays is defined as $\pi \sum_{i=1}^4 D_i^2 / (4p)^2$ which has the

maximal value of $\pi/4$ when the NWs take up the largest volume percentage of the unit cell [147]. The length L of the NW is set as $2 \mu\text{m}$ for all following cases [148].

Figure 3.1 Schematic of vertically aligned III-V NW arrays arranged squarely with inset explaining the unit cell.

To analytically determine each geometrical parameter of NW arrays, the optimization problem for maximal solar energy harvesting should be decomposed into two processes. The first one is the NWs' diameter-determinant resonant mode control and the second one is FR-affected minimal reflectance and transmittance of incident solar energy. We construct the relationship of individual geometrical parameter with respective determinant process. Therefore, the optimal value of each geometrical parameter can be separately identified. Two

diameters NW arrays are chosen as the example for illustration. The diameters of one pair of NWs are named as primary diameter $D_{primary}$, and the rest two are named as secondary diameter $D_{secondary}$. As a simpler case, the optimal geometrical dimensions of single diameter NW arrays can be acquired during the derivation. The diameters and periodicity for four diameters NW arrays can also be calculated as an extension of the design example.

It is reported that NWs can support LMR which lead to strong absorption peaks. The waveguide characteristics of NWs suggest that more resonant modes are supported by the NW with a larger diameter. Consequently, the optimal diameter of NW should be large enough to support more modes so as to include larger number of absorption resonances. However, too large diameters of NWs are less preferable since the higher order modes possess more nodes which couple less efficiently to the incident plane waves [146]. As a result, it is proved that the NWs that support two resonant modes locating inside the absorbing region are able to best improve the light absorption [56]. This conclusion greatly narrows down the range of the optimal diameter of NWs but still cannot provide a clear clue to directly approach the exact value of the diameter. Besides, the material property and the incident solar spectrum place other limitations on the selection of the optimal diameter. Only when the resonant modes lie within the absorption region, they can contribute to the photocurrent. The absorption region is defined by the superposition of the material absorbing range of up to critical wavelength and the incident AM 1.5G spectrum [67].

As shown in Fig. 3.2, to quantitatively determine the $D_{primary}$ of the NW arrays, LMR is initially adopted to calculate the respective resonant wavelengths for different diameters of NWs [48]. This gives the distribution of the resonant modes in the absorption region. The optimal $D_{primary}$ should support two modes and satisfy all of the rest criterions. Secondly, Mie theory is adopted to calculate the normalized absorption efficiencies of the primary NWs. Strictly speaking,

Mie theory cannot be applied to the situation when the incident wavevector aligns perfectly parallel to the axis of NWs since the eigenvalue equation is ill-defined [134]. However, this situation can be approximated as the glazing incident of the incoming light (very small incident angle θ with respect to the axis of NWs as shown in Fig. 3.1). At the interface of incident light and the NW arrays, the wave front of the incident light will be perturbed by the high index of NWs which introduces transverse components to the wavevector allowing the adoption of Mie theory [140]. Therefore, the optimal $D_{primary}$ is the one who supports two modes while keeps the full width at half maximum (FWHM) of the normalized absorption efficiency spectrum of the lowest resonant mode within the absorption region. After acquisition of $D_{primary}$, the $D_{secondary}$ is calculated on the following condition. The secondary NWs should support one mode for reducing reflection and their resonant wavelength should match the valley of the $D_{primary}$'s normalized absorption efficiency spectrum.

Figure 3.2 Flowchart of analytically geometrical dimension design for two diameters NW arrays.

The periodicity of the NW arrays can be computed by construction of an effective medium layer. This artificial layer represents the reflection and transmission of the NW arrays which is only related to the FR of the material of the NWs. As a

result, the diameter, periodicity, and the arrangement of the NW arrays are removed from the calculation. In this way, the transmittance and reflectance of NW arrays can be evaluated by applying Fresnel equations on this effective medium layer and therefore the optimal FR can be analyzed. Based on the relationship of FR and periodicity, the periodicities for the squarely arranged NW arrays are obtained. Detailed description of our proposed method is presented in the following sections.

3.2.2 Optimal Diameters of Nanowire Arrays for the Highest Solar Energy Absorption

To increase the solar energy absorption, the number of resonant modes leading to strong absorption peaks should be maximized within the absorption region. On the blue end of the absorbing region, incident AM 1.5G spectrum confines 300 nm as the high energy region. On the red end of the absorbing region, the critical wavelength λ_c corresponding to the material absorption band edge limits on the low energy region. The critical wavelength λ_{criti} is defined as $E_g q = hc/\lambda_{criti}$ where E_g is the band gap energy; q is the elementary electron charge; h is plank constant; c is the speed of light in the vacuum. According to the above requirements, the range of primary diameter can be calculated from the eigenvalue equation derived from Maxwell's equations [140]. Considering the anti-symmetric in-plane field distribution of the incident plane waves, only the HE_{1m} modes can be effectively excited to contribute to the absorption of vertically-aligned NWs [138]. These HE_{1m} modes satisfy the eigenvalue equation and the resonant wavelengths can be obtained assuming that the real part of the propagation constant $Re(\beta_z)$ of the mode along NWs axial direction approaches zero as shown in Eq. 3.1. k_{cyl} and k_{air} are the transverse components of the wavevector inside the NWs and in the air whereas ϵ_{cyl} and ϵ_{air} are the respective permittivities. J_1 and $H_1^{(1)}$ are the first order Bessel and Hankel functions of the first kind, respectively. As a consequence, the range that primary diameter falls in can be received on the

condition that the corresponding HE₁₁ and HE₁₂ mode lie within the absorbing region.

$$\frac{\varepsilon_{cyl} J_1'(k_{cyl} D_{prim} / 2)}{k_{cyl} J_1(k_{cyl} D_{prim} / 2)} - \frac{\varepsilon_{air} H_1^{(1)'}(k_{air} D_{prim} / 2)}{k_{air} H_1^{(1)}(k_{air} D_{prim} / 2)} = 0. \quad (3.1)$$

According to the Mie theory, the absorption efficiency Q_{abs} of NWs is defined by the ratio of the energy collecting area over the geometrical size of the NWs. In the realm of physical optics, when the diameter of a NW is smaller than the illuminating wavelength, Q_{abs} can be much bigger than 1. This means that the NWs can collect light from a region much larger than its geometrical boundary. Although Q_{abs} is different from the absorption efficiency of NW arrays whose value ranges from zero to unity, when normalized to its maximum value, the two efficiencies will display the same trend. Therefore, the Q_{abs} can be used to evaluate the absorbing properties without seeking to time-consuming simulations. Confirmed by both experiments and simulations [48], Mie theory provides a feasible way to predict the absorption efficiency of NWs with large illuminating angles θ as shown in Fig. 3.1. At small illuminating angle, Mie theory loses its accuracy in predicting the absorption efficiency since the length of NWs is not considered in its formulation. However, in our case, the longitudinal absorption play a minor part in determination of the diameter, and that is the reason we can also use Mie theory to estimate the low order mode absorption at the grazing incidence. The analytical expression of absorption efficiency Q_{abs} is given in Eq. 3.2 and 3.3 and the exact mathematical formalism of Mie theory can be found in the reference [44]. Here $\bar{n}=n+ik$ is the complex refractive index, as mentioned above J_i and $H_i^{(1)}$ is the Bessel and Hankel functions of first kind of order i .

$$Q_{abs,TM} = \frac{2}{x} \text{Re}(b_0 + 2 \sum_{i=1}^{\infty} b_i) - \frac{2}{x} [|b_0|^2 + 2 \sum_{i=1}^{\infty} |b_i|^2] \quad (3.2)$$

$$Q_{abs,TM} = \frac{2}{x} \text{Re}(a_0 + 2 \sum_{i=1}^{\infty} a_i) - \frac{2}{x} [|a_0|^2 + 2 \sum_{i=1}^{\infty} |a_i|^2]$$

$$a_i = \frac{\vec{n}J_i(\vec{n}x)J'_i(x) - J_i(\vec{n}x)J'_i(x)}{\vec{n}J_i(\vec{n}x)H_i^{(1)'}(x) - J'_i(\vec{n}x)H_i^{(1)}(x)} \quad (3.3)$$

$$b_i = \frac{J_i(\vec{n}x)J'_i(x) - \vec{n}J_i(\vec{n}x)J'_i(x)}{J_i(\vec{n}x)H_i^{(1)'}(x) - \vec{n}J_i(\vec{n}x)H_i^{(1)}(x)}.$$

After acquisition the Q_{abs} , the FWHM of each HE_{11} mode corresponding to different diameters of NWs can be found out. Therefore, the optimal diameter for maximal light harvesting is determined. For single diameter of NW arrays, the diameter of all NWs is obtained at this stage. For two diameters of NW arrays, the secondary diameter is confirmed on the condition that its normalized absorption peak wavelength should match the normalized absorption efficiency valley of the primary diameter of NWs. For four diameters NW arrays, the third and fourth diameters are determined in a similar way. Their normalized absorption efficiency peaks should match the valleys of the superposition of normalized absorption efficiency spectrum of the primary and secondary NWs.

3.2.3 Optimal Periodicity of Nanowire Arrays for the Highest Solar Energy Absorption

Various published work has disclosed that with fixed diameters of NWs, the absorption efficiency of the NW arrays initially increase with the FR and then drop after certain optimal value [146]. The rise of light absorption is usually attributed to the increase of volume percentage of the semiconductor materials with high absorption coefficients. As FR further grows, the average refractive index of the NW arrays increases and thus the reflection rises which reduces light

absorption. Therefore, an upper limit on the FR should be found to maximize the absorption of the NW arrays. Figure 3.3 schematically illustrates that an effective medium layer with complex refractive index is created to represent the refraction and transmission of the NW arrays. In this way, the diameter, periodicity, and the arrangement of the NW arrays are removed from the calculation.

Figure 3.3 (a) Reflected and transmitted light of zeroth and higher orders of NW arrays and (b) the effective medium layer showing the first two terms of the infinite Fabry-Perot reflection and transmission series.

The real part of the refractive index of the effective medium layer n_{em_real} are determined by Bruggeman formulation [149] in Eq. 3.4 where $\mathcal{E}_{em}$, $\mathcal{E}_{air}$, and $\mathcal{E}_{NW}$ are the permittivities of the effective medium layer, air, and NW respectively.

$$(1-FR)\frac{\epsilon_{air}^2-\epsilon_{em}^2}{\epsilon_{air}^2+2\epsilon_{em}^2}+FR\frac{\epsilon_{NW}^2-\epsilon_{em}^2}{\epsilon_{NW}^2+2\epsilon_{em}^2}=0$$

$$n_{em_real} = \text{Re}(\sqrt{\epsilon_{em}}).$$
(3.4)

The imaginary part of the refractive index n_{em_imag} is calculated by Volume Averaging Theory [150, 151] in Eq. 3.5 where the n_{NW_real} , n_{NW_imag} , n_{air_real} , and n_{air_imag} , are the real and imaginary parts of the refractive index of the NWs and air.

$$A = FR(n_{NW_real}^2 - n_{NW_imag}^2) + (1-FR)(n_{air_real}^2 - n_{air_imag}^2)$$

$$B = 2FRn_{NW_real}n_{NW_imag} + 2(1-FR)n_{air_real}n_{air_imag}$$

$$n_{em_imag} = \sqrt{\frac{-A + \sqrt{A^2 + B^2}}{2}}.$$
(3.5)

Therefore, the complex refractive index of the effective medium layer is shown as below.

$$n_{eff_md} = n_{em_real} + i n_{em_imag}.$$
(3.6)

The Fresnel coefficients of the air/effective medium and effective medium/SiO₂ interfaces are calculated for each value from zero to the largest value of FR which is $\pi/4$ for squarely NW arrays.

$$r_{air_med} = \frac{n_{air} - n_{em_real}}{n_{air} + n_{em_real}}$$

$$t_{air_med} = \frac{2n_{air}}{n_{air} + n_{em_real}}$$
(3.7)

$$r_{med_SiO_2} = \frac{n_{em_real} - n_{SiO_2}}{n_{em_real} + n_{SiO_2}}$$

$$t_{med_SiO_2} = \frac{2n_{em_real}}{n_{em_real} + n_{SiO_2}}.$$
(3.8)

The transmittance and reflectance are then obtained using the Fresnel equations, with the propagation constant within the effective medium layer as $\beta_z = 2\pi n_{eff_med} / \lambda$.

$$r(\lambda) = \frac{r_{air_med} + r_{med_SiO_2} e^{2i\beta_z h}}{1 + r_{air_med} r_{med_SiO_2} e^{2i\beta_z h}}$$

$$t(\lambda) = \frac{t_{air_med} t_{med_SiO_2} e^{i\beta_z h}}{1 + r_{air_med} r_{med_SiO_2} e^{2i\beta_z h}}.$$
(3.9)

In the presence of the substrate with refractive index n_{SiO_2} and superstrate with n_{air} the reflection and transmission spectra are:

$$R(\lambda) = r(\lambda) r(\lambda)^*$$

$$T(\lambda) = \frac{\text{Re}(n_{SiO_2})}{\text{Re}(n_{air})} t(\lambda) t(\lambda)^*.$$
(3.10)

We integrate the spectra after weighting them by the solar flux to arrive at a single averaged value for each FR. For instance, the average absorption is obtained from the average reflection and transmission as shown in Eq. 3.11 where λ_{low} is the lower limit from the solar spectrum. $\xi(\lambda) = I(\lambda)\lambda/hc$ describes the number of photons incident at that wavelength where $I(\lambda)$ is the irradiance as given in the AM 1.5G. The optimal FR_{opt} is defined as the FR which allows maximal absorptance $Abs(\lambda)$.

$$\begin{aligned}
 T_{average}(f) &= \frac{\int_{\lambda_{low}}^{\lambda_{criti}} \xi(\lambda) T(f, \lambda) d\lambda}{\int_{\lambda_{low}}^{\lambda_{criti}} \xi(\lambda) d\lambda} \\
 R_{average}(f) &= \frac{\int_{\lambda_{low}}^{\lambda_{criti}} \xi(\lambda) R(f, \lambda) d\lambda}{\int_{\lambda_{low}}^{\lambda_{criti}} \xi(\lambda) d\lambda} \\
 Abs(f) &= 1 - R_{average}(f) - T_{average}(f).
 \end{aligned} \tag{3.11}$$

At this stage, the optimal diameters and the FR are both determined and the corresponding periodicity can be acquired based on the definition of the FR. With the optimal geometrical dimensions, the NW arrays should harvest maximal solar energy. Short-circuit current density J_{sc} is mostly used to measure the solar radiation harvesting capability assuming that every absorbed photon leads to an exciton separation followed by a successful carrier collection. The definition is shown in Eq. 3.12 where $A(\lambda)$ is the absorption inside NWs as a function of the incident wavelength and $\xi(\lambda)$ is the number of photons per unit area per second for the incident wavelength from the standard solar spectrum.

$$J_{sc} = q \int_{AM1.5G} A(\lambda) \xi(\lambda) d\lambda. \tag{3.12}$$

GaAs and InP are both considered in this chapter to achieve maximal solar energy absorption as two of the most widely used III-V semiconductor materials for photovoltaic applications. The algorithm is applied to single, two, and four diameters of NW arrays to demonstrate the wide suitability of the proposed method. Compared with our proposed method, optimal geometrical dimensions of the NW arrays are also found out by intensive number of FDTD numerical simulations (Lumerical FDTD Solutions 8.15). The boundary condition in the simulation is set as periodic boundary condition along x and y directions whereas perfect matching layer in the z axis as shown in Fig. 3.1.

3.3 Maximal Solar Energy Harvesting of Single Diameter III-V Nanowire Arrays

As shown in Fig. 3.4, the absorption efficiencies of the GaAs and InP NW arrays are obtained from FDTD simulation when FR is 0.05. The refractive index and the extinction coefficients of the respective materials are supplemented in Fig. 3.4 insets. The band gaps and corresponding critical wavelengths are listed in Table 3.1. Figure 3.4 also illustrates the red-shifted evolvement of the resonant wavelength for HE_{11} mode with the increase of diameter of NWs. Using the dispersion relation in section 3.2.2, we calculate the resonant wavelengths of HE_{11} and HE_{12} mode related to each diameter from 50 to 200 nm for both GaAs and InP NWs. The calculated resonant wavelengths are marked on respective peaks. The well agreement of the calculated resonant peaks and those obtained from FDTD simulation demonstrates the effectiveness of our method for both GaAs and InP material. On one hand, both calculation and simulation results show that diameter of 140 nm is the turning point from one mode to two modes resonance within a GaAs NW. On the other hand, the resonant peak of 869 nm corresponding to the diameter of 174 nm is the upper limit of the absorbing region

for GaAs material. Similarly with GaAs NWs case, the optimal diameter for InP NWs lies among 160 and 200 nm.

Table 3.1 Band gaps and critical wavelengths for GaAs and InP materials.

Material	Band gap (eV)	Critical wavelength (nm)
GaAs	1.43 [152]	869
InP	1.34 [153]	927

Figure 3.4 Absorption efficiencies of (a) GaAs and (b) InP NW arrays change with incident wavelength when FR is 0.05 and the insets illustrate the complex refractive indexes for the respective materials.

The normalized absorption efficiencies Q_{abs} for both GaAs and InP NWs where two modes existed are calculated by Mie theory as shown in Fig. 3.5. It clearly displays that the largest diameter for GaAs is 168 nm while keeping FWHM lying within the absorption region. For InP NWs, the largest diameter is 184 nm without any additional peak. Interestingly, the up-to-date highest power conversion efficiency of InP NWs solar cells adopted the optimal diameter of 180 nm. In their work, the diameters of NWs were experimentally optimized ranging from 50 to 300 nm with 10 nm as the increase step [55]. Compared with our prediction of 184 nm, a narrow tolerance of 4 nm demonstrates the accuracy of our method. Also, the highly efficient GaAs NWs solar cells of 15.3% reported early last year [154] who had a core diameter of 165 nm. Compared with our analytical prediction, there is only 3 nm tolerance.

Figure 3.5 Normalized absorption efficiencies of (a) GaAs and (b) InP NWs calculated by Mie theory.

The FRs for GaAs and InP are optimized according to the method described in section 3.2.3. Figure 3.6 shows the absorption efficiencies of the effective medium layers for both GaAs and InP materials. Both absorption efficiencies rise initially with the increase of FR and then fall down after reach their optimal values. The optimal FRs correspond to the ones that maximize the solar energy absorption of the effective medium layers considering the Fresnel reflection and

transmission. The trend is mainly due to the variation of the transmission and reflection of the effective medium layer due to FR variation. When FR grows from 0.05 to the optimal value, the buildup of the III-V material increase light absorption and reduce transmission. However, too large portion of NWs will increase the reflection of the incident light which has also been confirmed in the publication [146]. Thus, the optimal FR for GaAs NW arrays is 0.22 whereas that for InP NW arrays is 0.2. According to the definition of FR, we can calculate the optimal periodicities of the single diameter GaAs and InP NWs as 328.68 and 364.63 nm respectively.

Figure 3.6 Absorption efficiencies for effective medium layers of GaAs and InP NW arrays as a function of FR.

Short-circuit current densities for single diameter NW arrays are shown in Fig. 3.7. Among the FDTD simulation results, the optimal values obtained from the proposed method are marked in bold. For GaAs NWs, the maximal value for the J_{sc} obtained from the FDTD is 28.18 mA/cm² whereas the maximum J_{sc} calculated from our proposed method is 28.10 mA/cm². For InP NWs, the maximum value obtained is 32.21 mA/cm² whereas that from our analytical

calculation is 32.11 mA/cm^2 . The calculation error for GaAs NWs is 0.28% whereas that for InP NWs is 0.33%. This confirms that our proposed method is effective in predicting the maximal light absorption for single diameter NW arrays.

Figure 3.7 Theoretical predicted maximal short-circuit current densities compared with FDTD simulations for single diameter (a) GaAs and (b) InP NW arrays.

3.4 Maximal Solar Energy Harvesting of Two Diameters III-V Nanowire Arrays

Adding another diameter of NWs in the unit cell has been investigated by many researchers with the purpose to further boost the light absorption [56, 58]. This is because adding a secondary diameter NWs can supplement the selectively absorption spectrum due to the LMR and thus improve energy harvesting capability. However, the secondary diameter is usually chosen and validated by intensive numerical simulations [61]. Using our method, the secondary diameter is still required to support one resonant mode and the absorption valley of primary NWs should be complemented by the resonant wavelength of the secondary NWs. As a result, from the normalized absorption efficiency of primary diameter of 168 nm GaAs and 184 nm InP NWs in Fig. 3.5, their absorption valleys are found to locate at 600 and 585 nm respectively. According to the dispersion relation, diameters of 114 nm for GaAs and 119 nm for InP NWs satisfy the selection criteria of the secondary diameter. At the same time, the FRs calculation method is still valid leading to 0.22 for GaAs and 0.2 for InP NWs. According to definition of FR, periodicities are calculated to be 270 nm for GaAs NWs whereas 307 nm for InP NWs. Meanwhile, FDTD simulations are carried out across diameters ranging from 50 to 200 nm. The FRs also vary to gain a full picture of the short-circuit current densities generated from different geometrical parameters combinations.

Figure 3.8 Short-circuit current densities change with different primary and secondary diameters combinations as well as FRs for squarely (a) GaAs and (c) InP NW arrays where (b) and (d) are the extracted slices for GaAs and InP NWs when FR is 0.22 and 0.2 respectively.

As shown in Fig. 3.8, short-circuit current densities vary with different primary and secondary diameter combinations as well as FRs for GaAs and InP NWs.

Figures 3.8(a) and (c) give the overall view of the three parameters changing whereas Figs. 3.8(b) and (d) are the extracted slices of the optimal FRs for GaAs and InP NWs. The influence of FR is similar with the trend that predicted by effective medium layer method. The short-circuit current densities generally increase with FRs, rise to its maximal value and then fall down. Although only three FRs are displayed for each material, they are deliberately chosen to gain a whole picture of the FR's influence according to Fig. 3.6. Obviously, large values of short-circuit current densities have been achieved with optimal FRs for both GaAs and InP NWs. We marked the short-circuit current densities on the Fig. 3.8(b) and (d) for our purposed method as 29.4 and 32.96 mA/cm² for GaAs and InP NW arrays respectively. The symmetrical distribution of the short-circuit current density coincides with the symmetrical distribution of two diameters NWs in the unit cell. To estimate the tolerance, the maximal short-circuit current densities obtained from FDTD are 29.56 and 33.34 mA/cm² for GaAs and InP material leading to tolerance of 0.5% and 1.1%.

Besides, we also investigate the hexagonal InP NW arrays having two different diameters NWs in the unit cell. Schematic for hexagonally arranged InP NW arrays is shown in Fig. 3.9. The diameter of the center NW is $D_{primary}$ and the diameters of the NWs at the peripheral are $D_{secondary}$. Similar with the squarely arranged NW arrays, the FR for hexagonal NW arrays is defined as

$$\pi \sum_{i=1}^2 D_i^2 / (4\sqrt{3}p^2) \text{ with the maximal value of } \pi\sqrt{3} / 6 \text{ [58].}$$

Same mathematical derivations for optimal geometrical dimensions are applied for the hexagonal InP NW arrays and both the calculation prediction and the FDTD simulation results are shown in Fig. 3.10.

Figure 3.9 Schematic of vertically aligned InP NW arrays arranged hexagonally with an inset explaining the unit cell.

Short-circuit Current Density for Hexagonally Arranged InP NWs

Figure 3.10 Short-circuit current densities change with different primary and secondary diameter combinations as well as FRs for (a) hexagonal InP NW arrays and (b) is the extracted slice for InP NWs when FR is 0.2.

Filling ratio of 0.2 leads to periodicity of 329.95 nm for hexagonal arrangement of InP NW arrays. Figure 3.10(a) provides an overview of the short-circuit current densities variation as a function of $D_{primary}$, $D_{secondary}$, and the FR of NW arrays. Generally, the short-circuit current density increases with FR, reaches its maximal value and falls down. When FR is 0.2, Fig. 3.10(b) displays the highest J_{sc} of 32.95 mA/cm² for hexagonal InP NWs. Compared with the maximal values from FDTD simulations as 33.26 mA/cm², the tolerances is 0.9%.

Compared with squarely InP NWs in Fig. 3.8(c), Fig. 3.10(a) shows similar maximal J_{sc} which is found at the same FR and diameters for two arrangements of NW arrays. This indicates that the proposed method is effective regardless of the arrangement of NWs. When FR is 0.4, on average, the J_{sc} of hexagonally arranged InP NW arrays is higher than that of squarely NW arrays. This is attributed to light the coupling among neighboring NWs. When the NWs are

close, power can transfer to the neighboring NWs who support the same leaky mode causing the competition of the incident energy [136] which is detrimental to overall light absorption. When the FR is the same for squarely and hexagonal arrangements, the periodicities for both arrangements have the relationship of $p_{square}^2 / p_{hexagonal}^2 = \sqrt{3} / 2$. Therefore, the $p_{hexagonal}$ is 1.08 times of the p_{square} which means less mode coupling among NWs for hexagonally arranged NW arrays and high light harvesting. When FR is 0.05, both NW arrays have few light coupling and similar values of J_{sc} are found in the two arrangements. This coincides with the conclusions drawn by other researchers [58, 155, 156].

3.5 Maximal Solar Energy Harvesting of Four Diameters III-V Nanowire Arrays

It is reported that higher absorption efficiency is obtained when multiple diameters are involved in the unit cell compared with single or two diameters NW arrays [56]. Near-unity absorption is achieved across the solar spectrum for four diameter NW arrays which points out a fascinating feature for high efficiency solar cell application [57]. However, due to the numerous simulation cases needed, only a few design examples are provided to demonstrate the multiple diameters NW arrays in improving the light absorption. Validation across parameter spaces of reasonable number of diameters of NWs combinations has seldom been reported because of the large amount of time for data acquisition. In our case, the total time taken to finish all of the calculations using our method equals to the time taken by only one FDTD simulation using the same personal computer. In this section, we will demonstrate the effectiveness of our proposed method in predicting the largest solar energy absorption by directly providing the geometrical parameters of four diameters NW arrays. FDTD simulations are also accompanied to prove the effectiveness of our method.

Similarly with two diameters NW arrays, the third and the fourth diameters of NWs are chosen to match the absorption valley of the superposition of the primary and secondary NWs' normalized absorption efficiency spectrum as shown in Fig. 3.11. The absorption valleys can be easily witnessed as 523 and 720 nm for GaAs whereas 486 and 704 nm for InP respectively. According to the resonant wavelengths calculated in section 3.2.2, the diameter of NWs whose resonant wavelength matches the absorption valley of respect curves are chosen as 92 and 140 nm for GaAs NWs whereas those for InP NWs are 92 and 148 nm.

Figure 3.11 Normalized superposition of the absorption efficiencies of the primary and the secondary diameters for GaAs and InP NWs.

Since all of the four diameters of NWs are determined, according to the optimal FRs obtained in section 3.2.2 and the definition of FR, the periodicities are calculated to be 248.67 and 277.41 nm for GaAs and InP NW arrays respectively. Intensive numerical FDTD simulations are provided running across each diameter parameter space. Considering there are four different diameters to be independent variables, it is difficult to have a direct view of the results in conventional two or three dimensional figures. Enumeration method is employed to demonstrate simulation results as shown in Fig. 3.12 and 3.13. There are two sets of coordinate systems. The x and y axes of the inner coordinate system

represent the values of primary and secondary diameters. The x and y axes of the outer coordinate system denote the third and fourth diameters. Each intersect of the dash lines indicates different combinations of the third and fourth diameters whereas the primary and secondary diameters run through 50 to 200 nm. Due to the limited length of the paper, representative values are chosen in the way to have a full picture of the result. For both GaAs and InP, 80 nm denotes single mode existence within NWs and 110 nm is selected to show the transition from single mode to two modes. 140 nm represent the starting of the two modes within the NWs and 170 nm demonstrates the absorbing edge of the NWs. The short-circuit current densities for our proposed calculation method are obtained as 29.88 and 33.13 mA/cm² for GaAs and InP NW arrays which are not marked on the Figs. 3.12 and 3.13 due to limited combinations of diameters of NWs. Compared with full simulation, the tolerances are 1.5% and 2.2% respectively.

Figure 3.12 Short-circuit current densities change with different primary, secondary, third and fourth diameter combinations for GaAs NW arrays when FR is 0.22.

Figure 3.13 Short-circuit current densities change with different primary, secondary, third and fourth diameter combinations for InP NW arrays when FR is 0.2.

Figure 3.14 and 3.15 give the individual NWs with optimal diameters in the four diameter III-V NW arrays from FDTD simulation. It clearly shows that near-unity light absorption efficiency could be obtained with the calculated diameter of NWs. Beyond the critical wavelength of 869 nm (corresponding of 1.43 eV band gap for GaAs [152]), the absorption coefficients are not extrapolated. The high absorption is mainly due to the photonic band gap trapping. Photons are confined within the NW arrays. The trapped energy contains both the photons that will contribute to the photocurrent (energy is larger than the band gap of GaAs) and those that will lose within the active layer and cannot get out due to the photonic band gap formed. It is true that photons with smaller energy than 1.43 eV will not contribute to the short-circuit current density. However, they are still trapped within active layer which means they are not reflected back or transmitted through the active layer. Similar phenomenon can be found in Fig. 2(c) of the published work [56].

Figure 3.14 Absorption spectrum wavelength for optimal four diameter GaAs NW arrays including each individual NW in the optimized diameters.

Figure 3.15 Absorption spectrum wavelength for optimal four diameter InP NW arrays including each individual NW in the optimized diameters.

3.6 Conclusion

In this chapter, an effective and efficient algorithm is proposed to calculate the optimal geometrical dimensions of NW arrays for maximal solar energy absorption. Specifically, the diameters of NWs and periodicity are analytically determined with low tolerance and within a short period of time as compared to conventional three dimensional FDTD simulation. Single, two and four diameters of GaAs and InP NW arrays are designed to pursue the largest short-circuit current densities. The primary diameters of 168 nm for GaAs and 184 nm for InP NWs are obtained both from LMR and Mie theory to excite two resonant modes while remain their FWHM of HE_{11} mode in the absorbing region. For single diameter NW arrays, compared with the experimental work, the optimal diameter is only 4 and 3 nm difference to the reported highest efficiency InP and GaAs NWs solar cells which demonstrate the effectiveness of our method. By matching the absorption valley of the primary NWs, the optimal diameters for

the secondary GaAs and InP NWs are 114 and 119 nm. Through comparison of squarely and hexagonally arranged InP NW arrays, we demonstrate that the proposed method is valid regardless of the arrangement of NWs. Moreover, broadband high absorption is achieved for four diameters NW arrays through matching their respective resonant wavelengths to the valleys of the superposition of the primary and secondary NWs' normalized absorption efficiency spectrum. Therefore, the third and fourth diameters are 92 and 140 nm for GaAs NWs whereas 92 and 148 nm for InP NWs. At the same time, the effective medium layer method combining with Fresnel reflection and transmission lead to the optimal FR of 0.22 for GaAs and 0.2 for InP NWs despite various diameters combinations. The optimal geometrical dimensions of four diameters NW arrays lead to the highest short-circuit current densities of 29.88 and 33.13 mA/cm² for GaAs and InP respectively. Through intensive numerical simulations across the parameter spaces, the tolerance of the predicted maximal short-circuit current densities lie within 2.2% for all NWs cases. The wide suitability, high precision and time saving capability in predicting the geometrical dimensions of NW arrays for maximal light absorption demonstrate the effectiveness of the proposed method in design of future efficient solar cell.

Chapter 4 A Coupled Opto-electrical Design for Fully Infiltrated Nanowires Based HSCs

In this chapter, we present a coupled opto-electrical model that both optimizes the light absorption and predicts electrical performance of fully infiltrated inorganic semiconductor nanowires (NWs) based hybrid solar cells (HSCs). Followed by the introduction and motivation, a hybrid active layer was created consisting of GaAs NWs as acceptor and poly(3-hexylthiophene-2,5-diyl) (P3HT) as donor. Absorption characteristics of the hybrid active layer were investigated focusing on both the material properties and the geometrical dimensions of the NW arrays. Codesigned of the solar energy harvesting of the hybrid active layer, the electrical performance of the HSCs was also numerically studied. In the last part, the validity of the coupled opto-electrical model was also proved by the well prediction of the published experimental work indicating an effective guidance for future high performance HSC design.

4.1 Introduction and Motivation

Interdigital ordered heterojunctions formed by the vertically aligned NWs with organics fully infiltrated around [33, 43, 157] are considered as the ideal hybrid active layer structure for NWs based HSCs [32, 33]. Along the NW radial direction, the reduced exciton diffusion distance improves the exciton diffusion and dissociation efficiencies. Along the NW axial direction, the NWs and the organics provide direct pathways for the carriers to transport to the respective electrodes increasing the carrier transport efficiency [16]. Up-to-date, fully infiltrated organics mixing with Si or GaAs semiconductor NWs are the most widely reported HSCs. The highest power conversion efficiency (PCE) reaches 13.2% [95]. To further boost the PCE and lower the time and material cost, great efforts have been devoted to the numerical modeling for developing highly

efficient HSCs design. However, most of the investigations about the light harvesting of the hybrid active layer end with short-circuit current density without digging into the electrical performance of the HSCs. Besides, although the electrical performances of the NWs based HSCs were reported, they either neglected the absorption of NWs [64] or limited the diameter of NWs below 50 nm [68]. Apparently, optical or electrical optimization alone is not sufficient to guide high performance NWs based HSC design. A coupled opto-electrical model is desired to fully evaluate the light absorbing and the photovoltaic performance of the device accounting both the geometrical dimension of NWs and the intrinsic material property [70, 71].

In this chapter, a coupled opto-electrical model is presented to thoroughly explore the performance of fully infiltrated NWs based HSC. In particular, the GaAs NWs/P3HT HSCs were simulated. Finite-difference time-domain (FDTD) simulations were employed to study the light absorbing characteristics of the GaAs NWs/P3HT hybrid active layer and compared with GaAs NWs/air layer. Along with the material property of P3HT, geometrical parameters of the NWs such as diameter and filling ratio (FR) were discussed about their influence on the light absorption. Upon solar illumination, photogeneration profile of the hybrid active layer was incorporated into our electrical model to determine the generation, diffusion, dissociation and transportation of the excitons and electron-hole pairs. Therefore, this opto-electrical model was able to calculate the exciton diffusion efficiency, photocurrent density, external quantum efficiency (EQE), current density-voltage (J - V) characteristic, and PCE of the NWs based HSCs. The validity of the model was proved by the well prediction of the published experiment work implying an effective guidance of HSC design.

4.2 Construction of the Opto-electrical Model for Nanowires Based HSCs

4.2.1 Photovoltaic Process in Nanowires Based HSCs

Photovoltaic process for HSC has been explained in details in Chapter 2. In this section, we give a brief description about the photovoltaic process for NWs based HSCs. Schematic of energy level arrangement and the photovoltaic process of the GaAs NWs/P3HT HSC is shown in Fig. 4.1. Upon illumination, photons are absorbed by both the inorganic NWs and organics, and then excitons are generated. Excitons diffuse to the donor-acceptor (DA) interfaces and are dissociated into free carriers. Electrons are held by the inorganic NWs which have higher electron affinity whereas holes are captured by the polymer with low ionization energy. The carriers then transport to the respective electrodes through either inorganic NWs (for electrons) or polymer (for holes) to generate the photocurrent. Photon absorption efficiencies for NWs and polymer are η_{Abs_NW} and η_{Abs_Poly} . Diffusion efficiencies η_{diff_NW} and η_{diff_Poly} are used respectively to measure the number of excitons that reach the DA interface to the total number of excitons generated in the respective materials. Transport efficiencies η_{trans_NW} and η_{trans_Poly} are introduced to evaluate the number of excitons that form the photocurrent to the number of excitons that reach the DA interface. External quantum efficiency is defined to measure the percentage of the number of charge carriers that generate the photocurrent to the number of photons incident on the device [158]. Therefore, EQE equals to the product of the photon absorption efficiency, diffusion efficiency and transport efficiency.

Figure 4.1 Schematic of the energy level arrangement and photovoltaic process for inorganic NWs based HSC (LUMO: lowest unoccupied molecular orbital; HOMO: highest occupied molecular orbital; CB: conduction band; VB: valence band; $h\nu$: incident photon energy).

4.2.2 The Unit Cell of Nanowires Based HSCs

Configuration of the inorganic NW/polymeric HSC is schematically shown in Fig. 4.2. Inorganic NWs are immersed in the polymer forming the active layer which is sandwiched between the anode and cathode. Figures 4.2(a) and (b) show the side and top view of the HSC. The simulated region is a unit cell which is the minimal repeatable unit of the HSC. Characteristic dimensions of the unit cell are provided in Fig. 4.2(c). The diameter of the NW is D and the periodicity of the unit cell is p which is equal to the center to center distance of the adjacent NWs. Filling ratio is defined as $\pi D^2/4p^2$ which has a maximal value of $\pi/4$ for the case that the cylindrical NW fills in the maximal volume percentage of the unit cell [147]. The length of the NWs is L . Since the thickness of the polymer-only layer L_{Poly} , as shown in Fig. 4.2(a), is less than 1/100 of the total length of NWs, the thickness of the active layer is approximated as L . In this work, NWs length of 2 μm is chosen for the following simulations. The total photocurrent generated is acquired by summing all the current generated in the unit cells.

Figure 4.2 Schematic of the NWs based HSC including (a) side view, (b) top view and (c) a unit cell illustrating characteristic dimensions for the simulation.

4.2.3 Codesign of the Light Absorption and Electrical Characteristics

Spectral absorptance of the inorganic NW/polymeric active layer was thoroughly analyzed using the full-field three-dimensional (3D) FDTD electromagnetic simulations (Lumerical FDTD Solutions 8.15). The simulation was carried out in the unit cell in Fig. 4.2(c) with the periodic Bloch boundary condition applied along x and y directions and infinite boundary condition applied in z direction. The complex refractive indexes of GaAs were obtained from the Palik material data provided by Lumerical whereas the optical constants for P3HT were taken from the reference [73]. The band gaps of GaAs and P3HT were acquired from the published references [68]. The absorbed energy was calculated from the total energy illuminated upon the active layer deducting both the reflected and transmitted energy. The electromagnetic field distribution in the inorganic NW/polymer active layer was obtained from the simulation. Accordingly the number of excitons generated per unit volume per unit time, namely, the photogeneration rate in the unit cell was calculated. Through incorporating the photogeneration rate into the electrical model, the photocurrent density and EQE were obtained accounting the exciton diffusion efficiency under terrestrial AM 1.5G illumination [67]. The J - V curves of the devices were then acquired and from which the important electrical parameters such as the open-circuit voltage

(V_{oc}), short-circuit current density (J_{sc}), and PCE were determined. In the proposed opto-electrical model, the following assumptions were made: (1) excitons only generated within the diffusion length to the DA interface would contribute to the photocurrent [64]; (2) excitons were dissociated into electron-hole pairs only at the DA interface; (3) carriers dissociated from the excitons would not recombine since the electrons transported through the inorganic semiconductor NWs and the holes transported through the polymer.

4.3 Light Absorption Analysis of Fully-infiltrated Nanowires based HSCs

In this section, the light harvesting capability of the GaAs NWs/P3HT hybrid active layer was thoroughly explored as a function of NW diameters and FR. Light absorption of GaAs NWs/air layer was firstly presented for comparison with the hybrid active layer. Two-dimensional model analysis was also provided to gain an insight of the light absorbing properties.

4.3.1 Model Analysis of GaAs Nanowire Arrays in the Air

For GaAs NWs/air layer, we could find the selectivity of the absorption wavelength from Fig. 4.3. When the FR was 0.05, the leaky mode resonance dominated light absorbing behavior of sparsely distributed NWs [56] as discussed in details in Chapter 3. Redshift of the HE_{11} mode resonant wavelength as the increase of diameter of NWs could also be observed in Fig. 4.3. An additional mode of HE_{12} began to appear when the diameter of NWs reached around 140 nm. Redshift of HE_{12} became obvious at larger diameter of NWs which had been discussed in Fig. 2 in reference [138]. Detailed model analysis was provided below.

Figure 4.3 Light absorption efficiency changed with diameter of NWs for GaAs NWs/air layer when FR was 0.05.

A two-dimensional model analysis of the GaAs NWs/air was carried out to gain an insight of the above mentioned light absorbing properties. The normalized electric field intensity $|\vec{E}(r)|^2$ was presented along the vertical cross-section through the middle of the NWs. The 160 nm diameter GaAs NWs in the air was selected at the incident wavelength of 400, 600 nm and resonant wavelength of HE_{11} mode as shown in Fig. 4.4. According to the literature review in Chapter 2, we are aware that there are three kinds of optical phenomena when the electromagnetic waves illuminate upon the NWs. They include the radial resonant mode, the nearfield evanescent mode coupling, and the Fabry-Perot (F-P) modes along the axial direction of NWs,[136]. The model analysis in Figs. 4.4(a) and (b) clearly showed the F-P modes along the longitudinal direction of NWs at different incident wavelength. Figure 4.4(c) displayed the dipole-like HE_{11} mode which had two distinct maximal values along the radial direction of the NWs. This resonant mode occurred when the incident wavelength of 809 nm coupled strongly with the NWs. As described in Chapter 3, this wavelength was the electromagnetic wave solution to the radial boundary conditions of the NWs.

Figure 4.4 Electric field intensity distribution of GaAs NWs/air unit cell in plots (a)-(c). Top, middle and bottom plots corresponded to: (a) 400, (b) 600, and (c) resonant wavelengths of 809 nm for HE₁₁ modes in GaAs NWs/air where the white lines indicated the edges of the NWs.

4.3.2 Light Absorption for GaAs Nanowire Arrays in Poly(3-hexylthiophene-2,5-diyl) (P3HT)

Compared with GaAs NWs/air layer, the GaAs NWs/P3HT structure displayed different light absorbing features as shown in Fig. 4.5. When the incident wavelengths were shorter than the P3HT absorption edge (650 nm), the absorption efficiency was high and uniform across the incident spectrum. The large amount of P3HT in the unit cell governed the light absorptance when FR was 0.05. The absorption efficiency dropped sharply beyond 650 nm since the absorption was mainly contributed by GaAs NWs at this spectral range. Beyond the absorbing edge of P3HT, the resonant HE_{11} mode took the lead and the selectivity of wavelength absorption appeared. Moreover, the resonant wavelengths oscillated as the peaks red-shifted with the enlarging of NWs diameter. The reason was due to the F-P effect of the P3HT thin film which tuned the resonant peaks of GaAs NWs as shown in Fig. 4.5(b). Although at long wavelengths the photons could not be absorbed to generate excitons by P3HT, they were still effectively trapped inside the active layer due to the high refractive index of P3HT serving as the dielectric shell [72]. Therefore, an average absorption enhancement could be observed compared with GaAs NWs/air layer.

Figure 4.5 Light absorption efficiency changed with diameter of NWs for (a) GaAs NWs/P3HT layer where (b) was the extracted absorption efficiencies for the given diameters of NWs when FR was 0.05.

Compared with GaAs NWs/air, the electric field intensity distributions for GaAs NWs/P3HT were more concentrated which were around the periphery of NWs for 400 and 600 nm incident light. From Figs. 4.6(a) and (b), the existence of P3HT helped absorb light effectively below the absorbance band gap. Therefore the electrical field intensity attenuated rapidly along the NWs axis and did not

reach the bottom of the NWs. Besides, the oscillation of the electrical field intensity became obvious in Fig. 4.6(c), which was mainly because of the F-P mode by P3HT layer. Since the FR was fixed at 0.05 for the simulated NWs, the HE_{11} leaky modes were concentrated in and around the NWs and thus were not affected by the adjacent NWs.

Figure 4.6 Electric field intensity distribution of GaAs NWs/P3HT unit cell.

Top, middle and bottom plots corresponded to: (a) 400, (b) 600, and (c) resonant wavelength of 827 nm for HE_{11} modes where the white lines indicated the edges of the NWs.

Figure 4.7 shows the contour plot of the light absorption efficiency spectra of the GaAs NWs/P3HT active layer as a function of FR with the NW diameter of 80 and 160 nm, respectively. When the incident wavelengths were below the band edge of P3HT, the absorption efficiency of the active layers decreased with the increase of FR for both the 80 and 160 nm diameters. This was mainly due to the model coupling among adjacent NWs. From the model analysis shown in Fig. 4.6, we found that the radial extent of the HE_{11} resonance mode leaked to the boundary of the unit cell. When the distance between the adjacent NWs narrowed down as the FR increased, the competition of the incident photons among the NWs caused the decrease of the absorption. For 80 nm NWs, when the incident wavelength was longer than 650 nm, the absorption peaks oscillated and the resonant wavelength red shifted as the FR increased. This oscillation originated mainly from the F-P modes [136] in the NWs rather than in P3HT since the volume ratio of NWs rose. The F-P modes in the NWs were generated as a result of the longitudinal boundary conditions at the two ends of the NWs. Besides, as FR increased, the F-P modes mostly passed through GaAs. Since the absorption coefficients of GaAs was much higher than those of P3HT, the absorption built

up with the increase of FR. For 160 nm NWs, Fig. 4.7(b) showed a blue shift at longer incident wavelength which was contrary to the trend displayed in Fig. 4.7(a). According to a recent publication from Sturmberg *et al.* [146], the first coefficient of the Rayleigh identity was calculated to be negative for 160 nm GaAs NWs/P3HT active layer. This indicated the destructive interference of the HE_{11} mode of the nearest neighboring NWs. Therefore, the blue shift of the resonance peak was observed indicating the destructive interference.

Figure 4.7 Light absorption efficiency changed with incident wavelength and FR when diameters of NW were (a) 80 and (b) 160 nm.

4.4 Opto-electrical Modeling for Nanowires/Organics HSCs

4.4.1 Electrical Characteristics of GaAs Nanowires/P3HT HSC

Based on the understanding of the absorbing characteristics of the hybrid active layer, light absorption of the HSC could be evaluated. The exciton diffusion length S_D was assumed as 20 nm for P3HT. Therefore, within a unit cell, only the NWs and their peripheral of 20 nm thickness polymeric shells would devote to the device photon harvesting. This organic-inorganic region was thus named as effective region as shown in the dashed cylindrical area in Figs. 4.8(a) and (b). In Fig. 4.8(c), light absorption efficiency of the unit cell was calculated under terrestrial AM 1.5G illumination condition with an intensity of (100 mW/cm^2) as a function of diameter and FR. The highest light absorption was 0.39. On one hand, a variety of combinations of diameters and FR could enter the high absorption region about 0.38. The two high absorption zones were both with large FRs resulting in less redundant polymeric area within unit cell outside the red dashed cylinder as shown in Fig. 4.8(b). Besides, when FR was fixed, the

consumption of GaAs materials remained the same regardless of different diameters. Considering the high extinction coefficients of GaAs, high absorption was obtained at large FR. On the other hand, there was a gentle decrease between two high absorption regions. This could be explained as resonant wavelengths variation when diameter changed. When the diameter was below 120 nm, the resonant peaks in Figs. 4.3(b) and 4.5(b) positioned in the blue end below the P3HT absorptance edge (650 nm). The enhanced optical field distribution due to the model resonance would also increase the light absorption of P3HT. When diameter of the NWs increased to 140 nm, the resonant wavelengths moved beyond the P3HT absorption edge. The enhanced optical field had little effect on the absorption of P3HT. Due to the small amount of P3HT at high FR, the decrease existed but was minor. When the diameter continued to rise, another resonant mode appeared in the blue end of the spectral inside the NWs as shown in Fig. 4.3(b), and thus the absorption efficiency grew again.

Figure 4.8 Top view (a) and isometric view (b) for effective region and (c) light absorption efficiencies as a function of FR and diameter at AM 1.5G illumination.

According to the photovoltaic process in Fig. 4.1, excitons were generated upon light absorption. The photogeneration rates were calculated for the effective region from the divergence of Poynting vector $\vec{P}$ for each configuration. Equation 4.1 gave the expression where ε'' was the imaginary part of the complex permittivity and $\vec{E}$ was the electric field intensity [159]. The photogeneration rates were then exported to electrical model and important electrical characteristics such as J_{ph} , EQE, $J-V$, and PCE were all achieved for GaAs NWs/P3HT HSC.

$$G_{opt} = \frac{1}{2\hbar\omega} \text{re} \left\{ \vec{\nabla} \cdot \vec{P} \right\} = \frac{\epsilon'' |\vec{E}|^2}{2\hbar} \quad [cm^{-3} \cdot s^{-1}]. \quad (4.1)$$

Only the excitons generated within the diffusion length to the DA interface would contribute to the photocurrent. For inorganic semiconductor like GaAs, the diffusion length was on the order of micrometers which was much larger than the radius of the NWs [160, 161]. Therefore, η_{diff_NW} could be taken as unity. For organic materials, η_{diff_Poly} was closely related to the distance between the locations where the excitons were generated to the DA interface Δs as shown in Fig. 4.8(a). Only when Δs was smaller than S_D , the excitons could diffuse to the DA interface to be dissociated. In this case, the diffusion efficiency η_{diff_Poly} could be expressed as $\eta_{diff_Poly} = \exp(-\Delta s/S_D)$ [64]. Besides, after dissociation at organics/inorganics interface, it was assumed that the carriers would not recombine since the electrons transported through the inorganic semiconductor NWs whereas the holes transported through the polymer. Therefore, the carrier transportation efficiency within the NWs and polymer, η_{trans_NW} and η_{trans_Poly} , were taken as unity in the simulation [34]. The total absorbed photons could be obtained by three-dimensional integration of photogeneration rates along the unit cell axes. As a result, the photocurrent density of unit cell J_{ph_Unit} of HSC contributed both from P3HT and GaAs NWs could be determined by dividing unit cell illuminating area $Area_{Unit}$ as shown in Eq. 4.2. Correspondingly, the photocurrent density J_{ph} and $EQE_{AM1.5G}$ of the device under terrestrial AM 1.5G illumination condition were received by Eqs. 4.3 and 4.4 where q was elementary charge, λ was wavelength, $I(\lambda)$ was light intensity, h was Plank constant and c was speed of light in vacuum. The material parameters of P3HT and GaAs used in the calculation were listed in Table 4.1.

$$J_{ph_Unit}(\lambda) = [i_{ph_Poly}(\lambda) + i_{ph_NW}(\lambda)] / Area_{Unit} \quad (4.2)$$

$$J_{ph} = \int_{\lambda} I(\lambda) J_{ph_Unit}(\lambda) d\lambda \quad (4.3)$$

$$EQE_{AM1.5G} = J_{ph} / \int_{\lambda} \frac{q\lambda I(\lambda) d\lambda}{hc}. \quad (4.4)$$

Table 4.1 Summary of the parameters used in the simulation

Band gap of GaAs	1.43 eV
Diffusion lengths of exciton within P3HT	20 nm
HOMO of P3HT	-5.2eV
LUMO of P3HT	-3.3 eV
Length of NWs	2 μ m
Temperature	300 K

4.4.2 Photovoltaic Performance Evaluation

Figure 4.9 showed the photocurrent density and $EQE_{AM1.5G}$ changing with diameter of GaAs NWs and FR. In general, dependence of J_{ph} on the diameter of NWs and the FR showed very similar values for large range of parameters. This indicated that GaAs NWs/P3HT active layer had high tolerance to manufacturing process. It was important to notice that the best potential values of J_{ph} was 22.55 mA/cm². For the low FR value of 0.4, a general increase of the J_{ph} could be observed when increasing diameter of NWs from 80 to 190 nm. This trend arose from the excitation of multiple resonance modes for a fixed FR, as discussed above. On the other hand, for a fixed diameter of NWs, the increase of FR would generally lead to the rise of J_{ph} and $EQE_{AM1.5G}$. This was because when FR was small, there was large portion of P3HT in the unit cell. Due to the short diffusion length, the excitons outside the effective region would recombine and lost before they transported to the DA interface to be dissociated. When FR increased, NWs accounted for more volume ratio within the unit cell, and at the same time, larger percentage of photons generated from P3HT would contribute to the photocurrent. However, further increase of FR would result in a decrease of J_{ph} . When FR was larger than 0.4, the NWs were so closely packed that the competition of incident

photons among adjacent NWs reduced the J_{ph} . $EQE_{AM1.5G}$ had a resembling trend as J_{ph} and the highest value was 36.76% at diameter of 161.5 nm.

From the device fabrication point of view, the P3HT had long and entangled molecular chains. Too large value of FR made P3HT difficult to penetrate into the gaps among the NWs. The narrowest spacing for P3HT to infiltrate into would vary due to the polymeric concentration and fabrication process. From the published experimental results, we set 20 nm as the minimum spacing S_{min} among adjacent NWs to ensure the full penetration of P3HT. This requirement was marked as the black dash-dot line in the Fig. 4.9. Along the S_{min} , the J_{ph} was about 20 mA/cm² and $EQE_{AM1.5G}$ was 32%.

Figure 4.9 Photocurrent density (a) and external quantum efficiency ($EQE_{AM1.5G}$) (b) changed with diameter of NWs and FR.

We adopted the equivalent circuit in Chapter 2. Figure 4.10 showed the simulated J - V curves of the GaAs NWs/P3HT HSCs with different NW diameters and the FRs. The equivalent circuit of the HSC adopted in this simulation was included in the inset of Fig. 4.10(b). The photocurrent source J_{ph} described the ability of converting photons into free carriers under illumination. A diode parallel to the photocurrent source generated the dark current, which represented how device behaved like a diode without illumination. The series resistance R_s originated from the resistance of active layer and contact resistance with electrodes whereas the shunt resistance R_{sh} accounted for the leakage current in the device. Since the R_{sh} was usually an order of magnitude greater than the series resistance, it was neglected in the analysis [65]. The final form of the J - V relation of the HSC was displayed in Eq. 4.5. Reverse saturation current density J_{sat} was less affected by the FR of NWs according to the Richardson's thermionic emission equation and was set as 10^{-10} A/cm² [133]. T was absolute temperature and k_B was Boltzmann constant. Since the carrier mobility within the inorganic NWs was a few orders

of magnitude higher than those in polymers, therefore the R_s was chosen as a fixed value which was on the order of $10^{-3} \Omega\text{m}^2$ [43].

$$J = J_{sat} \left[\exp\left(\frac{V - qJR_s}{k_B T}\right) - 1 \right] - J_{ph}. \quad (4.5)$$

From the calculated J - V curves of the GaAs NWs/P3HT HSCs, their PCEs were calculated by the ratio of the maximum power over the incident light energy as shown in Eq. 4.6.

$$\eta_{PCE} = J_m V_m / P_{in}. \quad (4.6)$$

As shown in Fig. 4.10(a), the open-circuit voltage was almost the same for all the devices with different NW diameters and FRs. This was because V_{oc} of a HSC was mainly affected by the electron affinity of the acceptor and the highest occupied molecular orbital (HOMO) of the donor [34]. Since only the diameter and spacing of the NWs had changed, V_{oc} of the cell remained unaffected. The short-circuit current density J_{sc} of the device was primarily determined by the photocurrent density. In the ideal case, the upper limits of J_{sc} could be taken as the J_{ph} when R_s was very small and R_{sh} was sufficiently large [43]. Therefore, J_{sc} had similar trend as the J_{ph} . Two specific FRs were chosen for analysis. For a fixed FR, despite the diameters of the NWs, the amount of NWs' material consumption was the same. The larger FR was, the higher the amount of GaAs material consumed and thus the higher the cost of the device. Besides, the FR should not be too large, so that there was sufficient spacing among the NWs. For FR was 0.6, the rise of diameter of NWs would decrease the J_{ph} and PCE. This was because of the destructive interference among NWs as shown in Figs. 4.3 to 4.6. At the same time, the FR should also be larger than 0.3 since too low FR would lead to PCE to below 9% as shown in Fig. 4.10(b). When FR had a small value of 0.3, the coupling among NWs was reduced and with the increase of

diameter, the light harvesting efficiency increased which resulted in high J_{ph} and PCE. Moreover, since P_{in} was a constant for a given illumination in Eq. 4.6 and voltage for maximum power generated for the HSC V_m varied within a small range in the J - V curve for different diameters of NWs and FRs in Fig. 4.10(b). The current density for maximum power J_m determined the maximum output power, P_m . Since J_m could be approximated as J_{sc} which was proportional to $EQE_{AM1.5G}$ by a factor of constant incident illumination density, therefore the trend of PCE was also similar with that of $EQE_{AM1.5G}$.

Figure 4.10 Current density-voltage ($J-V$) curves (a) and PCE (b) of the GaAs NWs/P3HT HSC changed with diameter and FR.

Using this model, the PCE of the GaAs NWs and P3HT HSC published by Jiun-Jie Chao *et al.* was calculated [31]. The PCE of the solar cell was 10.1% with the cell's structure parameters given, which was very close to the experimental results of 9.28%. Considering the exciton recombination during transportation and carrier collection loss in actual device, the predicted value demonstrated the effectiveness of our opto-electrical model.

4.5 Conclusion

In this chapter, a coupled opto-electrical model for GaAs NWs/P3HT HSCs was presented. Light absorption of the GaAs NWs/P3HT active layer was studied using the three-dimensional FDTD simulation. Compared with that of a GaAs NWs/air layer, an increased light harvesting was received. Along with the leaky resonant modes of the GaAs NWs for light trapping, the polymeric layer served

as dielectric shell which confined light both below and beyond the absorptance band edge of P3HT. Geometrical parameters including diameter of NWs and FR were assessed on their influence of the light absorption efficiency. The light absorption efficiency of 2 μm thickness hybrid active layer was also evaluated at solar illumination achieving the highest value of 0.39. Moreover, photogeneration rates were calculated and incorporated to an electrical model which was built relating to the diffusion efficiency of the excitons in the organics. Current density-voltage characteristics illustrated that the open-circuit voltage remained unchanged for various unit cell dimensions whereas the short-circuit current density changed following the trend of photocurrent density. In general, device's PCE rose with FR but it was also limited by both P3HT infiltration spacing and high cost. For a high FR, the device's PCE decreased with the rose of diameter of NWs, whereas opposite trend was observed when the FR was small. This corresponded to the light absorption efficiency variation trend in the optical simulation. The proposed opto-electrical model was used to reconstruct published work and the well match of the device performance indicating the effectiveness of the model.

Chapter 5 Fabrication and Characterization of GaAs Nanowires/P3HT HSCs

In this chapter, we experimentally fabricated and characterized vertically-aligned GaAs nanowires (NWs) based hybrid solar cells (HSCs) to study the influence of the geometrical dimensions of the NW arrays on the performance of the device. Followed by the introduction and motivation, vertically aligned GaAs NW arrays were formed by combining nanospheres lithography and dry etching. The periodicities of the NW arrays were well controlled by the size of the nanospheres whereas the diameters of the NWs were tuned by plasma etching. Then, GaAs NWs/poly(3-hexylthiophene-2,5-diyl) (P3HT) HSCs were fabricated, characterized, and investigated as a function of NWs' geometrical parameters. These results unraveled the role of geometrical dimensions of the GaAs NW arrays in HSCs which was indispensable of guiding future highly efficient inorganic/organic HSC design.

5.1 Introduction and Motivation

As stated in the previous chapters, the light absorption of NW arrays are seriously affected by their geometrical dimensions. Therefore, the study about the influence of the geometrical parameters of the NW arrays on the photovoltaic performance of HSCs are critical. Although the opto-electrical model [68, 162] was presented in Chapter 4 to unravel the effect of the geometrical dimensions of the NW arrays in the fully-infiltrated GaAs NWs/P3HT HSCs, lacking of experimental study makes the conclusions less persuasive. Large area III-V NW

arrays can be fabricated by either bottom-up growth [120, 121, 125] via vapor-liquid-solid (VLS) mechanism [113] or top-down method using wet or dry etching such as inductively coupled plasma reactive ion etching (ICP-RIE) [111, 163]. Considering the diameter-dependent length of NWs for bottom-up growth [164-166], top-down method is mostly preferred in which the diameters and periodicities of the NW arrays can be well-controlled using the patterned masks. Early in 2009, the first report combining P3HT polymer with vertically aligned n-type GaAs achieved power conversion efficiency (PCE) of 1.04% [101]. Up to now, the highest PCE reported reached 9.2% [31]. Despite the efforts devoted which mainly focused on fabrication techniques (solvent mixing ratio, surface passivation, polymer thickness, etc.), the role of NWs' geometrical parameters such as diameter and periodicity in the photovoltaic process of HSC has not been investigated clearly.

In this chapter, we fabricated and characterized GaAs NWs/P3HT HSCs with well controlled NW arrays of various diameters and periodicities. Serving as etching masks, hexagonally arranged monolayer polystyrene (PS) nanospheres of various sizes were obtained by both spin-coating technique and self-assembly at ethanol-water surface method. The diameters of the nanosphere masks were controlled by plasma etching whereas the periodicities were tuned by the size of the nanospheres. Through optimization of the etching condition, vertically aligned GaAs NWs with controlled diameters and periodicities were received. Moreover, HSCs were fabricated by spin-coating the P3HT over the forest of NW arrays. Characterization of the HSCs were also presented to unravel the influence of the geometrical dimensions of the NWs. Along with the experimental study, the opto-electrical model were adopt to supplement and analyze the electrical performance of the device. These results deepen the understanding of the

geometrical dimensions of GaAs NWs in HSCs and are crucial for future HSC design.

5.2 Fabrication of GaAs Nanowires

One of the prerequisites of making high efficiency HSC is to obtain well-controlled GaAs NW arrays. In this section, we fabricated vertically aligned GaAs NW arrays using nanospheres lithography and ICP-RIE. The periodicities of NW arrays were controlled by the diameters of nanospheres whereas the diameters of the NWs were tuned by plasma etching. Through variation of the dry etching condition including the chlorine and methane-based chemistries, vertically aligned GaAs NW arrays were realized.

The experimental process for fabrication the GaAs NW arrays is schematically shown in Fig. 5.1. Monolayer of hexagonal arranged PS nanospheres were used as the etching mask and various diameters of PS nanospheres (Polysciences, Inc.) were selected. Specifically, Si-doped n-type (100) GaAs wafer (AXT, Inc.) with a carrier concentration of $0.8\sim 4 \times 10^{18} \text{ cm}^{-3}$ was cut into $5 \times 5 \text{ mm}^2$ square pieces and then they were treated for ultrasonication in acetone, isopropanol, and deionized (DI) water for 5 min each. Then, those pieces of wafer were dried by nitrogen. After surface treatment for hydrophilicity of the sample, monolayer of PS nanospheres was formed on top of GaAs pieces. In the next step, the diameters of PS nanospheres were reduced by plasma cleaner (Harrick Plasma PDC-32G-2) using medium power of different etching time as shown in Fig. 5.1(b). The patterned PS nanospheres covered wafers went through ICP-RIE (Beijing NMC Co.,Ltd.) at optimized condition and uniformly distributed GaAs NW arrays were received with PS nanospheres riding on their tops as illustrated in Fig. 5.1(c).

Next, the PS nanospheres were removed as shown in Fig. 5.1(d). In the following sections, formation of monolayer of PS nanospheres, size reduction of the nanospheres, dry etching of GaAs NWs, and how to remove the remaining PS nanospheres will all be described in details.

Figure 5.1 Schematic for GaAs NWs fabrication process including (a) formation of monolayer closely packed PS nanospheres, (b) diameter reduction of PS nanospheres, (c) ICP-RIE etching of GaAs, and (d) removal of PS nanospheres.

5.2.1 Formation of Monolayer of Nanospheres of Various Sizes

Polystyrene nanospheres have been widely adopted as etching masks in nanospheres lithography. Monolayer closely packed PS nanospheres of various diameters have attracted lots of research interests. Techniques have been successfully developed for the formation of colloidal crystals of excellent quality [167], including spin-coating [168, 169], vertical deposition [170], and self-assembly at the gas-liquid interface solvent evaporation [171]. In this chapter we mainly adopted the spin-coating and the self-assembly at the ethanol-water interface method to achieve hexagonal arrangement of monolayer PS

nanospheres of various diameters.

Before applying the above mentioned techniques for PS nanospheres arrangement, the surface of the sample should be treated as hydrophilicity. After cleaning of the wafers, the samples were functionalized by soaking in 1 wt% polydiallyldimethylammonium chloride (PDDAC) solution (Polysciences Inc.) for 60 min. After that, the samples were rinsed with deionized water for 30 s, followed by nitrogen drying. Figure 5.2 gave the comparison of the surface hydrophilicity of GaAs samples with and without surface treatment. Both samples were dropped 5 μ L deionized water on the surface. Obviously, the droplet formed a dome shape on the surface of GaAs sample without any treatment whereas the droplet of deionized water quickly spread uniformly on the surface of the sample after treatment.

Figure 5.2 Comparison of the GaAs surface hydrophilicity with and without surficial treatment.

Spin-coating technique is widely adopted for PS nanospheres arrangement because the spin-coating process is simple, rapid and compatible with wafer-scale processes for mass production. Schematic of spin-coating process is shown in Fig. 5.3 which is divided into four stages. In the first stage, the PS nanospheres suspension is dropped onto the stationary GaAs wafer and a spherical crown shape puddle is formed due to the surface tension as shown in Fig. 5.3(a). After

wetting for 1 min, some suspension is spun away from the substrate whereas the rest of it stays on the surface of the substrate in Fig. 5.3(b). The suspension gradually evaporates along with the spin-coating process. The PS nanospheres begin to self-assemble and monolayer of colloidal-crystal films are formed in Fig. 5.3(d) [168].

Figure 5.3 Schematic of spin-coating process for the formation of closely packaged monolayer of PS nanospheres.

The packaging quality of the PS nanospheres is mainly affected by the spin speed, acceleration, and the hydrophilicity of the substrate [167]. During the process, forces acting on the PS nanospheres suspension depend on the sizes of PS nanospheres. Therefore, different spin speeds and accelerations should be applied for PS nanospheres of various diameters to keep them in a balance state. In addition, spin speed and spin acceleration can be well controlled by adjusting the parameters of spin-coater which simplifies the fabrication processes and improves the reproducibility of this fabrication. In this section, we mainly optimized the spin speed and the acceleration for 500, 350, and 200 nm diameter of PS nanospheres. A JEOL JSM-7000F field emission scanning electron microscope (FESEM) was used to characterize the morphology of PS

arrangement under different spin-coating condition.

From Figs. 5.4 to 5.6, for all sizes of PS nanospheres, they displayed similar trend that too high the spin speed would “tear up” the closely packaged PS monolayer whereas too low the spin speed would cause the pile up of the nanospheres. This was because the spin speed mainly affected the centrifugal force that applied on the PS nanospheres and the velocity and turbulence of the air above the PS suspension. Well-packed PS nanospheres were obtained at the balance among the forces applied to shear the PS suspension towards the edge of the wafer and the drying rate. At this point, the nanospheres moved along the surface of the substrate and self-assembled in hexagonal manner and therefore monolayer of PS nanospheres could be formed. If the spin speed was too low, it destroyed the balance of the forces acted upon on the PS nanospheres. The slowed speed of evaporation of the PS nanospheres suspension caused the aggregation and the pile up of the nanospheres. At the same time, if the spin speed was too high, the centrifugal force and the evaporation rate increased further and a mass of the PS nanospheres suspensions were thrown away. As a result, the rest of the PS nanospheres were dried and fixed before packing in order.

Similar with spin speed's effect, the acceleration of the spin speed toward the targeted speed also affected the quality of the PS monolayer. Unlike the spin speed causing a radial force, acceleration provided a twisting force to the nanospheres suspensions. At low acceleration, the sample was spun at a low speed for a longer time and therefore the nanospheres would accumulate and form multilayers. At high acceleration, large amount of the suspension was spun off the substrate at the initial stage and the leaving PS nanospheres fixed before arranged in order [168]. More information were obtained from Fig. 5.7, where

the samples were observed under low magnification.

Figure 5.4 Morphology variations of 500 nm PS nanospheres with spin speed and acceleration.

Figure 5.5 Morphology variations of 350 nm PS nanospheres with spin speed and acceleration.

Figure 5.6 Morphology variations of 200 nm PS nanospheres with spin speed and acceleration.

Figure 5.7 Different magnifications of closely packed PS nanospheres of 500, 350 200 and 100 nm diameters.

From the above discussion, although spin-coating method has advantages for mass production, the dislocations and defects will jeopardize the arrangement of NW arrays if they are used as the etching masks. Therefore, the self-assembly at the ethanol-water interface method was also investigated. Large area monolayer of PS nanospheres were formed of various sizes. Before applying the self-assembly at the ethanol-water interface method, the surface of a piece of glass was treated by UV ozone cleaner (PSD Series Digital UV Ozone System) for 15 min. This piece of glass was used to arrange the monolayer of PS nanospheres which were transferred to GaAs samples at a later stage. The hydrophilicity of the surface of the glass was checked as shown in Fig. 5.8. It was obvious that the droplet of deionized water quickly spread over the surface of the glass after UV ozone treatment.

Figure 5.8 Hydrophilicity of the surface of glass with and without UV ozone treatment.

Process flow of the preparation of self-assembly at the ethanol-water interface method for monolayer PS nanospheres is shown in Fig. 5.9. After surface hydrophilic treatment of the piece of rectangular glass, it was used for the formation of PS nanospheres monolayer of various sizes. Next, the surface of the glass was covered by a layer of deionized water as shown in Fig. 5.9(a) to (c). Suspension of PS nanospheres was mixed with ethanol at the volume ratio of 1:1 which was gradually injected from the corner of the glass. Upon the dropping of

the mixed PS suspension on the still water, they quickly spread on the deionized water surface and a temporary ethanol-water bilayer was formed. The PS nanospheres gradually self-assembled on the water surface along the ethanol flow direction as shown in Fig 5.9(d) and (e). In the next step, the deionized water below the layer of closely packed PS nanospheres was absorbed by a piece of filter paper as shown in Fig. 5.9(f). After that, the monolayer of PS nanospheres was transferred to the surface of deionized water in a glass beaker. Figure 5.9(g-1) and (g-2) gave the monolayer of PS nanospheres of diameters of 500 and 200 nm. The reflected color provided a roughly guidance of the different sizes of PS nanospheres. In the last step, a piece of GaAs wafer was taken out with monolayer of PS nanospheres covered its surface. Figure 5.10 clearly showed the surface coverage on the GaAs wafers. The FESEM images in Fig. 5.11 provided detailed view of the large area monolayer of PS nanospheres for 500, 350, and 200 nm diameters. High quality and monolayer of PS nanospheres were well arranged on the top of GaAs wafers. Compared with Fig. 5.7, this self-assembly method has demonstrated itself to be an effective way of formation of large area hexagonally arranged nanospheres with less defects and dislocations for nanospheres lithography.

Figure 5.9 Process flow for the self-assembly at the ethanol-water interface method: (a) to (c) showed deionized water coverage on the surface of glass; (d) to (f) showed the dispersed PS nanospheres floating on the ethanol/water surface; (g-1) to (h) showed scooping transfer of the monolayer of PS nanospheres to the GaAs wafer surface where (g-1) and (g-2) gave monolayers of 500 and 200 nm nanospheres respectively.

Figure 5.10 Transfer results for (a) 500, (b) 350, and (c) 200 nm PS nanospheres monolayer.

Figure 5.11 FESEM images for large area PS nanospheres monolayer of (a) 500, (c) 350, and (e) 200 nm where (b), (d) and (f) were the lower magnification of the respective sizes of PS nanospheres.

Table 5.1 Comparison of the advantages of the spin-coating method and the self-assembly method for the formation of the monolayer of the PS nanospheres

	Defects density	Range of monolayer	Coverage
Spin-coating method	high	large	Only the center part of the sample
Self-assembly method	low	small	Whole size of the sample

After the acquisition of the monolayer of PS nanospheres, the diameter of the PS nanospheres was reduced by plasma cleaner. The etching speed of the plasma cleaner was summarized in Fig. 5.12. After a period of 1 min, the etching speed became at 20 nm/min and rapid increase of the etching was observed at longer etching time of 4 min. The morphology of PS nanospheres after plasma treatment was illustrated in Fig. 5.13 for period ranging from 1.5 to 4 min.

Figure 5.12 Diameter of 500 nm PS nanospheres changed with plasma etching time.

Figure 5.13 The 500 nm diameter PS nanospheres under plasma treatment for (a) 1.5, (b) 2, (c) 2.5, (d) 3, (e) 3.5, and (f) 4 min.

5.2.2 Fabrication of GaAs Nanowires

GaAs NW arrays with large aspect ratio were reported by several groups using various recipes [110, 111, 163]. In an ICP-RIE system, there are multiple parameters that affect the morphology of the dry-etched nanostructures. The two radio-frequency sources separately control the plasma generation and the bias between the plasma and the wafers [172]. The etching chemistry also plays an important role. Chlorine based etch chemistries are reported to strongly etch the III-V materials at the cost of side wall smoothing [110, 111]. On the contrary, methane based etch chemistries produce smoother side surfaces but the etch rates are below satisfactory [163]. In this part, optimal combinations of both chlorine and methane-based chemistries were explored to achieve reasonable etch rates and smooth side walls. Meanwhile, the PS nanospheres should sustain during the etching process to maintain cylindrical shape of NWs. The FESEM images of the etched GaAs NWs were used for morphology assessment.

Boron trichloride has previously been mixed with chlorine to anisotropically etch structures in GaAs [173]. Figure 5.14 showed that with the increase of the Cl_2 and BCl_3 flow rates, the profiles of the GaAs became vertical at first and then the anisotropically etching became obvious. This could be explained that with the increase of chlorine flow rate, the number of heavy ions increased for physical sputtering which enhanced isotropic etching. In the light of these results, the Cl_2 flow rate was fixed at 25 sccm and BCl_3 flow rate was fixed at 30 sccm since they led to high selectivity with steep sidewalls of the NWs.

Figure 5.14 GaAs profiles changed as a function of chlorine chemistry. The flow rates were (a) 20, (b) 25, and (c) 30 sccm for Cl_2 where the BCl_3 was fixed at 30 sccm; the flow rates were (d) 25 and (e) 35 sccm where Cl_2 was fixed at 25 sccm.

We also increased the etching time and it was obvious from Fig. 5.15 that the length of the GaAs NWs rose with the prolonged etching time.

Figure 5.15 GaAs profiles changed as a function of etching time where (a), (b) and (c) were 20, 40, and 80 s respectively.

Figure 5.16 showed the profiles of the NWs changed with the ICP power. When the power increased from 50 to 300 W, ions with higher velocities bombarded the surface, resulting in a higher etch rate. Also, the increase of the anisotropy etching resulted in the smooth side walls. When the power further rose to 350 W, the stronger bombardment caused the serious etching of the PS nanospheres which also deformed the side walls of the NWs. After this parameters study, the optimized chemistry was obtained as Cl_2/BCl_3 and with gas flows of 25, and 30. The ICP power was 300 W and the operating pressure was 5 mTorr.

Figure 5.16 GaAs profiles changed as a function of ICP power where (a), (b) and (c) were 50, 300, and 350 W respectively.

How to remove the PS nanospheres after ICP-RIE is also an important technical problem. We developed a new technique that combined the solution soaking and ultrasonication without causing serious damage to the GaAs samples. In the following, 500 nm diameter PS nanospheres were chosen as an illustration. The GaAs NWs with PS nanospheres riding on their tops were soaked in chloroform for 15 min and then the FESEM inspection of the samples with and without

ultrasonication of 30 min were compared in Fig. 5.17. It clearly showed that after soaking into the chloroform for 15 min, the PS nanospheres gradually dissolved into the solution. Without ultrasonication, those PS material lied on the tops and the peripheral of the GaAs NW arrays. At the same time, observation in Fig. 5.17(a) also indicated that the soaking time was not long enough since there was still polystyrene on the tops of the GaAs NWs.

Figure 5.17 Comparison of with (a) and without (b) ultrasonication to remove PS nanospheres on GaAs samples.

We optimized the soaking time of the GaAs samples in the chloroform as shown in Fig. 5.18. Variation of soaking time in chloroform for GaAs NW arrays to removal PS nanospheres had been shown as an effective method. From 15 to 40 min, the PS stain on top of GaAs NWs became smaller and smaller and finally disappeared at 40 min. The same technique had been applied to GaAs NWs samples with diameter of 200 and 350 nm nanospheres. The optimized PS-removal condition is summarized in Table 5.1.

Table 5.2 Optimized condition for various sizes PS nanospheres removal on top of GaAs NWs

Size of PS nanospheres	Chloroform soaking time	Ultrasonication time
------------------------	-------------------------	----------------------

(nm)	(min)	(min)
200	90	30
350	60	30
500	40	30

Figure 5.18 Removal of PS nanospheres on top of GaAs NW arrays by optimization of chloroform soaking time of (a) 15, (b) 20, (c) 25, (d) 30, (e) 35, and (f) 40 min.

The morphology of GaAs NW arrays of various diameters under optimized ICP-RIE etching condition are shown in Fig. 5.19. Uniformly distributed NW arrays using 500, 350 and 200 nm PS nanospheres as etching masks were shown in Figs. 5.19(a) to (c). Large area NW arrays were provided in the insets of respective NW arrays. Polystyrene nanospheres were successfully removed from the top of the NW array as observed from Fig. 5.19(a) with flat top surfaces of NWs. Figure 5.19(d) and (e) displayed 350 nm NW arrays which underwent the same etching condition but with prolonged etching time for 80 s. The PS nanospheres were deformed but the side wall of the NWs remained smooth.

Figure 5.19 GaAs NW arrays by ICP-RIE of different sizes where (a), (b), and (c) were 500, 350, and 200 nm diameter GaAs NW arrays; (d) was the top view of the NW array and (e) was the glancing view of the NW arrays.

5.3 Fabrication and Characterization of GaAs Nanowires/P3HT HSCs

5.3.1 GaAs Nanowires/P3HT HSCs Fabrication Process

The fabrication process of GaAs NWs/P3HT HSC is schematically shown in Fig. 5.20. When the GaAs NW arrays were obtained, a layer of 200 nm thickness Ag was then thermally evaporated on the back of the GaAs wafers as shown in Fig. 5.20(a). The sample was spin-coated by a mixed solution of regioregular P3HT as shown in Fig. 5.20(b). Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS) was mixed with DMSO (95:5) and add 1% FS-30 to change its surface property. Then the PEDOT:PSS was also spin-coated on top of GaAs NWs/P3HT at 4000 rpm for 50 s as shown in Fig. 5.22(c). After that, the sample was stick to ITO and cured at 140 °C for 10 min. In the next step, polydimethylsiloxane (PDMS) was moulded and cured around the fabricated cell exposing the top Ag electrode as cathode. Then, the silver paste filled along the channel created on the top of

PDMS. After that, the silver paste was cured. Figures 5.22(g) and (h) gave the real image of the fabricated cell. The GaAs NWs/P3HT processing, and testing processes were all conducted under ambient air condition. Samples were stored under a vacuum of <0.1 mTorr if any step was not performed immediately. The morphology of the samples before and after spin-coating was examined by FESEM. Current density and voltage characteristics were measured by illuminating the devices using a solar simulator with an AM 1.5G filter to provide 100 mW cm^{-2} (1 Suns) of power.

Figure 5.20 Schematic of the fabrication process of GaAs NWs/P3HT HSC.

5.3.2 Hybrid Active Layer of Various Diameters and Periodicities of GaAs Nanowire Arrays

The common procedure to prepare P3HT solution is by mixing P3HT with chlorobenzene (CB) or dichlorobenzene. However, this well-adopted method is not suitable for creation of NWs/organics hybrid active layer. P3HT prepared in this way will not penetrate into the forest of NW arrays and in most of the cases, it is spun off the sample. In this section, we dissolved P3HT (Sigma-Aldrich) in a mixed solution of CB and ortho-dichlorobenzene (ODCB) with volume ratios of 4:1 according to the optimized ratio in the parameters study in reference [101]. It was reported that the utilization of mixed solvent with different boiling points (132 °C for CB and 180 °C for ODCB) would achieve the optimal P3HT coverage onto the GaAs NWs [31]. After dissolving the P3HT into the mixed solution, the spin speed was optimized to form the desired fully infiltration coating over the NWs surface. Next, all of the samples were cured at 120 °C for 10 min.

Hybrid active layers for GaAs NWs/P3HT of different diameters and FRs are provided in Fig. 5.21. From Figs. 5.21(a) to (c), we observed that as the decrease of spin speed from 7000 to 2000 rpm, the P3HT firstly infiltrated to the base of the NW arrays and then it gradually covered the whole NW arrays. Therefore, through optimization of spin speed, we achieved fully infiltrated hybrid active layer for various periodicities and FRs. Tilt view of 45° in Figs. 5.21(d), (e) and (f) were obtained by peeling off the samples from ITO glass. Even for the highest FR of 0.7, the spacing among NWs was well covered by P3HT for both 350 and 200 nm periodicities of NW arrays as indicated in Figs. 5.23(d), (e), (f), and (i).

Figure 5.21 Hybrid active layer for GaAs NWs/P3HT of different periodicities and FRs where (a), (b) and (c) were 500 nm periodicity of GaAs NW arrays infiltrated by P3HT of spin speed of 7000, 5000, and 2000 rpm respectively; (d) and (e) were for 350 nm periodicity GaAs NW arrays with FR of 0.7 covered by P3HT where (d) gave the tilt view and (e) was cross-sectional view of the same sample; (f), (g) and (h) gave 200 nm periodicity GaAs NWs with FR of 0.7, 0.58 and 0.44 respectively and (i) showed the cross-sectional view of the same sample in (f).

5.3.3 Photovoltaic Performance Evaluation

The photovoltaic performance of GaAs NWs HSCs were investigated both numerically and experimentally. The opto-electrical model that we developed in Chapter 4 was adopted to evaluate the performance of HSCs. Finite-difference time-domain (FDTD) simulations (Lumerical FDTD Solutions 8.15) were provided to verify and compare with experimental results. The parameter space for diameters of NWs were chosen from 100 to 500 nm whereas the FR ranged from 0.05 to the maximal value of $\pi\sqrt{3}/6$ for hexagonal NW arrays. The model was built according to the FESEM inspection of the morphology of the NWs.

The length of NWs was 900 nm and the base of GaAs was 2.6 μm . Incident light illuminated from the top of NW arrays and the complex refractive indexes of GaAs were obtained from the Palik material data provided by Lumerical whereas the optical constants for P3HT were taken from the reference [73].

An overall view of the $\text{EQE}_{\text{AM1.5G}}$ variation as a function of diameter of NWs and FRs was displayed in Fig. 5.22(a) which was obtained by FDTD simulation with experimental measurements marked with white crosses. In general, the experimental measurements were in accordance with the simulation results. Since the extinction coefficients for GaAs was an order of magnitude higher than P3HT [73] and only the 20 nm thickness P3HT shell around GaAs NWs would contribute to the photocurrent, the variation of $\text{EQE}_{\text{AM1.5G}}$ was mainly attributed to the GaAs NW arrays. For a fixed periodicity, the $\text{EQE}_{\text{AM1.5G}}$ decreased when FR increased and similar trend could be found for all periodicities. This was mainly due to the light coupling among adjacent NWs. As the diameter became larger, for a fixed periodicity, the spacing among neighboring NWs got smaller. This would cause the competence of incident photon energy leading to the decrease of exciton generation. Although the redundant P3HT that could not contribute to the photocurrent became larger as the reduction of the FR, they still served as dielectric shell over the NWs and improved the light absorption of NWs.

Moreover, for a fixed value of FR, the $\text{EQE}_{\text{AM1.5G}}$ decreased when the periodicity rose from 200 to 500 nm. This was mainly due to the reduced coupled efficiency of the incident light to the NWs. As stated in the previous chapters, it was the resonant modes that drove strong absorption peaks to contribute to the light harvesting. These modes were mainly diameter-dependent and the larger the diameter, the higher modes they could support. However, the fields of higher

order modes also had greater number of mode nodes at the cross-section of NWs which coupled less well to the incident plane waves. This reduced coupled efficiency of the incident light and increased the light reflectance resulting less absorption. Besides, when FR was 0.7, the spacing among NWs was 28, 80, and 120 nm for periodicity of 200, 350, and 500 nm NWs samples. As mentioned before, only the periphery of 20 nm P3HT shell around the NWs could devote to the photocurrent. Therefore, the redundant P3HT that could not contribute to the photocurrent increased as the rise of the periodicity which also led to lower $EQE_{AM1.5G}$.

Figure 5.22(b) and (c) show the experimental measurements of EQE of GaAs NWs/P3HT HSC as a function of incident wavelength. Beyond 650 nm, an obvious decrease of EQE was found due to the band edge of P3HT material. Beyond 650 nm, P3HT served as the dielectric shell over GaAs NWs but would not contribute to excitons generation. Below 650 nm, both the P3HT and the GaAs NWs contributed to the photocurrent. However, for a fixed periodicity of 200 nm as shown in Fig. 5.24(b), the EQE decreased as the increased of FR since the incident of photons were competed among closely packed NWs. For a fixed FR, the hybrid active layer possessed the same amount of GaAs material as shown in Fig. 5.24(c). However, the increase of periodicity would lead to the increase of diameter of NWs. The higher order modes that the larger diameter NWs supported would decrease the light absorption which was also confirmed by the appearance of additional peaks at high incident energy region.

Figure 5.22 EQE_{AM1.5G} of GaAs NWs/P3HT HSC of various periodicities and diameters from (a) FDTD simulation results whereas experimental measurements were included; (b) and (c) gave the EQE measurement for fixed periodicity and FR respectively.

Power conversion efficiency (PCE) of GaAs NWs/P3HT was shown in Fig. 5.23. Figure 5.23(a) combined the FDTD simulation results with experimental measurements. The measurements were marked as white crosses at respective FR and diameters locations in the same figure. Generally speaking, the PCE demonstrated similar trend with $\text{EQE}_{\text{AM1.5G}}$. A gradual decrease of PCE was observed as the increase of FR for a fixed periodicity. Similar trend could be found at periodicities of 200, 350 and 500 nm. Besides, for a fixed value of FR of 0.7, the maximal PCE of 3.3% was found at periodicity of 200 nm. For all experimental measurements, the maximal PCE was 4.6 % when periodicity was 200 nm with FR of 0.44.

Table 5.3 The photovoltaic characteristics of the GaAs NWs/P3HT HSC with different FR (diameters) of NWs and periodicity

FR	Periodicity (nm)	V_{oc} (V)	J_{sc} (mA/cm ²)	R_s (Ωcm^{-2})	R_{sh} (Ωcm^{-2})	FF (%)	PCE (%)
0.44	200	0.59	13.68	6	1768	0.58	4.6
0.58	200	0.58	12	13	659	0.53	3.7
0.7	200	0.58	11.9	6.4	620	0.47	3.3
0.7	350	0.58	11.13	10.6	807	0.50	3.2
0.7	500	0.58	10.45	19.9	1282	0.50	3.0

The J - V curves of GaAs NWs/P3HT were shown in Fig. 5.23(b) and (c) and the important photovoltaic characteristics were provided in Table 5.2. Irrespective of the diameters and periodicities of NWs, an open-circuit voltage was found to be at 0.58 V which was mainly due to the band gap of GaAs and highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)

levels of P3HT. For a fixed periodicity of 200 nm as shown in Fig. 5.23(b), an obvious increase of J_{sc} was observed as the decrease of FR which corresponded to the variation of $E_{QEAM1.5G}$ trend in Fig 5.22(a). At the same time, according to Table 5.2, the noticeable drop of R_{sh} also indicated the rise of recombination as the FR increased. The area of DA interfaces $DA_{NW_Organics}$ was estimated as $DA_{NW_Organics} = A_{device} / A_{UnitCell} \times 4\pi R_{NW} \times L = A_{device} / \sqrt{3} p_{UnitCell}^2 \times 4\pi R_{NW} \times L$ where L was the length of the NWs. Defined by the overlapping area of cathode and anode, the active area of the device A_{device} was the same for all devices. For a fixed periodicity, the devices in Fig. 5.25(b) possessed the same size of unit cell $A_{UnitCell} = \sqrt{3} p_{UnitCell}^2$. Consequently, the $DA_{NW_Organics}$ was proportional to the radius of NWs for a fixed periodicity. In this situation, the rise of FR would lead to larger diameter of NWs and therefore the $DA_{NW_Organics}$ was correspondingly enlarged. This boosted the higher possibility of nonradiative recombination which caused the drop of R_{sh} .

At the same time, for a fixed FR of 0.7, the increase of periodicity from 200 to 500 nm decreased the PCE. This was mainly attributed to the rise of periodicity and therefore the diameter of NWs which reduced the light coupling efficiency of the incident light and reduce the short-circuit current density. However, we had also noticed that the obvious increase of the R_{sh} as the rise of the periodicity in Table 5.2. This indicated a decrease of surface recombination rates. According to the definition of FR, for a fixed FR, a relationship between the radius of the NWs and the periodicities among various unit cells was obtained as $2\pi R_{NW}^2 / \sqrt{3} p_{UnitCell_R}^2 = 2\pi r_{NW}^2 / \sqrt{3} p_{UnitCell_r}^2$. This relationship of the radius of NWs and the periodicity between different cells could be substitute to the definition of $DA_{NW_Organics}$. It was calculated that $DA_{NW_Organics}$ was reciprocally

proportional to the radius of NWs. For a fixed FR, the rise of periodicity would lead to the increase of the radius which would reduce the value of the $DA_{NW_Organics}$, and lowered probability of surface recombination. However, according to the experimental measurement results, this rise of the nonradiative recombination had minor effect over the PCE trend. Therefore, the highest PCE was still found at the 200 nm periodicity for the fixed FR of 0.7.

Figure 5.23 Power conversion efficiency of GaAs NWs/P3HT HSC of various periodicities and diameters from (a) FDTD simulation results whereas experimental measurements were included with J - V curves shown in (b) with fixed periodicity and (c) with fixed FR.

Table 5.4 The represented published work about GaAs NWs/P3HT HSCs

Year	Reference	Structure	Power conversion efficiency
2009	[101]	GaAs:P3HT	1.04%
2010	[102]	GaAs:PEDOT	5.8%
2010	[104]	GaAs:P3HT	0.6%
2012	[31]	GaAs:P3HT:PEDOT	9.2%

The represented published work are compared in the Table of 5.4. Since the first work published in 2009 till the highest reported PCE of 9.2. Considering the fabrication of the ordered NW arrays by ICP-RIE, there may be more surface damages to the side walls of the NWs as compared with bottom up growth method. Several groups have considered this surface passivation issue in their work. Examples can be found by adding a thin shell of amorphous TiO_x coated onto the GaAs NWs to passivate the NW surface and further enhanced the device performance [106]. There is other report that mentioned that the rectification ratio

(current ratio measured at +3 V versus -3 V) increased by almost a factor of 2 from 81 to 155 for the untreated and treated InP NWs HSCs [133]. In this project, the role of surface passivation on the performance of the device was not investigated experimentally since the focus was mainly put on the influence of the geometrical dimensions of the NW arrays. However, the effect of the surface passivation was considered in the Figs. 5.22(a) and 5.23(a) by a factor of 65%. To further boost the performance of the device, it is worthy of investigation the surface damages and the techniques of surface passivation in the future.

The actual size of the piece of the GaAs sample with NWs formed on its top was about $5 \times 5 \text{ mm}^2$ which is difficult to operate and test the J-V curve. Too large size of the GaAs sample makes it very fragile for some device fabrication techniques such as polystyrene nanosphere removal using the ultrasonication for 30 min and spin-coating the organics over the GaAs NW arrays/P3HT HSC etc.. Moreover, the contact layer between the PEDOT:PSS and the ITO was very easy to detach and the poor contact may be the possible reason for the poor J-V curve.

5.4 Conclusion

In this chapter, HSCs based on GaAs NWs/P3HT were demonstrated which unravel the influence of geometrical dimensions of GaAs NWs in photovoltaic performance. Uniform GaAs NW arrays with well-controlled various diameters and periodicities were experimentally fabricated by nanospheres lithography and ICP-RIE etching. Spin-coating and self-assembly at ethanol-water interface techniques were investigated to form low defects density and closely packaged PS nanospheres. Spin-coating speed and acceleration were optimized and analyzed to form monolayer PS nanospheres of 500, 350, and 200 nm diameters

on GaAs wafers. Besides, millimeter-scale and low defects density monolayer PS nanospheres were realized by self-assembly at ethanol-water interface technique serving as the etching masks for GaAs NWs. The diameters of the nanosphere masks were controlled by plasma etching whereas the periodicities were varied by the selection of the sizes of the PS nanospheres. Optimal etching condition of GaAs NWs was found through parameters study of the etching chemistries, power and time. Hybrid solar cells were fabricated by infiltrating the P3HT into the forest of GaAs NW arrays of various diameters and FRs. Along with the numerical study, the influence of the geometrical dimensions of the NW arrays on $EQE_{AM1.5G}$ and PCE of HSCs were characterized. In general, the rise of periodicity (and therefore the diameter) of NW arrays would decrease the photon harvesting when FR was 0.7 which was mainly due to the low coupling efficiency of the incident light to the NWs. When the periodicity was fixed, the rise of FR would cause the competence of energy harvesting among adjacent of NWs which lowered the PCE. The highest PCE achieved was 4.6% for 200 nm periodicity and FR was 0.44. This study clarified the role of GaAs NWs in HSC which also demonstrated the potential of inorganics/organics HSC for large-scale application.

Chapter 6 A Prototype of HSC Based on the Direct Growth of Freely Standing GaAs Nanowires on Indium Tin Oxide (ITO)

In this chapter, a prototype of hybrid solar cell (HSC) is developed based on the direct growth of GaAs nanowires (NWs) on transparent conductive substrate. Freely standing GaAs NWs of high crystal quality have been grown on indium tin oxide (ITO) glass using Au nanoparticles (NPs) as catalysts by metal organic chemical vapour deposition (MOCVD). Followed by the introduction, an area density controllable Au NPs deposition method is presented. The influence of the growth condition and the catalysts on the growth of NWs are systematically investigated. A prototype of GaAs NWs based HSC was fabricated and characterized which unravel an alternative way of fabricating low-cost photovoltaic device.

6.1 Introduction and Motivation

In the early work, to form the ideal interdigital heterojunctions for high performance HSCs, the inorganic NWs of cadmium compound (CdS, CdSe) and metal oxides (ZnO and TiO₂) were grown on transparent conductive substrates [87, 174-177]. However, the toxicity of the cadmium compounds may cause severe damage to the environment, whereas TiO₂ and ZnO have the energy band gaps higher than 3 eV leading to a poor power conversion efficiency of below 5% [43]. Considering the direct band gap, high absorption coefficients, and high carrier mobility of III-V material, GaAs NWs based HSCs will demonstrate great potential. Up-to-date, the best performance reported reached energy conversion efficiency of 9.2% [31]. Nevertheless, most of the fabricated III-V semiconductor NWs based HSCs possess about two hundreds micrometers underlying III-V substrate. In order to further lower the material cost, attention has been put on directly integrate III-V NWs on low-cost transparent conductive substrates for

developing new types of HSCs. In 2008, there was the first report of InP NWs directly growth on ITO glass. GaAs NWs were also grown on aluminium-doped zinc oxide substrate [132]. However, most of the as-grown III-V NWs in the publications have noticeable kinks and worm-shape defects which seriously degrade the crystal quality of the NWs. Moreover, due to the polycrystalline nature of ITO glass and large lattice mismatch between the GaAs and the substrate [178], it is difficult to directly grow GaAs NWs with free-standing morphology and high crystal quality on ITO.

In this chapter, we developed a prototype of HSCs based on the direct growth of the freely standing GaAs NWs on ITO glass. Metal organic chemical vapour deposition (MOCVD) was used to grow the GaAs NWs who were catalyzed by Au NPs of various sizes. A centrifugal method was proposed to deposit Au NPs and well control over their area densities on ITO glass was realized. Following that, a quantitatively examination of the influence of the growth parameters on the growth of NWs were carried out including the growth temperature, precursor flow rate, growth time, and Au NPs size. At the same time, the area density of GaAs NWs was effectively controlled by centrifugal deposition of Au NPs. Moreover, few crystal defects were found along the entire length of the NWs of various diameters indicating that the GaAs NWs had high crystal quality. In the last part of this chapter, a prototype of HSC combining the GaAs NWs and organics was demonstrated pointing out an alternative way of fabricating low-cost photovoltaic device.

6.2 Au Nanoparticles Deposition Control for GaAs Nanowires Growth

In order to directly grow GaAs NWs on ITO, bottom-up growth method was adopted using the vapor-liquid-solid (VLS) mechanism which was firstly reported in 1964 [113]. The supersaturated liquid alloy was formed inside the foreign metal catalyst by the reactants in vapour phase [179]. The precipitation

of precursors to the interface of the liquid-solid was caused by the chemical potential difference. The eutectic alloy began to crystallize at the liquid-solid interface by continuously providing the reactants, and thus the NWs were formed [125]. According to the VLS mechanism, the position of the foreign catalysts such as Au NPs constrained the distribution of the as-grown GaAs NWs. Therefore, well control over the Au NPs deposition was one of the prerequisite for the growth of NWs.

In most of the Au NPs catalyzed NWs growth, the liquid suspension containing the NPs are usually dropped onto the substrate. The excessive suspension is then blown away by nitrogen while some of the Au NPs are left on the substrate. For this simple technique, the size distribution of the NPs is constrained by the synthesis method. Normally, the commercial products of Au NPs have 15% tolerance for size distribution. At the same time, another effective method of forming Au NPs is by evaporation of a few nanometers of Au thin film followed by thermal annealing [180]. Through varying the thickness of the Au thin film, time and temperature during the thermal annealing, the size and area density of the Au NPs can be changed. Adoption of this method, the average area density of Au NPs can reach about $80 \text{ NP}/\mu\text{m}^2$ with broad size distribution [128]. There are also reports that focus on the position control of Au NPs including manipulating Au NPs through atomic force [181], applying templates [182] or masks [64]. However, the high cost and the multiple process steps limit their wide application. In this section, we develop an Au NPs deposition method that is simple, cheap, with narrow size distribution, and area density controllable.

We firstly adopted the dropcast method for Au NPs deposition taking the advantages of polydiallyldimethylammonium chloride (PDDAC) solution to attach the Au NPs onto ITO. Next, we presented an Au NPs deposition method by centrifugation. Morphology inspection had revealed that significant increase of the area density by the proposed method. Through tuning the centrifugal

parameters, rational control over the area density of Au NPs had been realized. Moreover, a numerical model was present to quantitatively and qualitatively describe the NPs' area density on ITO surface. Both experimental and numerical analysis proved the validity of this centrifugation method in depositing of various sizes of Au NPs on ITO surface which was the foundation of the VLS NWs growth.

6.2.1 Centrifugal Deposition of Au Nanoparticles on ITO

Without surface treatment of ITO, Au NPs were difficult to be attached onto the hydrophobic surface of ITO. In the following, we used PDDAC solution to treat the surface of ITO since it was reported that a layer of positive charged could be formed which helped attract the negatively charged NPs [183]. Optimal PDDAC soaking time and the suspension of Au NPs deposition time were investigated for maximal area density in reference [127].

The ITO glass (Xinyan Technology Ltd.) was cut into $5 \times 5 \text{ mm}^2$ pieces and cleaned by acetone, isopropanol and deionized water in the ultrasonicator. The samples were dried by nitrogen, and they were soaked into the PDDAC solution (1 wt%) for 1 h. In the next step, the samples were cleaned by deionized water and then dried by nitrogen. After that, the ITO glasses were stuck onto the cap of centrifugal tube with ITO surface facing the inside of the tube as shown in Fig. 6.1. The suspension of Au NPs (Nanocs Ltd.) of 10 and 20 nm diameters of $\sim 1.8 \times 10^{13} \text{ NP/mL}$ was injected into the centrifugal tubes. This tube was moved into the centrifugal tube who was suitable for the centrifuge (Sartorius 2-5). Before the start of centrifugation, there was no contact of the Au NPs and the ITO glass. We gave a parameter study of the rotation speed of 1000, 2000, and 4000 revolutions per minute (RPM). The centrifuge had the radius R of 13.4 cm, and we calculated the relative centrifugal forces of 150, 599, and 2397 g using relationship of $1.12 \times R \times (\text{RPM}/1000)^2$. Investigation of centrifugal time was

also carried out from 1 to 32 min. Droplet only method was included to compare with our proposed technique. In this method, the suspension of Au NPs was drop-casted onto the surface of the ITO and lasted for 3 h before it was blown away by nitrogen. All of the samples were dried on the hotplate at 100 °C for 3 min. The number of Au NPs within one square micrometer was defined as the area density in the following discussion. LEO 1550 Gemini field emission scanning electron microscopy (FESEM) was used for morphology inspection.

Figure 6.1 Centrifugal deposition schematic for Au NPs on the surface of ITO.

Morphology inspection in Fig. 6.2 obviously showed that compared with droplet only method of about 10 NP/ μm^2 , the dramatic increase of the area density had demonstrated the effectiveness of the proposed method. When the centrifugal time increased, the area density rose significantly for a fixed gravitational force of 2397 g regardless of the size of the Au NPs.

Figure 6.2 FESEM inspection of the Au NPs distribution on the ITO. Droplet only samples were in (a) and (e) for 10 and 20 nm respectively. The rest images were for centrifugal method where (b) to (d) were for 10 nm Au NPs and (f) to (h) were for 20 nm samples.

Figure 6.3 summarized the area densities of Au NPs on ITO as a function of relative gravitational force and centrifugal time. In general, the area density increased with the rise of the relative gravitational force. When the time was below 10 min, the area density of the Au NPs initially rose with prolonged centrifugal time for a fixed gravitational force. However, they began to saturate after 16 min. The largest area density was $509 \text{ NP}/\mu\text{m}^2$ for 10 nm Au NPs at 2397 g for 32 min. Similar trends could be found regardless of the size of the Au NPs. For 20 nm Au NPs, the highest area density was $130 \text{ NP}/\mu\text{m}^2$.

Figure 6.3 Au NPs area density variation for (a) 10 and (b) 20 nm as a function of the centrifugal time and relative gravitational force.

6.2.2 A Numerical Model for Centrifugal Deposition of Au Nanoparticles on ITO

In this section, the variation of the area density of Au NPs was analyzed by an effective numerical model. This model collaboratively designed the diameter of

the NPs, relative gravitational force (rotation speed), and the time of centrifugation. To construct this model, there were three assumptions: 1) before the centrifugation, the resultant velocity towards the surface of the ITO of the Au NPs was zero; 2) there was no contact of Au NPs with ITO surface; 3) the size distribution of Au NPs and the difference of the electrical charges on each Au NPs were all neglected.

As shown in Fig. 6.4, we gave the Au NPs kinetic and dynamic analysis along the normal direction of ITO glass which was also the radial direction of rotor. Based on assumption one, the resultant electrostatic force was zero for an Au NP in the suspension before the centrifugation. When the centrifugation started, there were four forces exerting upon the Au NP including: 1) inertial centrifugal force F_{ic} ; 2) centripetal force F_c ; 3) fluid resistance f ; 4) the electrostatic force F_e by the rest of Au NPs on ITO. Analytical expression of these four forces were provided from Eqs. 6.1 to 6.7.

$$u_T = \omega_T R = 2\pi\Omega R / 60 \quad (6.1)$$

$$F_{ic} = (\pi/6)d^3 \rho_{Au} (u_T^2 / R) \quad (6.2)$$

$$F_c = -(\pi/6)d^3 \rho (u_T^2 / R) \quad (6.3)$$

$$f = -\xi(\pi/4)d^2 \rho (u_r^2 / 2) \quad (6.4)$$

$$\xi = 24 / Re = 24\nu / u_r d. \quad (6.5)$$

The relationship among tangential velocity of the centrifugal rotor u_T , angular velocity ω_T and the rotation speed Ω was given in Eq. 6.1. Considering the small amount of the suspension, the distance between the positions of the Au NPs to the central axial of the rotor were approximated as the radius of the rotor R . Therefore, the centrifugal force and inertial centrifugal force were given in Eqs. 6.2 to 6.3 where the density of the solvent and Au NPs in the suspension were ρ and ρ_{Au} respectively. Taken the positive direction as pointing towards the ITO

surface, the fluid resistance was described in Eqs. 6.4 and 6.5 including the velocity of the Au NP u_r , the diameter of the Au NP d , and the kinematic viscosity of the solution ν .

Figure 6.4 Schematic of the kinetic and dynamic analysis of the Au NPs during the centrifugation with four forces applying on the Au NPs along the normal direction of ITO surface.

Figure 6.5 Schematic explaining the electrostatic force acting upon the Au NP.

When the Au NP was near to the surface of the ITO, the resultant electrostatic force was given in Eq. 6.6. Each Au NP on the surface of ITO had a connecting direction of the approaching Au NP. The angle θ_i described the connecting direction to the ITO surface normal. Other parameters included the shortest

distance between the approaching Au NP and the ITO surface h , the amount of electrical charge Q for each Au NP, and the Coulomb's constant k . Therefore, assuming circular symmetry of the ITO glass with radius R_{ITO} , the F_e could be obtained by summing each electrostatic forces by Au NPs staying along each radius of ITO F_{e-r} . This assumption of uniform distribution of Au NPs on ITO was supported by the FESEM images in Fig. 6.2. After substitution of θ_i , the F_{e-r} was expressed in Eq. 6.7 where n_0 was the number of Au NPs on ITO surface.

$$F_e = -\sum kQ \cdot Q / (h / \cos \theta_i)^2 \quad (6.6)$$

$$\begin{aligned} F_{e-r} &= -\sum \frac{kQ^2}{(h / \cos \theta_i)^2} \times \cos \theta_i \\ &= -\sum \frac{kQ^2}{h^2} \times \cos \theta_i^3 \\ &= -\sum \frac{kQ^2}{h^2} \times \left[\frac{h^2}{h^2 + (iR_{ITO} / n_0)^2} \right]^{3/2}. \end{aligned} \quad (6.7)$$

Therefore, the dynamic equation in Eq. 6.8 was constructed by substitution of the four forces exerting on the Au NP in which $a_r = du_r / dt$ was the acceleration of the Au NP along the radius of the centrifuge which was also the surface normal direction of ITO.

$$\sum F = F_{ic} + F_c + f + F_e = ma_r. \quad (6.8)$$

Based on the above equations, the relationship among the rotation speed Ω , the centrifugal time t , the size of the Au NPs, and the area density of the Au NPs $D_{Area}(\Omega, t)$, was constructed in Eqs. 6.9 and 6.10. The area of ITO that was in contact with the Au NPs suspension was A_{ITO} and the concentration of the Au NPs suspension was D_{Au} . For each centrifugal trial, the maximal distance traveled by the Au NPs was S_n within which the Au NPs could arrive at the ITO surface.

$$D_{Area}(\Omega, t) = D_{Au} \times A_{ITO} \times S_n(\Omega, t) \quad (6.9)$$

$$S_n = \int_{t=0}^t u_r(t) \cdot dt. \quad (6.10)$$

Our objective was to quantitative determine the area density of the Au NPs with centrifugal parameters and the size of the NPs. For the movement of Au NPs during the centrifugation process, we provided a qualitative analysis. Upon the start of centrifugation, the u_r was small and therefore the f was negligible and the resultant F_e for the given Au NP was zero since it was far from ITO. Consequently, a large acceleration towards ITO a_r was generated which was then gradually reduced by the increase of f . This acceleration was turned to zero when the balance of the forces was reached and the Au NP would travel with constant speed with acceleration of zero. When it approached the adjacent region of ITO surface, all of the Au NPs that had already arrived on the surface of ITO would act electrostatic force on the Au NP. The resultant F_e led to an $-a_r$ which would slow down the approaching Au NP until it rested on the ITO surface.

From the above analysis, we knew that the larger number of Au NPs accumulated on the ITO surface, the stronger F_e was. Therefore, the electrostatic force was negligible when the centrifugal time was short. As a result, the Au NP would travel following the constant speed until it was stopped by the ITO. Consequently, the area density of the Au NPs would linearly increase as the centrifugal time prolonged which was named as linear region. However, if the centrifugal time was long enough, the accumulated Au NPs would generate strong F_e and the Au NP would be stopped before it reached the ITO surface. In this case, even we prolonged the time of centrifugation, the area density of the Au NPs would not increase anymore which was named as saturated region. In the following, we showed quantitative expressions for the linear and saturated region.

Figure 6.6 Quantitatively study in linear and saturation regions and qualitatively study for transition region of Au NPs during centrifugation where 10 and 20 nm were given in (a) and (b) respectively.

Linear region

When the centrifugal time was small, the Au NP fell into the linear region in which it followed the uniform linear motion without being exerted the F_e . Therefore the dynamic equation in Eq. 6.8 would come to $\sum F = F_{ic} + F_c + f = 0$. As a result, the velocity of the Au NP towards ITO in linear region u_{r0} could be expressed in Eq. 6.11. By substituting Eqs. 6.1 and 6.6 into 6.11, this velocity could be calculated in Eq. 6.12. In this way, the Au NPs' area density on ITO for various rotation speed, centrifugal time, and the diameter of Au NPs could be acquired in Eq. 6.13 in which the A_{ITO} was considered as $1 \mu\text{m}^2$. During the calculation, one of the experimental measurement was selected for parameter correction and all the rest curve fittings were calculated. As shown in Fig. 6.6, the experimental matched well with the fitting curves.

$$u_{r0} = \sqrt{\frac{4d(\rho_{Au} - \rho)u_T^2}{3\xi\rho R}} \quad (6.11)$$

$$u_{r0} = \frac{d^2(\rho_{Au} - \rho)}{18\nu\rho R} \times \frac{4\pi^2\Omega^2 R^2}{3600} \quad (6.12)$$

$$D_{Area}(\Omega, t) = D_{Au} \times A_{ITO} \times \frac{d^2(\rho_{Au} - \rho)}{18\nu\rho R} \times \frac{4\pi^2\Omega^2 R^2}{3600} \times t. \quad (6.13)$$

Saturated region

The ideally maximal number of Au NPs per micrometer square could be estimated by multiplication of the density of Au NPs in the suspension D_{Au} , the contact area A_{ITO} and the thickness of the suspension S_{max} . Compared the ideally maximal number of Au NPs and the experimental results in Fig. 6.2, there was enough available Au NPs in the suspension. In the supersaturated region, the accumulated Au NPs exerted F_e on the new arriving Au NP. If F_e was strong enough this Au NP would be stopped before it got to the surface of ITO. New

balances of forces was built as Eq. 6.14. Mathematical derivation took two approximations including one is $\lim_{n_0 \rightarrow \infty} (1/1^3 + \dots + 1/i^3 + \dots + 1/n_0^3) < 1.5$ and the other is $R_{ITO}/n_0 h \gg 1$.

$$\sum F = F_{ic} + F_c + F_e = 0 \quad (6.14)$$

$$\begin{aligned} F_{e-r} &\approx -\frac{kQ^2}{h^2} \left[\frac{n_0^3}{(R_{ITO}/h)^3} + \dots + \frac{n_0^3}{(iR_{ITO}/h)^3} + \dots + \frac{n_0^3}{(n_0 R_{ITO}/h)^3} \right] \\ &= -\frac{kQ^2 n_0^3 h}{R_{ITO}^3} \left[\frac{1}{1^3} + \dots + \frac{1}{i^3} + \dots + \frac{1}{n_0^3} \right] \\ &\approx -\frac{kQ^2 n_0^3}{R_{ITO}^3} \times Const_{n_0, h} \end{aligned} \quad (6.15)$$

$$n_0 = \sqrt[3]{\frac{R_{ITO}^3 \pi d^3 (\rho_{Au} - \rho)}{kQ^2 Const_{n_0, h} \times 6 \times R} \times \frac{4\pi^2 \Omega^2 R^2}{3600}} \quad (6.16)$$

$$\begin{aligned} D_{Area} &= \pi \times R_{ITO}^2 \times n_0 \\ &= \pi \times R_{ITO}^2 \times \sqrt[3]{\frac{R_{ITO}^3 \pi d^3 (\rho_{Au} - \rho)}{kQ^2 Const_{n_0, h} \times 6 \times R} \times \frac{4\pi^2 \Omega^2 R^2}{3600}}. \end{aligned} \quad (6.17)$$

Transition region

Between the linear and saturated region, there was transition region and all four forces applied on the Au NPs. Analytical expressions were hard to find but through curve fitting, we could still receive the area density variation with the centrifugal parameters and the size of Au NPs.

In this part, a new high and controllable area density and cost-effective Au NP deposition method with narrow size distribution by centrifugation is proposed. According to the experiment results, area densities as high as 509 NP/ μm^2 for 10 nm and 130 NP/ μm^2 for 20 nm are obtained with relative centrifugal force of 2397 g and larger than 16 min centrifugation time. Compared with the droplet only method, centrifugation is able to greatly increase the Au NPs area density

50 times for 10 nm Au NPs and 13 times for 20 nm size. Through control of the relative centrifugal force and time wide range area densities can be obtained. A theoretical model has been built to describe the Au NP motion under centrifugation which also predict and describe the area density with respect of centrifugation parameters and the Au NP size. According to Au NPs motion in different phases, analytical solutions are given which can well predict the Au NPs area density. In linear region, few Au NPs on ITO surface to exert electrostatic force, inertial centrifugal force, centripetal force and fluid resistance construct a balance and the Au NPs follow the uniform linear motion. The area density increases linearly with centrifugation time. In saturated region, while there are a number of Au NPs on ITO, the electrostatic force cannot be neglect and new force balance is built. At this stage, the velocity is reduced to zero and correspondingly the fluid resistance is reduced to zero in which case the area density does not change with time. The transition region describes the changing phase between the two. The expressions given for linear and saturated region match well with experiment results. These results show potential of centrifugation method to be used in the Au NPs induced NWs based hybrid solar cell application.

6.3 Metalorganic Chemical Vapour Deposition (MOCVD) Growth of Freely Standing GaAs Nanowires on ITO

Previous studies report that the variation of the growth parameters will seriously affect the morphology as well as crystal quality of the as-grown III-V NWs [125]. There are other reports that focusing on the kinetics and mass transport model during the growth of NWs [113, 165, 166, 184-186]. However, there are few studies focusing on the control of III-V NWs growth on metal oxide substrates. In most of the cases, the III-V NWs are found to have kinks or worm-shaped defects and the crystal quality of the NWs are seriously degraded.

After acquirement of the control over the deposition of Au NPs, we used

MOCVD to directly grow GaAs NWs on ITO. In this section, we firstly demonstrated a successful growth of GaAs NWs on ITO, followed by a detailed growth parameters study. In the meantime, a kinetic model had been adopted to analyze and control the growth rate of NWs. Area density of the NWs was tuned by centrifugation technique followed by the crystal quality characterization. Through the realization of the well-control of NWs on ITO with high crystal quality, we were ready to fabricate low-cost GaAs NWs based HSCs.

6.3.1 GaAs Nanowires Morphology Inspection

The commercial ITO glass (Xinyan Technology LTD.) was cut into $5 \times 5 \text{ cm}^2$ pieces and cleaned in the same process as mentioned in the previous section. The surface of ITO were functionalized by PDDAC for 60 min. They were rinsed several times by deionized water, and then dried by nitrogen. Apart from the area density study of the NWs, droplet only method was selected for deposition of Au NPs suspension for growth parameter study since the morphology of NWs could be easily observed in low area density of NWs. The droplet of various sizes of Au NPs suspension (Nanocs Ltd.) stayed on the surface of ITO for 3 h and then the excessive suspension was blown away and dried by nitrogen. The empirical Au suspension deposition time and its effect on the area density of Au NPs could be referred to Fig. 1 in Ref. [127]. Growth parameters study mainly focused on 40 nm Au NPs as catalysts for NWs growth and 2, 5, 10, 20 nm Au NPs were also chose for catalyst size study. We completely dried the samples on the hot plate and then transferred them into the reactor chamber of MOCVD (Aixtron 200).

The precursor for group III was Trimethylgallium (TMGa) whereas tertiarybutylarsine (TBAs) was selected for group V. During the rise of the temperature, the TBAs was firstly introduced by the carrier gas of hydrogen. When the growth temperature T was reached, TMGa was incorporated. For all the growths, the reactor chamber was set as 50 mbar. The molar flow rates of

TMGa Q_{TMGa} varied from 0.91, 1.36, to 1.81 $\mu\text{mol/s}$ whereas the molar flow rates of TBAs Q_{TBAs} was calculated with the same V/III ratio of 9.5. Growth temperature changed from 410 to 480 $^{\circ}\text{C}$. Unlike otherwise stated, the growth time was set as 30 s. The morphology of NWs were obtained from FESEM inspection.

In general, Fig. 6.7 gave a general view of the GaAs NWs standing on ITO for various sizes of Au catalysts. The Q_{TMGa} was 1.36 $\mu\text{mol/s}$ and the growth temperature was 430 $^{\circ}\text{C}$ for 120 s growth. It was found that on the surface of ITO there were straight and free-standing GaAs NWs of various diameters with almost no observable kinks or worm-shape NWs.

Figure 6.7 GaAs NWs standing on ITO surface which were catalyzed by (a) 5, (b) 10, (c) 20, and (d) 40 nm Au NPs.

The vertically aligned NWs were highly desirable for photovoltaic applications. However, there were no one preferred growth direction for all of the NWs on ITO glass. This was attributed to the polycrystalline of ITO. However, from the cross-sectional view, most of the NWs grew away from the ITO surface. In Fig. 6.8,

we summarized the tilting angles α with respect of the surface of ITO for the 40 nm Au NPs catalyzed NWs. From a sample of 200 NWs, we drew the histogram which clearly summarized their orientations. The NWs who had tilt angles larger than 45° accounted for 96.1% of the total NWs. More than half of the NWs had their tilt angles fell into range of 70 to 90° . This free-standing morphology was also favorable for the HSC fabrication. In the following, the growth rate of NWs was defined as the time dependent growth. Due to the different growth directions of NWs, the lengths of the NWs were calculated from a zoom-in view which was illustrated in the inset of Fig. 6.8(a).

Figure 6.8 GaAs NWs catalyzed by 40 nm Au NPs of the same growth condition of Fig. 6.7(d) where (a) gave cross-sectional view. The tilt angle was explained in the inset. Histogram in (b) summarized the tilt angle distribution of the GaAs NWs.

Figure 6.9 showed the morphology of GaAs NWs changing with different growth temperatures and precursor flow rates. Apparently, the growth temperature played a more important role in varying the shape of the NWs. Cylindrical NWs were changed into cone shaped NWs with wider bases. During the growth of NWs, the adatoms not only impinged on the Au NPs, but also diffused along the substrate and climbed along the surface of the NWs. The tapered NWs were attributed to those adatoms who nucleated on the sides of NWs. Besides, Fig. 6.9(d) also indicated that the length was almost linear proportional with the

increase of growth time.

Figure 6.9 GaAs NWs catalyzed by Au NPs of 40 nm whose length changed with TMGa molar flow rates of (a) 0.91, (b) 1.36, and (c) 1.81 $\mu\text{mol/s}$; (d) showed time dependent length change at 460 °C with fixed TMGa molar flow rates.

6.3.2 A Theoretical Model of the Growth Parameters Effect on the GaAs Nanowires Growth

In order to rational control and analyze the growth of GaAs NWs on ITO, a theoretical model of the growth parameters effect over the growth of the NWs was presented in this section. Indepth understanding of the VLS growth

mechanism was the foundation for the construction of this kinetic model. Schematic of the VLS mechanism was shown in Fig. 6.10. Firstly, the vapor precursors of TMGa and TBAs began to decompose in the reactor chamber and the adatoms would transport to the metal catalysts where the liquid eutectic droplets were formed [187]. In the second step, the adatoms entered the eutectic droplets at the vapor-liquid interface. Thirdly, the adatoms met the liquid-solid interface through diffusion [185]. Finally, at the liquid-solid interface, GaAs crystalized [166] and by continuously providing the growth precursors, NWs were obtained. Analytically determination of the relationship of the NWs' growth rate and the growth parameters allowed us to rationally control the growth of NWs. To acquire these relationships several assumptions were adopted including: 1) during the growth of NWs, the total number of adatoms entering the eutectic metal catalysts at the vapor-liquid interface was equal to the number of adatoms that crystalized at the liquid-solid interface; 2) the NWs were considered as cylinders with hemispherical Au caps riding on their tops which was reasonable according to the FESEM inspection; 3) considering the growth condition in the reactor chamber with low pressure and high temperature, the behavior of the vapor precursors should be able to be described by ideal gas law.

Figure 6.10 Schematic of a GaAs NW grown on ITO based on VLS mechanism.

Due to the over flow of the TBAs, the flow rates of TMGa were used in our calculation. The net incident flux of the precursor per unit time per unit area at the surface of the NWs was taken as J . Based on the first assumption, we built the relationship of the number of adatoms that were incident upon the Au catalyst and the number of adatoms that crystalized at the liquid-solid interface as shown in Eq. 6.18. The radius of the cylindrical NW R was also the radius of the Au catalyst. k_g was the growth rate of the NW. Ω_s was the atomic volume in the GaAs NW (solid phase) which could be calculated as a^3/n . The lattice constant was a and n denoted the number of As atoms per unit cell where the atoms in group V was much larger than atoms in group III.

$$2\pi R^2 \times J = (\pi R^2 / \Omega_s) \times k_g. \quad (6.18)$$

Hertz-Knudsen equation in Eq. 6.19 described the net incident flux of precursor who adsorbed to a surface [184] where m was the mass of Ga atom, T was the absolute temperature and k_B was Boltzmann constant. The Ga pressure in the vapor phase and within the Au droplet were P_{Ga} and P_R respectively. P_{Ga} could be acquired by $P_{Ga} = \varepsilon_{pyro} P_{TMGa}$ where ε_{pyro} was pyrolysis efficiency and P_{TMGa} was precursor partial pressure in the reactor. At the same time, P_{TMGa} can be estimated as $P_{TMGa} = [Q_{TMGa} / (Q_{TMGa} + Q_{TBAs} + Q_{H_2})] \times P_{Chamber} \approx [Q_{TMGa} / Q_{H_2}] \times P_{Chamber}$ where $P_{Chamber}$ was the chamber pressure [125]. The adsorption coefficient α was taken as unity for fully adsorption of the incident adatoms since we considered the net incident flux of the precursor. α describes the probability of the available atoms being adsorbed into the NWs. In our case, α is set as 1 since all the adatoms incorporated into the Au catalysts contributes to the NW growth in the model formulation.

$$J = \alpha(P_{Ga} - P_R) / \sqrt{2\pi m k_B T}. \quad (6.19)$$

Ostwald–Freundlich equation gave the expression of P_R as shown in Eq. 6.20 [125]. The Ga pressure in vapor phase and in equilibrium with the flat surface was P_∞ where the radius was infinite. Atomic molar volume within the Au NPs was Ω_l . The surface energy density at the interface of the eutectic Au NPs and the vapor was σ_{lv} .

$$P_R = P_\infty \exp(2\Omega_l \sigma_{lv} / Rk_B T). \quad (6.20)$$

Based on the third assumption, the chemical potential of the ideal gas within the reactor chamber was $\mu_g(T, P_{Ga}) = \mu_g(T, P_\infty) + k_B T \ln(P_{Ga} / P_\infty)$. The NWs growth was assumed to be at vapor-liquid phase equilibrium condition. Therefore the chemical potential difference inside and outside the Au NPs was calculated as $\Delta\mu_{gl} = k_B T \ln(P_{Ga} / P_\infty)$. As a result, the P_{Ga} could be expressed in Eq.6.21. By substituting the Eqs. 6.21, 6.20 into Eq. 6.19, we acquired the next flux expression in Eq. 6.22 and the growth rate of NWs was obtained in Eq. 6.23. In this way, we quantitatively analyzed the growth parameters' effect on the growth rate of NWs focusing on the growth temperature, precursor flow rates, growth time as well as the catalyst size.

$$P_{Ga} = P_\infty \exp(\Delta\mu_{gl} / k_B T), \quad (6.21)$$

$$J = \alpha \times \frac{P_\infty \exp(\Delta\mu_{gl} / k_B T) - P_\infty \exp(2\Omega_l \sigma_{lv} / Rk_B T)}{\sqrt{2\pi m k_B T}}, \quad (6.22)$$

$$k_g = 2 \times \frac{a^3}{n} \times \alpha \times \frac{P_\infty \exp(\Delta\mu_{gl} / k_B T) - P_\infty \exp(2\Omega_l \sigma_{lv} / Rk_B T)}{\sqrt{2\pi m k_B T}}. \quad (6.23)$$

6.3.3 Analysis of the Growth Parameters Effect on the GaAs Nanowires Growth

Temperature effect

Figure 6.11 described the effect of the precursor flow rate and the growth temperature on the variation of the NWs' growth rate. In this part, the growth temperature rose from 410 to 480 °C whereas the Q_{TMGa} increased from 0.91 to 1.81 $\mu\text{mol/s}$. Generally speaking, the growth rate rose with the increase of the growth temperatures for various precursor molar flow rates. This behavior was mainly attributed to the enhancement of the pyrolysis efficiency due to the alleviated of the growth temperature. More adatoms was available for the growth of NWs which increased the growth rate. For the highest temperature of 480 °C and the precursor flow rate of 1.81 $\mu\text{mol/s}$, the largest growth rate was found as 51.48 nm/s. It had been verified that Au NPs of 40 nm size was large enough to neglect the Gibbs-Thompson effect [165, 186]. Consequently, the growth rate of the NWs could be simplified from Eq. 6.23 to 6.24. The lattice constant a was 0.565 nm. The number of As atoms within the unit cell n was 4. The mass of the Ga atom was 1.158×10^{-25} kg. Substituting all these values into Eq. 6.24, we acquired the curves of the growth rate under various precursor flow rates and temperatures in Fig. 6.11.

$$k_g = 2 \times a^3 / n \times \alpha \times P_{Ga} / \sqrt{2\pi m k_B T}. \quad (6.24)$$

Figure 6.11 (a) gave the growth rate of GaAs NWs changing as growth temperatures at different precursor flow rates where (b) provided the relationship of the reciprocal of the growth temperature and the logarithmic of the growth rate of NWs.

To understand the effect of ITO substrate on the crystallization of NWs, the molar activation energy E_A was also calculated. It was compared with the activation energy of the GaAs NWs of the same diameter that were grown on GaAs (111)B substrate. According to the Arrhenius equation, the NWs' growth rate proportionated to $\exp(-E_A / k_B T)$ in which the molar activation energy was used to quantitatively evaluate the energy of crystallization at the liquid-solid interface [133]. Figure 6.11(b) gave the relationship of logarithmic of the growth rate and the reciprocal of the growth temperature $\ln k_g = f(1/T)$, and the E_A was acquired from the slope of the curves. For the three precursor flow rates of 0.91, 1.36, and 1.81 $\mu\text{mol/s}$, the E_A were 65.86, 65.53 and 63.59 kJ/mol respectively. These E_A values were quite similar to the values for GaAs NWs grown on the substrate of GaAs (111)B which were among 67 to 75 kJ/mol [176, 188]. This fact drew the conclusion that the ITO substrate did not increase the kinetic barrier for the growth of NWs.

Precursor flow rates effect

Figure 6.12 presented the effect of the molar flow rate on the growth rate of the GaAs NWs induced by 40 nm Au NPs on ITO. During the growth of the NWs, Q_{TBAs} was redundant and therefore the growth rate limiting factor was Q_{TMGa} . From Eq. 6.24, we concluded that the growth rate would increase linearly with P_{Ga} at a given temperature. This partial pressure increased as the rose of the Q_{TMGa} from the above analysis in Section 6.3.2. At the same time, this P_{Ga} was closely related to the pyrolysis efficiency ε_{pyro} which had larger value as the enhancement of the growth temperature. As a result, the growth rate also increased due to the rise of the net precursor flux at alleviated growth temperature.

Figure 6.12 TMGa molar flow rate dependent growth rate of GaAs NWs at various growth temperatures of 410, 430, 460, and 480 °C.

Growth time effect

We chose the 40 nm Au NPs induced samples who grew under the condition of Q_{TMGa} 1.36 $\mu\text{mol/s}$ at two growth temperatures of 430 and 460 °C. Growth time varied from 30 to 120 s. From Fig. 6.13, we observed that the prolonged growth time had negligible effect on the growth rate of NWs. This finding allowed us to grow desired length of NWs since the length of the NWs could be tuned in proportional to the growth time.

Figure 6.13 Time dependent GaAs NW growth at two growth temperatures of 430 and 460 °C.

Catalyst size effect

Catalyst played an important role in the VLS growth mechanism. They also determined the position, area density, diameter of the as-grown NWs [189]. For a fixed Q_{TMGa} of 1.36 $\mu\text{mol/s}$, we studied the growth rate variation as a function of the size of Au NPs as shown in Fig. 6.14. In general, the diameter of Au NPs had demonstrated similar influence on the growth rate of GaAs NWs at different growth temperatures. The growth rate rose quickly with the increase of the size of the NPs and then the effect of the catalyst size became smaller at larger size of the catalyst. The highest growth rate of 35.27 nm/s was found at growth temperature of 480 °C for 40 nm Au NPs induced NWs whereas 23.29 nm/s for 5 nm induced NWs. This phenomenon was commonly attributed to the Gibbs-Thompson effect which described that for a given T , the smaller of the catalyst size, the higher the reactant pressure [175, 176]. According to Eqs. 6.19 and 6.23, the growth rate of GaAs NWs proportionated to the reactant's pressure difference inside and outside of the Au catalyst. Consequently, the larger NPs induced NWs

had higher growth rate than the smaller NPs catalyzed NWs. As a result, it was deduced that if the diameter of the Au NPs was too small, no NWs could be grown onto the substrates. The radius of this NPs was defined as critical radius R_c whose mathematical expression was $R_c = 2\sigma_{lv}\Omega_l / \Delta\mu_{gl}$. We calculated the R_c to be 2.14 nm with the atomic volume per molar of 10.20 cm³/mol and the surface tension σ_{lv} of 1.237 J/m² [125]. In our experiments, there were no NWs found on the ITO substrates using 2 nm Au NPs as catalysts. Moreover, the fitting curves in Fig. 6.16 matched well with experimental measurements with one experiment data for rectification of the proportional constant that related to our equipments.

Figure 6.14 The influence of the size of Au NPs on the growth rate of GaAs NWs at various growth temperatures where the TMGa molar flow rate fixed at 1.36 $\mu\text{mol/s}$.

6.3.4 Area Density Control of GaAs Nanowires by Centrifugal Deposition of Au Nanoparticles

In this part, the area densities of the NWs were controlled by centrifugal method

of deposition Au NPs on ITO. The desired area densities of different sizes of Au NPs were deposited on ITO by variation of the centrifugal parameters such as the rotation speed and centrifugal time. Details about this deposition method had been explained in Section 6.2.

For a fixed rotation speed of 3900 RPM corresponding to relative gravitational force of 2283 g, 10 and 20 nm Au NPs suspension went through different centrifugal time from 4 to 16 min as shown in Fig. 6.15. Droplet only method of deposition of Au NPs was also chosen as a comparison. The FESEM images in Fig. 6.15 had clearly denoted the rapid increase of the area density of the Au NPs on ITO. Figure 6.16 summarized the area density of the Au NPs for various centrifugation time with the curves calculated from the numerical model presented in Section 6.1.

Figure 6.15 FESEM images of the Au NPs distribution on the ITO with different centrifugation time. (a) to (e) were for the 10 nm and (f) to (j) were for 20 nm diameter Au NPs. (a) and (f) were droplet only samples.

Figure 6.16 Area density changed with respect of centrifugal time for 10 and 20 nm diameter Au NPs.

These samples were completely dried before they were transferred into the MOCVD chamber. The growth temperature was set as 430 °C with Q_{TMGa} of 1.36 $\mu\text{mol/s}$. The V/III ratio was also fixed as 9.5 and the growth lasted for 2 min. The FESEM images in Fig. 6.17 clearly demonstrated the dramatic increase of the area density for 10 and 20 nm Au NPs induced NWs compared with the droplet only method in Figs. 6.17(a) and (d). Especially from the cross-sectional view in Figs. 6.17(d) and (h), straight and elongated NWs were directly grown on ITO without the noticeable kinks or worm-shape defects. Similar with 40 nm Au NPs induced Au NPs in Fig. 6.9(a), most of the NWs stood a large tilt angle with the surface of the substrate. These high area density of NWs were greatly favorable for the HSC application [64].

Figure 6.17 The FESEM images of the 10 and 20 nm Au NPs catalyzed GaAs NWs with different Au NPs deposition method. (a) and (e) were droplet-only method and the rest were centrifugal method and (d) and (h) were cross sectional view of the GaAs NWs.

Figure 6.18 plotted the relationship of the growth rate of NWs and the centrifugal time. In fact, from the numerical model in Section 6.2, the area densities were accurately predicted as the prolonged of the centrifugal time. Therefore, Fig. 6.18 also reflected the effect of area densities of the NWs on their growth rate. The spacing among adjacent NWs L_{NW} had also been included in to Fig. 6.18 which was obtained as $1000 / \sqrt{\text{Area Density}}$ with nanometer as its unit. The area density could be referred to the experimental measurements in Fig. 6.16. Generally speaking, the growth rate of the GaAs NWs decreased with the increase of the area density of the NWs which was mainly attributed to the competition of the available adatoms for NWs growth since the spacing between neighboring NWs narrowed down. Considering the VLS growth of NWs, there were mainly two sources of providing the adatoms [166]. One was through direct impingement of the adatoms onto the eutectic Au NPs who rode on the tops of NWs. The other one was through diffusion of the adatoms along the side walls of the NWs. All of the samples that carried different area densities of Au NPs underwent the same growth condition. As a result, there was negligible difference in the impingement rate of the adatoms upon various samples. When the spacing among NWs was

larger than the diffusion length of the adatoms, there were enough adatoms available for the NWs. However, when the spacing was smaller than the diffusion length of adatoms, the available adatoms had to be shared among neighboring NWs. Therefore, the competition of adatoms started among neighboring NWs. Under similar growth conditions, it was reported that the diffusion length for Ga adatoms was about 100 nm [190]. It was larger than the spacing among NWs for both 10 and 20 nm Au NPs induced NWs as long as the centrifugal time was longer than 4 min. Consequently, a sharp reduction of the growth rates was found due to the competition of the adatoms of the NWs. As the centrifugal time further increased, the area density varied little since it entered the saturated region mentioned in Section 6.2.2. As a result, the spacing among NWs remained similar value which explained that the growth rate of the NWs had little influence by the increase of the centrifugal time from 8 to 16 min.

Figure 6.18 GaAs NWs growth rate and spacing between NWs as a function of centrifugal time. The inset schematic explained the spacing between NWs and the competition of the available adatoms.

6.3.5 Crystal Quality Characterization of the GaAs Nanowires on ITO

GaAs NWs with high crystal quality is highly favored in the photovoltaic application since the low crystal defect density will reduce the density of non-radiation centers which helps to improve the power conversion efficiency (PCE). The crystal quality inspection of the NWs were obtained by transmission electron microscopy (TEM: Philips Tecnai G2 F20 field-emission TEM, operated at 200 kV). GaAs NWs catalyzed by 40 nm Au NPs were grown under the condition of 430 °C with Q_{TMGa} of 1.36 $\mu\text{mol/s}$. They were examined using TEM along $\langle 110 \rangle$ zone axis. Before observation, the as-grown GaAs NWs were peeled off from their growth ITO substrates and randomly dispersed into the acetone. One droplet of the suspension that contained the NWs was drop-casted on the copper net for crystal quality observation. This approach is commonly adopted for characterization of the NWs [120-124]. Photoluminescence data for the NWs grown on ITO can be also performed to further characterize and confirm the quality of the NWs at larger scale. From Fig. 6.19(a), we drew the conclusion that there were few planar or twin defects along the entire length of NWs. The enlarged view of the tip of the GaAs NWs in Fig. 6.19(b) and the high-resolution TEM (HRTEM) image in Fig. 6.19(c) provided detailed structural information. The spacing among crystal planes indicating that the NWs followed growth in $\langle 111 \rangle$ direction. Proof of the zinc-blende structure of the NWs was shown in the Fourier transform of the NW crystal Fig. 6.19(d).

Figure 6.19 (a) to (c) were the TEM images of the 40 nm Au catalyst induced NWs whereas (d) gave the Fourier transform of the NW crystal; (e) compared the XRD measurements of ITO glass and the ITO with GaAs NWs grown on it.

Those TEM images in Fig. 6.19 provided the clues of the crystal structures for the GaAs NWs on ITO but this conclusion was hard to be directly generalized for the majority of NWs on the same sample. This was because that researchers had found that the different growth directions might lead to various crystal structures [191]. Therefore, in order to reveal more facts about the crystal quality of the GaAs NWs on ITO, the ITO glass with GaAs NWs covered went for X-ray diffraction (XRD) measurements using Cu K α radiation as shown in Fig. 6.19(e). Comparison of the ITO glass piece with and without GaAs NWs had shown that an additional diffraction peak was observed at 2θ angle of 27.30° which were indexed to the GaAs zinc-blende (111) plane. This characterization further confirmed the TEM measurements.

The crystal quality of the GaAs NWs catalyzed by other sizes of Au NPs were also investigated as shown in Figs. 6.20(a) to (f). Similar with 40 nm Au NPs induced NWs, 10 and 20 nm Au NPs catalyzed NWs also displayed high crystal quality. From the bright field TEM images in Figs. 6.20(a) and (d), there were no observable defects across the entire length of the NWs. The HRTEM in the Fig. 6.20(b) and (d) gave the detailed information about the single crystallinity. For

the 10 nm Au NPs induced NWs, the growth direction was along $\langle 0001 \rangle$ direction whereas $\langle 111 \rangle$ direction was found for the 20 nm Au NPs induced NWs. The selected area electron diffraction (SAED) pattern in Fig. 6.20(c) and (f) revealed that the 10 nm Au NPs catalyzed NWs had wurtzite crystal structure whereas zinc-blende structure for the 20 nm Au NPs catalyzed NWs. This was mainly attributed to the liquid saturation pressure difference since it was reported that the wurtzite structure usually observed at high liquid supersaturation at the Au-NWs interface whereas zinc-blende structure favored the low liquid supersaturation [129]. The Gibbs-Thomson effect had explained that supersaturation in the catalyst was reversely proportional to the size of the catalyst. This led to the conclusion that the supersaturation in the smaller the catalyst was higher than the supersaturation in the larger catalyst [192] which explained the observed phenomenon that the wurtzite and the zinc-blende structures were found for 10 and 20 nm Au NPs catalyzed GaAs NWs. These results also indicated that by varying the diameter the crystal structure could be changed for various applications. Moreover, the energy dispersive spectroscopy (EDS) analysis in Fig. 6.20(g) demonstrated that the Ga adatoms had been expelled from the Au NPs at the end of the growth. Besides, there were few traces of indium or tin constituents in the GaAs NWs.

Figure 6.20 TEM images and EDS analysis of the 10 and 20 nm Au catalyzed GaAs NWs. (a), (b) and (c) were BRTEM, HRTEM and SAED for 10 nm Au NPs induced NWs whereas (d), (e) and (f) were corresponding images for 20 nm Au induced NWs. (g) was EDS analysis obtained at the Au NPs and GaAs NWs neck region for two sizes of samples and were marked with the corresponding regions in (b) and (e).

6.4 A Prototype of HSCs Based on GaAs Nanowires Growth on ITO

In Section 6.1 to 6.3, we have successfully growth high crystal quality GaAs

NWs with favorable morphology on ITO. In this section, we propose a prototype of low-cost GaAs NWs/P3HT HSC. To the best of our knowledge, this is the first demonstration of a HSC of GaAs NWs growth directly onto a transparent electrode and thus showing promise as a low-cost alternative to the current hybrid photovoltaic designs.

6.4.1 Fabrication Process for Freely Standing GaAs Nanowires Based HSCs

Similar with the growth process of GaAs NWs in the previous chapters, the ITO glass was cut into $5 \times 5 \text{ mm}^2$ pieces and cleaned by acetone, isopropanol and deionized water using the ultrasonicator for 10 min each. After dried by nitrogen, they were soaked in PDDAC solution for 1 h and then they were cleaned by deionized water and dried by nitrogen. Droplets of 40 nm Au NPs suspension lasted for 3 h and the excessive solution were blown away by nitrogen. After completely dried, the samples were transferred into the MOCVD reactor chamber. The precursor flow rate of TMGa was $1.36 \text{ } \mu\text{mol/s}$ with a fixed V/III ratio of 9.5. The growth temperature was $430 \text{ } ^\circ\text{C}$. The growth time was chosen as 30 s. From the FESEM images from the previous sections, the NWs stood freely on the ITO glass and the random orientation of the NWs were due to the polycrystalline nature of ITO. This morphology would help the NWs to deep penetrate through the P3HT.

The P3HT was dissolved into the chlorobenzene at concentration of 10 mg/mL . After that, the P3HT was drop-casted onto the NWs/ITO samples and dried for several hours. The samples were then annealed followed by a layer of PEDOT:PSS spin-coated on the cured P3HT. A layer of 200 nm Al was also thermally evaporated on the top of PEDOT:PSS. Current density-voltage characteristics were measured by illuminating the devices using a solar simulator with an AM 1.5G filter to provide 100 mW/cm^2 (1 Suns) of power. Figure 6.21

showed the schematic and the actual device fabricated.

Figure 6.21 The schematic of the fabricated HSC (a) and (b) was the actual device.

6.4.2 Photovoltaic Performance Analysis

Schematic of the device structure and the band gaps were provided in the Fig. 6.22. Similar with the hybrid active layer in Chapter 5, both the P3HT and the GaAs NWs would absorb light upon illumination and generate excitons. Within the diffusion length the excitons diffused to the donor-accepter interfaces. The excitons were dissociated at the interface of the inorganic NWs/organics. The electrons were transported through the GaAs NWs whereas holes were captured through the P3HT. Photocurrents were observed when the carriers transport to electrodes through respective pathways. Unlike the hybrid active layer in Chapter 5, the ITO served as cathode while the Al was anode.

Figure 6.22 Schematic of the device structure (a) and the band gaps (b) of the HSCs.

To test the interface of ITO/GaAs NWs, the current-voltage measurements were carried out. About 200 nm thin layer of benzocyclobutene (BCB) was spun onto the ITO sample with GaAs NWs and a contrast ITO sample without GaAs NWs. This thickness of BCB layer was selected to exposed part of NWs. It was also reported that besides of its insulation property, the BCB also had great infiltration property which allowed it to penetrate into the bottom of the NWs. Both samples were annealed for 1 h at 250 °C, followed by a thermally evaporation of a 200 nm layer of Al. Figure 6.23 gave the current-voltage measurement of the interface of the GaAs NWs/ITO. From the observance of the contrast sample without NWs, it demonstrated that there was no current passing through the BCB which displayed the insulating nature of the material. The NWs shorted the circuit between the Al and ITO contacts. The linear relationship of the measured current

and voltage indicated that the contacts among the GaAs NWs and ITO was ohmic contact permitting the efficient carrier collection on the ITO.

Figure 6.23 Current-voltage measurement of the GaAs NWs on ITO and the contrast sample with inset illustrating each layer.

In order to investigate the photovoltaic effect of the GaAs NWs/P3HT HSCs, we also fabricated P3HT only device following the same processing steps. The only difference was that the contrast sample did not have GaAs NWs. In general, the observed current density-voltage curve originated from the interface among the P3HT which had a high hole mobility and the GaAs NWs grown on ITO. The P3HT only sample could not short circuit the device. Compared with this P3HT only sample, the inclusion of the GaAs NWs allows for improved light absorption and conduction of the carriers. From Fig. 6.24, we noticed that there were voids near the bottom of the NWs which would cause large resistance in the active layer. Besides, the low current density was partially due to the thick P3HT layer since in the majority of organic solar cells, the thickness of the organics was normally kept within one to two hundreds of nanometers due to the short diffusion length of the excitons and the poor mobility. However, in this prototype of HSCs, we had to make sure that the P3HT was thick enough to enclose all of the GaAs NWs. Otherwise, even if only one NWs was left unwrapped, the device would be short

circuited. Compared our device in the Chapter 5, the GaAs materials was greatly reduced whose NWs was 900 nm in length and an underlying substrate of about 260 μm . The prototype of GaAs NWs on ITO fabricated in this chapter undoubtedly saved great amount of the expensive GaAs materials. However, this also led to a poor light harvesting and therefore poor PCE.

Figure 6.24 Comparison of the photovoltaic performance of the ITO/GaAs NWs/P3HT/PEDOT:PSS/Al and ITO /P3HT/PEDOT:PSS device with inset showing the cross-sectional view of the ITO/GaAs NWs/P3HT/PEDOT:PSS/Al device.

From Table 6.1, we compared the photovoltaic performance of our device and the best published results in Nano Letters fabricated using similar method. In the published work, they directly grew the InP NWs on ITO and then drop-casted P3HT on to the forest of the InP NWs [133]. The authors mainly attributed the poor performance to the thickness of the P3HT which was several micrometers. From the FESEM image in the inset of Fig. 6.24, we estimated the thickness was about 710 nm which partially explained the improved short-circuit current density of our work over the reference. The material cost is one of the key sources that contribute to the high cost of the photovoltaic technology. Through direct growth of GaAs NWs on ITO, hundreds micro-meters thickness of expensive III-V wafers can be saved. Compared with the device that had the up-to-date highest

PCE, there was about 350 μm GaAs material underlying [31]. Through optimization of the fabrication techniques, the proposed structure will demonstrate more potential for the future NWs based HSCs.

Table 6.1 Comparison of the photovoltaic performance of our fabricated device
and the results from the best results in other's work.

	Our Work	The Best Published Results [133]
Nanowire Material	GaAs	InP
Organic Material	P3HT	P3HT
FF	38.06	41
V_{oc} (V)	0.11	0.18
J_{sc} ($\mu\text{A}/\text{cm}^2$)	27.8	2.2

To improve the performance of this type of HSCs with GaAs NWs directly grown on ITO glass, further experiments are required to overcome the above mentioned loss mechanisms. In our prototype of the HSCs, the P3HT was drop-casted directly onto the NWs which would result in the non-uniform thickness of the polymer layer across the HSCs. Besides, the voids appeared at the bottom of the NWs were to be dealt with. Therefore, an optimized polymer deposition technique is required. Dissolving the P3HT in a mixed solvent with different boiling points may be a viable method. Through selection and optimization of the mixed ratio of different solvents, an improved polymer deposition technique can enhance the performance of the HSCs.

Besides, future experiments are designed to study the thickness of the P3HT effect on the short-circuit current density. Too thick of the P3HT will lead to the loss of the excitons due to their short diffusion length, whereas too thin of the P3HT will jeopardize the reliability of the device since the NWs may short circuit the HSCs. Moreover, investigation on the passivation of the surface of the NWs can be carried out. It is proved by other researchers that sulfur passivation of the NWs is an effect way to reduce the leakage current [193-195]. Therefore, the

improvement of the quality of this organic/inorganic interfaces and the overall charge transfer can be obtained to improve the performance of this type of HSCs.

6.5 Conclusion

In this chapter, we presented a prototype of the GaAs NWs/P3HT HSCs based on the direct growth of GaAs NWs on ITO using Au NPs as catalysts by MOCVD. An area density controllable Au NPs deposition method on ITO was developed with narrow size distribution by centrifugation. Through tuning the centrifugal parameters the highest area densities were achieved as 509 NP/ μm^2 for 10 nm and 130 NP/ μm^2 for 20 nm Au NPs. Meanwhile, an analytical model was built to calculate the area density of the Au NPs on ITO which matched well with the experimental results. Secondly, we had demonstrated the direct growth of GaAs NWs catalyzed by Au NPs on ITO. Free-standing GaAs NWs had been received with few kinks or crawling defects. Growth control of various parameters had been studied including the temperature, precursor flow rates, growth time, the size of the Au catalysts etc.. A kinetic model was also adopted to quantitatively analyze each parameters. The thermally activated growth of GaAs NWs was observed and the activation energy of 65 kJ/mol was calculated which indicated that the ITO had no additional barrier on the growth of GaAs NWs. Also, the growth rate of the NWs was linearly proportional to the precursor flow rate of TMGa when the V/III ratio was 9.5 at various growth temperatures. At the same time, the growth rate was almost unchanged with the prolonged growth time. It was found that the growth rate increased with the rise of the catalyst size which was due to the Gibbs-Thomson effect. The smallest Au NPs to induce the growth of the NWs was calculated to be 2.14 nm. We had also demonstrated the well control of the area density of the NWs by tuning the area density of the Au NPs through centrifugation. Moreover, the crystal quality of the as-grown GaAs NWs was found to have almost no observable defects. For larger size of Au NPs (20 and 40 nm) induced NWs, they possess zinc-blende structure whereas wurtzite

structure was found for 10 nm Au NPs induced NWs. This was due to the supersaturation differences caused by the size of the catalysts. In the last part, we presented a prototype of the GaAs NWs/P3HT HSC to remove the need for the thick and expensive III-V underlying substrate. Staggered band gap alignment was designed and formed among the inorganic NWs and the organics. It was proved that the ohmic contact had been formed among GaAs NWs and the ITO. Photovoltaic performance was also measured and compared with the results reported using similar method for InP NWs HSCs. These results provided an alternative pathway of fabrication of low-cost organic/inorganic HSCs.

Chapter 7 Conclusion and Future Work

7.1 Conclusion

In this project, we study the role of III-V nanowires (NWs) for efficient and low-cost semiconductor NWs based inorganic/organic hybrid solar cells (HSCs) through theoretical modeling, numerical simulation, device fabrication and characterization. We focus on geometrical dimensions design and control of the III-V NWs which are vital to the light harvesting and electrical characteristics of the HSCs. We also carried out fundamental study on direct growth of GaAs NWs on low-cost transparent conductive oxide substrates and developed a prototype of HSCs based on these NWs.

In Chapter 3, we presented an effective and efficient analytical algorithm for optimal geometrical parameters of vertically aligned GaAs and InP NWs for maximal solar energy absorption. It was demonstrated that the diameters of NWs and periodicity of the arrays could be rationally calculated within short time. Nanowire arrays of GaAs and InP composed of single, two and four diameters arranged both squarely and hexagonal had all been investigated to pursue the highest light harvesting. Through adoption of leaky mode resonance and Mie theory to excite two resonant modes and maintaining the full width at half maximum (FWHM) of HE_{11} mode in the absorbing region, optimal diameters of 168 nm for GaAs and 184 nm for InP had been obtained for single diameter NW arrays. Compared with published experimental work, our optimal diameter was only 4 and 3 nm difference to the up-to-date reported the highest efficient InP and GaAs NWs solar cells which proved the effectiveness of our proposed method. For two diameters NW arrays, the normalized absorption efficiency of the secondary NWs matched the absorption valley of the primary NWs. The optimal secondary diameters were 114 and 119 nm for GaAs and InP NW arrays.

Moreover, near-unity broadband absorption was achieved for four diameters NW arrays. The third and fourth diameters were 92 and 140 nm for GaAs NWs whereas 92 and 148 nm for InP NWs. At the same time, the optimal volume filling ratios (FRs) were calculated to be 0.22 for GaAs and 0.2 for InP NWs using the effective medium layer method. The highest short-circuit current densities were 29.88 and 33.13 mA/cm² for GaAs and InP NW arrays respectively. We had proved that the arrangement of NWs had negligible effect on the maximal light absorption by comparison of squarely and hexagonal InP NW arrays. Besides, the widely adopted three dimensional full finite-difference time-domain (FDTD) simulations were carried out to find out the optimal geometrical dimensions of the GaAs and InP NW arrays. Compared with the simulation results, the predicted maximal short-circuit current densities lied within 2.2% for all cases. This analytical model was suitable for various materials with high precision in predicting the optimal geometrical dimensions of NW arrays for maximal solar energy absorption. It was demonstrated to be a useful tool in design of future efficient NWs based solar cell.

In Chapter 4, a coupled opto-electrical model for GaAs NWs/Poly(3-hexylthiophene-2,5-diyl) (P3HT) HSCs were proposed. Light absorption of the GaAs NWs/P3HT hybrid active layer was investigated using the three-dimensional FDTD simulations. Compared with GaAs NWs/air layer, an increased light harvesting was received. Along with the leaky resonant modes of the GaAs NWs for light trapping, the polymeric layer confined light both below and beyond the absorptance spectrum edge of the polymer. Geometrical parameters including diameter of NWs and FR were assessed on their influence of the light absorption efficiency. The light absorption efficiency of 2 μ m thickness hybrid active layer was also evaluated at solar illumination achieving the highest value of 0.39. Moreover, upon solar illumination, photogeneration rates were calculated and incorporated to the electrical model which was built considering the diffusion efficiency of the excitons both in organic and inorganic

materials. Current density-voltage characteristics illustrated that the open-circuit voltage remained unchanged for various geometrical dimensions of the NWs and FRs. The short-circuit current density variation followed the trend of photocurrent density. For a high FR of the NWs, the device's power conversion efficiency (PCE) decreased with the rise of diameter of NWs. This was because of competence of the incident photons. However, opposite trend of PCE was observed when the FR was small. This was because only a 20 nm thick of P3HT surrounded each NWs contributed to the photocurrent and redundant P3HT decreased the performance of the device. The validity of the presented model was tested by reconstruction of the published experimental work and the well prediction of the device's performance indicated the effectiveness of the model.

In Chapter 5, GaAs NWs/P3HT HSCs were fabricated and characterized which revealed the role of geometrical dimensions of the NWs. Uniform GaAs NW arrays with well-controlled diameters and periodicities were fabricated by nanospheres lithography and inductively coupled plasma reactive-ion etching (ICP-RIE). Spin-coating and self-assembly at ethanol-water interface techniques were investigated to form hexagonally packaged polystyrene (PS) nanospheres. Spin-coating speed and acceleration were optimized and analyzed to form monolayer PS nanospheres of 500, 350, and 200 nm diameters on GaAs wafers. Besides, large-scale and low defects density monolayer PS nanospheres were realized by self-assembly at ethanol-water interface technique serving as the etching masks. The diameters of the nanosphere masks were controlled by plasma etching whereas the periodicities were tuned by the selection of the sizes of the nanospheres. Optimal etching condition of GaAs NWs was found through parameters study of the etching chemistries, power and time. Hybrid solar cells were then fabricated by infiltrating the conjugated polymer of P3HT into the forest of GaAs NW arrays. The trend of PCE and external quantum efficiency under AM 1.5G illumination ($E_{QEAM1.5G}$) of the fabricated HSCs were investigated as the variation of the geometrical dimensions of the NW arrays.

When the periodicity was fixed, the rise of FR would cause the competence of energy harvesting among adjacent of NWs. When the FR was fixed at 0.7, the rise of periodicity (and therefore the diameter) of NW arrays would decrease the photon harvesting. The highest PCE achieved was 4.6% for 200 nm periodicity and FR was 0.44. This study further clarified the role of GaAs NWs in HSC which also demonstrated the potential of inorganics/organics HSC for large-scale application.

In Chapter 6, we have demonstrated a low-cost prototype of HSC based on the growth of freely standing GaAs NWs directly on indium tin oxide (ITO) using Au nanoparticles (NPs) as catalysts by metal organic chemical vapour deposition (MOCVD). An area density controllable Au NPs deposition method was developed by centrifugation. Upon the parameters study of the centrifugal time and rotation speed, the highest area density for Au NPs was 509 NP/ μm^2 for 10 nm and 130 NP/ μm^2 for 20 nm. Freely standing GaAs NWs were directly grown on ITO followed by a systematic study of the size of the catalysts and the growth parameters including the growth temperature, precursor flow rates, and growth time. A kinetic model was also adopted to quantitatively investigate their influence over the growth of GaAs NWs. Specifically, the increase of the growth rate of the NWs was found as the rose of the growth temperature. The calculated value of 65 kJ/mol for GaAs NWs on ITO indicated no additional barrier from the substrate. At the same time, it was found that the growth rate of the NWs linearly increased with the precursor flow rates of TMGa when the V/III ratio was 9.5 at various temperatures. The growth time had negligible effect on the growth rate of the NWs. Moreover, the growth rate of NWs increased with the size of the Au NPs until 40 nm which was attributed to the Gibbs-Thomson effect. We had calculated that the smallest Au NP to induce NWs growth to be 2.14 nm and experimentally proved that the 2 nm Au NPs failed to initiate the growth of the GaAs NWs on ITO. Moreover, the area density of the NWs was well tuned by the centrifugal deposition of Au NPs. In the meantime, high crystal quality of

the GaAs NWs were observed with no observable defects along the length of the NWs. Zinc-blende structure was noticed for 20 and 40 nm induced NWs whereas wurtzite was observed for 10 nm Au NPs catalyzed NWs. Based on the above results, a prototype of the HSC was presented by drop-casted P3HT over the GaAs NWs that grown on ITO. The current-voltage measurement revealed that ohmic contact had been built among the GaAs NWs and the ITO substrate. The photovoltaic performance was evaluated which demonstrated an alternative pathway of fabrication of low-cost organic/inorganic HSCs.

7.2 Recommendation for Future Work

There are several aspects of the present research work that can be further investigated.

Rational Design for the Geometrical Dimensions of Nanowire Arrays of IV and Perovskite Materials

In our study, orderly and vertically standing III-V NW arrays are mainly considered to maximize their light harvesting by optimizing the geometrical dimensions. Compared with FDTD simulations, the proposed algorithm has been demonstrated to be effective and efficient. However, there are also other promising photovoltaics-favorable or low-cost materials such as Si, Ge or the currently most popular perovskite that are worthy of investigation. Analytically design of the diameters and periodicities of the arrays of NWs can greatly narrow down the time and fabrication cost. Considering the low tolerance of the predicted values with experimentally reported the highest PCE of GaAs and InP NWs based photovoltaic devices, investigation and exploration of the proposed algorithm for other materials have great potential to guide high efficient NWs based solar cells design.

Photovoltaic Performance Investigation of Other Nanostructures Based HSCs Through Fabrication, Characterization, and Numerical Modeling

Numerical investigations have proved that other types of nanostructures such as nanocone, nanofunnel etc. to increase the solar energy harvesting capability. In our work, we mainly focus on cylindrical NW arrays based HSCs. The proposed hybrid active layer could be extended to mix the organics with other types of nanostructures. Coupled opto-electrical modeling can be adopted to predict and guide the design of the efficient HSCs. Through selection and optimization of the etching chemistries, time, and power, a variety of the nanostructures can be realized by combining nanospheres lithography and ICP-RIE. Fabrication and characterization techniques can be applied for high performance HSCs.

Performance Improvement of the HSCs Based on GaAs Nanowires Directly Growth on ITO

It is proved that bottom-up growth of NWs have superiority of high crystal quality as compared with those received by top-down method. In Chapter 6, we have successfully grown GaAs NWs directly on low-cost transparent conductive substrate with high crystal quality and freely standing morphology. Considering the material reduction and the well-control over the growth of the NWs, the prototype of GaAs NWs based HSCs that we presented has demonstrated an alternative possibility for future HSCs. To further improve the performance of the device, there are several aspects that can be explored.

Further experiments are required to study polymer deposition method. In Chapter 6, the P3HT was drop-casted directly onto the NWs and left dried. This drop-cast method would result in the non-uniform thickness of the polymer layer between the tops of the NWs and the electrode. Besides, the voids appeared at the bottom of the NWs were also to be dealt with. Therefore, an optimized polymer

deposition technique is required such as dip-coating to achieve more uniform layer. Dissolving the P3HT in a mixed solvent with different boiling points may also be a viable method. Through selection and optimization of the mixed ratio of different solvents, an improved polymer deposition technique can enhance the performance of the HSCs.

Besides, future experiments are designed to study the dependency of the short-circuit current density on the thickness of the P3HT. If the P3HT is too thick, many carriers are lost and the excitons will recombine due to their short diffusion length. This leads to small overall short-circuit current density. On the other hand, if the P3HT is too thin, the NWs may not be appropriately wrapped by the polymer which will jeopardize the reliability of the device.

Moreover, investigation on the device performance as a function of the surface treatment of the NWs is critically important to the performance of HSCs. The interface among the NWs and the polymer can be a leakage source. Proper surface passivation of the NWs helps reduce the surface recombination centers and improve the short-circuit current density. Therefore, the improvement of the quality of this organic/inorganic interfaces and the overall better charge transfer can be obtained to improve the performance of this type of HSCs.

Author's publications

Journal Publications

1. **D. Wu**, X. Tang, K. Wang, Z. He and X. Li, "An Efficient and Effective Design of InP Nanowires for Maximal Solar Energy Harvesting," *Nanoscale Research Letters* (2017) (submitted)
2. **D. Wu**, X. Tang, K. Wang, and X. Li, "An Analytic Approach for Optimal Geometrical Design of GaAs Nanowires for Maximal Light Harvesting in Photovoltaic Cells," *Scientific Reports*, vol. 7, p. 46504, 2017.
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