Hybrid solar cells based on Si and PEDOT : PSS

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Hybrid Solar Cells Based on Si and PEDOT:PSS

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Abstract

As the demand for renewable clean energy increases, extensive research has been directed towards photovoltaics (PV) energy owing to its inexhaustibility, abundance and availability anywhere on earth. Although the conventional crystalline bulk silicon (Si) solar cells which dominate the current commercial PV markets are highly efficient and reliable, the costly Si material and fabrication processes make them not as competitive as fossil fuels. To lower the cost, hybrid solar cells based on Si and organic materials have emerged as promising candidates to leverage on the advantages of the highly efficient Si material and the low cost and flexibility offered by organic materials. Si nanostructures have also drawn much attention and been widely incorporated into the hybrid cells due to their excellent capabilities in light trapping and carrier separation and collection. In this work, we fabricate and characterize different types of high efficient Si/PEDOT:PSS hybrid solar cells, that include planar cells and cells incorporated with Si nanowires (SiNWs) and Si nanocones (SiNCs). These cells were fabricated on both bulk Si wafers as well as Si thin films. The study of such hybrid cells using Si thin films is important to lower the material cost and render them suitable for practical application. Besides experimental studies, extensive theoretical simulation has been carried out to understand the optical characteristics and light trapping of the nanostructures.

Firstly, we study the performance of simple planar Si/PEDOT:PSS hybrid cells, focusing on the thickness of the PEDOT:PSS coating and the Si absorber layer on the light absorption behavior. Simple planar hybrid heterojunction solar cells have been fabricated based on n-type Si and the p-type PEDOT:PSS polymer using a simple low-temperature

spin-coating technique. Cells with different thicknesses of PEDOT:PSS layer have been fabricated to study the effect of the polymer thickness on the cell performance. It is found that an optimum PEDOT:PSS thickness of ~ 78 nm gives rise to the highest short circuit current density (J_{sc}) and external quantum efficiency (EQE) of 27.0 mA/cm^2 and 63.6%, respectively. Hybrid cells with different thicknesses of Si thin films from 2.2 to $15.5 \text{ }\mu\text{m}$ have also been fabricated to study their photovoltaic performance. It is found that a high power conversion efficiency (PCE) of 8.7% has been achieved for the cell with the thickest Si film thickness of $15.5 \text{ }\mu\text{m}$. It exhibits a J_{sc} of 20.4 mA/cm^2 , which is about 78% of that measured for a reference bulk wafer Si cell fabricated in the same process. Concurrently, we have performed optical simulations for the planar hybrid cell structure based on the finite element method. The effects of both the PEDOT:PSS thickness and the Si thickness on the light harvesting characteristics are investigated and compared with the experimental results. It is found that a high photocurrent density of $\sim 24 \text{ mA/cm}^2$ is achievable for a hybrid cell based on $10 \text{ }\mu\text{m}$ Si film using layer of PEDOT:PSS with an optimum thickness of 80~90 nm. Taken into account a larger resistance when a thicker PEDOT:PSS is used, our experimental and simulation results suggest that the optimum PEDOT:PSS thickness for thin film hybrid cells is around 70~80 nm. With only a layer of $15 \text{ }\mu\text{m}$ thick Si film, the planar hybrid cell based on the backPEDOT structure is able to achieve a high photocurrent density of 30.3 mA/cm^2 and a PCE of 13.2%.

Next we study the light harvesting capability and photovoltaic performance of Si/PEDOT:PSS hybrid cells incorporated with SiNWs arrays fabricated using the metal-catalyzed electroless etching (MCEE) technique. The surfaces of the SiNWs prepared

using this technique are typically defective and contaminated with Ag nanoparticles, which will lead to enhanced carriers recombination and adversely affect the performance of the cells. In this work, a simple two-step surface treatment method using ozone has been proposed to improve the surface quality of SiNWs in SiNWs/PEDOT:PSS hybrid cells. A remarkable PCE of 12.4% has been achieved, with a high J_{sc} of 30.8 mA/cm² and a high V_{oc} of 0.58 V. This is due to the enhancement of light absorption attributed to the light trapping by the SiNWs, and suppression of recombination loss arising from the removal of Ag nanoparticles and passivation of the SiNWs surface brought about by the proposed two-step surface treatment process. The PCE and V_{oc} are 29.8% and 13.7% enhanced respectively as compared to similar SiNWs hybrid cells without the surface treatment. Besides using bulk Si wafers, SiNWs/PEDOT:PSS based on the more cost-effective Si thin films have also been studied. The same two-step surface treatment process, using oxygen (O₂) plasma instead of ozone, has been applied to the thin film SiNWs/PEDOT:PSS cells to remove contaminants and passivate the SiNWs surface. The performance of the thin film SiNWs/PEDOT:PSS hybrid cells have been investigated in terms of the effects of the surface treatment and the SiNWs length. It is found that similar improvements in the SiNWs surface quality can also be achieved with the use of oxygen plasma treatment. In terms of cell performance, a maximum PCE of 7.83% has been obtained for a Si thin film of 10.6 μm thick under the optimized SiNWs length of 0.7 μm.

Periodic Si nanocones (SiNCs) have been fabricated by dry etching of Si substrate using assembled monolayer polystyrene (PS) nanospheres as mask, and incorporated into the Si/PEDOT:PSS solar cells. Compared with SiNWs, SiNCs are mechanically more robust

due to the larger base. Besides, they present a more gradual change in the effective refractive index that is important to help minimize light reflection and enhance light absorption in the solar cells. Hybrid Si/PEDOT:PSS solar cells have been fabricated based on the periodic SiNCs with different periodicities (P), and a highest PCE of 7.1% has been obtained for cells with a periodicity of 400 nm due to its strong light trapping around the peak of the solar spectrum and better current collection efficiency. The optical properties of the SiNCs/PEDOT:PSS cell have also been studied theoretically using simulation based on the finite element method and compared with the experimental results. For a SiNCs/PEDOT:PSS hybrid solar cell structure based on a 3.5 μm thin Si layer, it demonstrates great enhancement in light absorption with the incorporation of SiNCs and reveals a highest ultimate efficiency of 33.7% with a periodicity (P) of 600 nm when the top diameter to periodicity is fixed at 0.5.

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Chapter 1 Introduction

1.1 Background and Motivation

The demand for energy increases inevitably as our society develops. Fig. 1.1 summarizes the world total energy supply from 1971 to 2013[1], where it is clearly seen that energy consumption has been increasing over the past decades and is over two times as compared to the amount in 1971. Currently, the global power consumption is approximately 15 TW ($1 \text{ TW} = 10^{12} \text{ W}$) and is generated mainly by the combustion of fossil fuels [1, 2]. However, our current energy sources are not renewable and will run out eventually, resulting in serious energy crisis especially when faced with a prospective energy demand of up to 30 TW by the mid 21st century [3]. Moreover, the use of fossil fuels has large emission of carbon dioxide (CO_2) which is the main composition of the greenhouse gases (GHGs) that causes climate change [4, 5]. The climate change primarily caused by human activities has resulted in undesirable changes in surface air and free atmospheric temperature, sea level pressure, tropopause height and ocean heat content [6]. From combining climate modeling and paleoclimatic data, it is estimated that the sea-level will have a maximum rise of about 2.0 m under physically possible glaciological conditions [7]. To address the energy and environment issues, it is important to search for alternative energy sources that are both renewable and environmentally friendly, so as to sustain our society development. Moreover, in the long term the fossil fuels will become more expensive due to their depletion, and renewable energy investments will pay off economically, particularly with advancement of technologies [4].

Figure 1. 1 : World total primary energy supply from 1971 to 2013 [1].

Among the various renewable energy sources, sunlight is free, clean, environment friendly, widespread, abundant and inexhaustible. Solar energy has the potential to meet our high level of energy demand, as only one hour's solar radiation on the earth surface is almost able to provide enough energy for all human activities consumption in a year [8]. While for other renewable energy sources such as wind, hydroelectric, biomass and geothermal, their practical potential energy supply are estimated to be less than 10 TW [9].

There are three main solar active technologies, including concentrating solar power (CSP), solar thermal collectors for heating and cooling (SHC), and solar photovoltaic (PV) [10]. Among them, solar PV directly converts solar irradiation into electricity. Fig. 1.2 shows the total global capacity of solar PV during the period from 2004 to 2014 [10]. In

2004, the solar PV annual capacity had exceeded 3.7 GW and it has been growing at a fast rate over the past decade. In 2014, the new solar capacity came into operation is almost 39 GW, which increases the global total to almost 177 GW. In 2010, solar PV generated electrical energy accounts for only a small portion (40 GW out of 1320 GW) of the total renewable energy [11]. The electricity energy provided by solar PV is projected to account for 5% of global total consumption in 2030, and increasing to 11% in 2050, according to the International Energy Agency (IEA) solar PV roadmap vision [8]. By the year of 2100, the world energy share will be completely changed and dominated by solar energy with the depletion of coals, as predicted by the German scientific advisory board [12, 13]. Therefore solar energy is believed to be a very promising renewable alternative for our future energy supply.

Figure 1. 2 : Total global capacity of solar PV from 2004 to 2014 [10].

Unfortunately, despite its abundance, solar energy is one of the most expensive renewable energy sources, which is the primary reason that it takes up only a tiny fraction of the world energy share at present. Nowadays, the commercial PV market is dominated by the conventional inorganic solar cells such as single crystalline silicon and multi-crystalline silicon solar cells and such PV panels are widely used on roof top. These solar cells have high power efficiency owing to their high quality crystalline Si material used which has high carrier mobility. Moreover, the designs and fabrication processes of these conventional solar cells have benefited from mature technologies developed for the CMOS industry. A high efficiency of 25% has been reported by the University of New South Wales on a conventional single crystalline Si single junction solar cells [14, 15]. These solar cells have efficiencies approaching the theoretical limit predicted for Si solar cells of 30% [16], but suffer from the high cost of the expensive Si wafers and costly complex fabrication processes. Si material of over 200 μm thick is needed to efficiently absorb sunlight irradiated due to its indirect bandgap, and this expensive Si material accounts for more about 32% of the module cost [17]. Energy intensive processes involving high temperature and high vacuum conditions are extensively utilized in the fabrication processes of those cells [18], and these expensive processes further increase the total production cost. Therefore, more efforts are needed to make the solar PV more cost-effective as a reliable energy alternative.

To lower the material cost, thin film Si has drawn much attention and been explored to replace bulk Si in Si solar cells [19-24]. In addition to inorganic solar cells, extensive research has been done in the development of promising low-cost organic solar cells in

the past few decades owing to their low material cost, flexibility and low temperature simple processing [25-34]. However, there are still challenges to improve the efficiency of organic solar cells due to limitation of their inefficient carrier hopping transport and low dissociation probability of excitons [35, 36]. This led to the idea of hybrid solar cells based on a combination of inorganic and organic materials to leverage on their individual advantages. In 2002, this idea was reported for a hybrid cell fabricated using CdSe nanorods and a conjugated polymer which has a relatively low efficiency of 1.7% [37]. Since then, there have been remarkable progresses made in the studies of Si based hybrid solar cells, especially with the incorporation of Si nanowires (SiNWs) [38-40]. Si nanowires have excellent light trapping capability to enhance absorption and hence allow the use of thinner Si material. Besides, their nano-scale diameter and high surface-to-volume ratio are perfect for efficient carrier extraction in the SiNWs/organic solar cells [41]. Moreover, with the incorporation of SiNWs, lower quality silicon can also be used to fabricate the hybrid solar cells to further reduce the cost. Recently, a highly conductive transparent polymer, poly (3,4-ethylenedioxy-thiophene): poly (styrenesulfonate) (PEDOT:PSS) has been extensively used and studied to form hybrid solar cells with SiNWs in various designs, and a record efficiency of 13.01% has recently been reported [42]. Efficiency of over 10% has also been achieved for planar Si/PEDOT:PSS hybrid cells that do not employ any nanostructures [43]. Si/PEDOT:PSS solar cells have also been demonstrated on a 2.2 μm Si thin film [44], which shows the potential of realizing such highly efficient at lower cost. Despite the progress made, it should be noted that there are still challenges to address, such as the high surface recombination rate associated with the SiNWs resulting from the solution etching process [45], to further

improve the cell efficiency. Overall, hybrid solar cells incorporating nanostructures thin film Si and PEDOT:PSS are very promising to be low cost and high efficiency, and hence are potentially suitable for practical application.

In this project, we propose to fabricate and study Si/PEDOT:PSS solar cells using both planar and nanostructures Si designs. We characterize the performance of the hybrid cells including light harvesting and carrier extraction behavior both experimentally and theoretically.

1.2 Objectives

In this project, Si/PEDOT:PSS hybrid solar cells with both planar and nanostructures textured designs are studied. The scope of this research work includes the design, fabrication and characterization of planar Si, SiNWs and Si nanocones/PEDOT:PSS hybrid solar cells. Optical simulation is also performed for the Si/PEDOT:PSS hybrid structure with different configurations using the finite element method. The objectives of this study are summarized as follows:

- (i) Fabricate and characterize planar Si/PEDOT:PSS hybrid cells and investigate the effects of various parameters, including the thickness of the PEDOT:PSS layer and the Si absorber on their light harvesting performance. These light absorption behaviors of the planar hybrid cells are studied using optical simulation as well.

- (ii) Prepare SiNWs using the metal-catalyzed electroless etching (MCEE) method. Fabricate SiNWs/PEDOT:PSS hybrid solar cells with and without surface treatment of the SiNWs and compare their performances. We will study the effects of the surface treatment on the photovoltaic performance of these hybrid cells, including their short circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (PCE).
- (iii) Fabricate SiNWs/PEDOT:PSS hybrid solar cells on thin film Si of various thickness with different SiNWs lengths. The performances of the thin film hybrid cells will be optimized by tuning the SiNWs length. Surface treatment process will also be employed to improve the thin-film hybrid cell performance by lowering the surface recombination rate.
- (iv) SiNWs fabricated using the MCEE method are non-periodic and with a range of small diameters of 30 ~ 150 nm only. In this work we also study the fabrication of periodic Si nanocones (SiNCs) structures with controllable dimensions based on the dry etching of Si substrate patterned using monolayer polystyrene (PS) nanospheres as mask. SiNCs/PEDOT:PSS hybrid solar cells are then fabricated and characterized in terms of their optical, electrical and photovoltaic properties, as well as surface morphology. The influence of the SiNCs dimension on the hybrid solar cell performance will be studied.

1.3 Major contribution of the thesis

Planar hybrid solar cells based on crystalline Si and PEDOT:PSS material are fabricated with a simple spin coating approach. We study the cells fabricated with different PEDOT:PSS thicknesses as well as different Si absorber thicknesses. The change in the thickness of the PEDOT:PSS layer is found to have large effects on the reflection spectra of the planar hybrid cells, resulting in large J_{sc} variation from 24.4 to 27.0 mA/cm² when the thickness of PEDOT:PSS layer varies in the range of 64 ~ 135 nm. The optimum thickness of PEDOT:PSS is observed to be 70~80 nm, which gives rise to J_{sc} of 27 mA/cm². With same coating of PEDOT:PSS layer, the light absorption in the planar hybrid cells is found to increase continuously with the increase of Si absorber thickness, but with a decreasing increment per unit thickness. High power conversion efficiencies (PCE) of 5.4%, 6.6%, 8.3% and 8.7% are achieved for the 2.2, 5.5, 10.6 and 15.5 μ m planar thin-film Si/PEDOT:PSS cells, with J_{sc} of 12.7, 16.0, 19.2 and 20.4 mA/cm², respectively. Optical simulations are also performed to investigate the light harvesting capabilities of the planar Si/PEDOT:PSS hybrid cells as a function of Si film thickness. It is found that the J_{sc} increases with T and saturates at about $T = 15 \mu$ m. With a reflector incorporated at the back of the thin film Si to increase the optical path length, a remarkable short circuit current density as high as 27.5 mA/cm² can be achieved. With only a layer of 15 μ m thick Si film, the planar hybrid cell based on the backPEDOT structure is able to achieve a high photocurrent density of 30.3 mA/cm² and a PCE of 13.2%.

We have also proposed a two-step surface treatment method to improve the efficiency of the SiNWs/PEDOT:PSS hybrid solar cells. SiNWs of 500 nm length are fabricated using the MCEE method on bulk Si and then used to fabricate hybrid solar cells with PEDOT:PSS. To improve the surface quality, the SiNWs are treated by low temperature ozone to form a layer of surface sacrificial oxide and then dipped into hydrofluoric (HF) acid to partially remove the oxide, leaving only a thin layer of oxide to passivate the surface. The effects of the surface treatment of SiNWs on the cell performance are investigated. It is found that the surface recombination of the hybrid SiNWs hybrid cells is greatly suppressed, resulting in a remarkable improvement of ~ 0.07 V in V_{oc} and thus boosts the efficiency from 10% to 12.4%. The surface treatment process helps to remove residual impurities and defects near the surface of the SiNWs and effectively passivate the SiNWs surface.

Instead of bulk Si, epitaxial Si thin films have been used to fabricate SiNWs/PEDOT:PSS hybrid solar cells using same solution-based process. The performance of the hybrid thin film SiNWs/PEDOT:PSS cells with different Si thin film thickness are investigated in terms of the effects of the surface treatment and the wire length. For the cells with Si thickness of 5.5 and 10.6 μm , average PCEs of 6.20% and 7.27%, and maximum PCEs of 6.53% and 7.83% have been obtained respectively, under the optimized SiNWs length of 0.7 μm . For the case of a thicker Si thin film of 15.5 μm , an average PCE of 7.88% and a maximum PCE of 8.01% have been achieved with an optimized SiNWs length of 0.95 μm with the surface treatment. The promising efficiencies obtained for the thin-film

SiNWs cells demonstrate the possibility to realize highly efficient SiNWs/PEDOT:PSS hybrid solar cells using thin-film Si.

Finally, SiNCs have been fabricated by dry etching of Si substrate patterned using monolayer polystyrene (PS) nanospheres as mask. Based on the SiNCs realized, hybrid SiNCs/PEDOT:PSS solar cells are then fabricated and characterized in terms of their optical, electrical and photovoltaic properties. By varying the SiNCs periodicity of the hybrid cells, a PCE of 7.1% is achieved for the SiNCs hybrid cell with a 400 nm periodicity, owing to the strong light trapping near the solar spectrum peak and better current collection efficiency. In addition, we have studied theoretically the light absorption of the SiNCs/PEDOT:PSS hybrid cell using the finite element method on thin-film Si layer. With a top diameter to periodicity ratio of 0.5, the hybrid structure offers the highest ultimate efficiency of 33.7% at a periodicity of 600 nm.

1.4 Organization of the thesis

This thesis consists of seven chapters organized as follows:

Chapter 1: Background, motivation, objectives and major contributions of the project are presented.

Chapter 2: The overview of solar cells and fundamental principles of solar cell operation are presented. A detailed literature review of the development of Si based solar cells, organic solar cells, hybrid solar cells and the incorporation of nanostructures for light

harvesting is carried out. Simulation studies on light absorption in solar cell applications are discussed.

Chapter 3: Planar hybrid solar cells based on Si and PEDOT:PSS are fabricated and studied on bulk Si wafer and epitaxial thin-film Si material. The effects of thickness of the PEDOT:PSS layer and Si absorber on the hybrid cell performance are investigated. Optical simulation studies of the light absorption behaviors are also performed.

Chapter 4: The critical effects of the Ozone surface treatment of SiNWs prepared by MCEE method on the performance of SiNWs/PEDOT:PSS hybrid cells are studied.

Chapter 5: SiNWs are fabricated by MCEE method on epitaxial Si thin films of various thicknesses. The performance of thin-film SiNWs/PEDOT:PSS hybrid cells are studied in terms of the SiNWs lengths. Surface treatment of the SiNWs using O₂ plasma are proposed and applied to the thin-film hybrid cells.

Chapter 6: The fabrication process for SiNCs structures and hybrid SiNCs/PEDOT:PSS solar cells is presented. Optical simulation is performed and studied for the periodic SiNCs/PEDOT:PSS hybrid cells using thin-film Si, and the results are compared with those obtained experimentally.

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

Chapter 2 Literature Review

This chapter reviews the fundamentals of solar cells, and literature works on silicon solar cells, organic solar cells, hybrid solar cells and optical simulation related to solar cells. This chapter first introduces the fundamentals of solar cells and an overview of the material and technology involved. Following this, various categories of solar cells including silicon solar cells, organic solar cells, hybrid solar cells, and Si nanostructure based inorganic/organic solar cells will be discussed. Finally, simulation works on optical characteristics of solar cells are presented.

2.1 Overview and Fundamentals of Solar cell

2.1.1 Introduction of Solar Cell

Figure 2. 1 : Cross section of a solar cell [46].

A photovoltaic (PV) device or solar cell is a device that can directly convert incident solar energy into electrical current. It consists of a light absorbing material which is

connected to an external circuit asymmetrically, typically in the form of a semiconductor p-n junction as shown in Fig. 2.1 [47]. There are four key processes involved in the solar energy conversion: light absorption, charge separation, charge transportation and charge collection. When incident photons of light with energy greater than the band gap of the material are absorbed, electron-hole pairs (or excitons in organic solar cells) are generated, which are meta-stable and will recombine after a period of time equals to the minority carrier lifetime. If these photo-generated electron-hole pairs can reach the p-n junction in one minority carrier diffusion length, they can then be separated by the electric field built in the p-n junction and swept across the junction becoming majority carrier in the emitter or base without recombination. The carriers are then driven towards the front and rear contacts separately, passing through the external circuit as photo-generated current. The cell establishes a photovoltage at open circuit, and produces both current and voltage and delivers electrical energy when connected to an external load.

Figure 2. 2 : Efficiency and cost projections for the three generations of solar cells [48].

Currently, solar cells are generally classified into three generations, as shown in Fig. 2.2 [48]. The first-generation solar cells are single junction devices based on high quality single crystalline and multicrystalline bulk wafers, and account for 85-90% of the global annual PV market today [8]. They have high efficiency but suffer from high production cost. The second-generation solar cells are thin-film solar cells, and account for 10% to 15% of the global PV module market [8]. They have relative low efficiency and lower material cost. The materials widely used for this generation solar cells include Cadmium-Telluride (CdTe), Copper-Indium-Diselenide (CIS), Copper-Indium-Gallium-Diselenide (CIGS), amorphous and polycrystalline silicon [8], and among them, thin-film Si is a promising candidate [49]. The third-generation solar cells include various emerging technologies such as multi-junction cells, tandem cells, hot-carrier cells, nanostructure cells, multi-junction and tandem cells [8, 50, 51]. They aim to achieve high efficiency solar cells at lower manufacturing costs similar to the second-generation solar cells based on operating principles not limited by efficiency constraint of 31% of the conventional cells [48]. In addition, recently perovskites solar cell has emerged as a promising candidate for low-cost high-efficiency solar cell and is currently under intensive research as it has demonstrated high efficiency of 19.3% [52] through using thin material layers prepared by solution based chemicals. However, there are also challenges faced by the perovskites solar cells, such as stability issues due to their high sensitivity to moisture environment and the UV light [53, 54], and the ambiguous evaluation of efficiency due to hysteretic behavior of the current-voltage curves [55].

2.1.2 Modeling of Solar Cell

Figure 2. 3 : Equivalent circuit of solar cell including series and shunt resistances [56].

Solar cell is typically modeled as a current generator with a rectifying diode connected in parallel with it, as illustrated by the equivalent circuit shown in Fig. 2.3 [56]. It is noted that current density J is normally used instead of current for performance comparison to eliminate the dependency on illumination area. Two parasitic resistances are included to be in series and in parallel with the cell to describe the power dissipation in real solar cell devices [56]. The series resistance (R_s) is caused by the resistance of the materials of the cell and the contacts to the current flow, whereas the shunt resistance (R_{sh}) is due to the leakage of current. The current density in a real cell circuit including the parasitic resistances is given by the non-ideal diode equation [56],

$$J = J_L - J_0 \left(e^{\frac{q(V+JAR_s)}{nK_B T}} - 1 \right) - \frac{V+JAR_s}{R_{sh}} \quad (2.1)$$

where J_L is the photo-generated current density, J_0 is the diode saturation current density, K_B is the Boltzmann's constant, T is the temperature in Kelvin, A is the cell area and n is the ideality factor. The ideality factor measures how much the cell diode behavior deviates from the ideal diode, and is determined by the various recombination processes occurring in the cell [47]. To achieve high solar cell performance, low series resistance

and high shunt resistance are necessary and the recombination of carriers should also be minimized.

Figure 2. 4 : The current voltage and power-voltage characteristics of an ideal cell [56].

There are several important parameters that characterize solar cell performance. Fig. 2.4 shows the current-voltage and power-voltage characteristics of an ideal solar cell [56]. The open circuit voltage V_{oc} is the maximum voltage available from the cell when the circuit current is zero, and it defines the operating regime of the solar cell. A solar cell delivers power only in the region from 0 to V_{oc} . The short circuit current density J_{sc} is the current density drawn when the cell is short circuited, and it is dependent on the light illumination. Incident photon-current efficiency (IPCE) or external quantum efficiency (EQE) is an important quantity used to relate the J_{sc} to the incident solar spectrum. It is defined as the ratio of the number of carriers that the solar cell collects to the number of the total incident photons at a given irradiation, and thus includes the effects of reflection and transmission optical losses as well as the electrical losses due to recombination. V_m

and J_m represent the maximum voltage and maximum current density at the point that the cell delivers maximum electrical power to the external circuit. The power efficiency (PCE, η), which is the most critical parameter used to evaluate the performance of a solar cell, is defined as the ratio of the maximum output electrical power to the total incident solar power density, P_{in} . The PCE depends on the illumination condition and the temperature of the solar cell. The standard test for solar cell is done under Air Mass 1.5 spectrum of an incident power density of 1000 W m^{-2} at a temperature of 25°C [56]. The fill factor FF is defined as the ratio of the maximum output power ($V_m J_m$) to the product of V_{oc} and J_{sc} , to relate the efficiency to V_{oc} and J_{sc} . The V_{oc} , J_{sc} , EQE , PCE and FF are the most important parameters used to evaluate the performance of a solar cell, and they are related by the following equations for an ideal cell [56]:

$$V_{oc} = \frac{K_B T}{q} \ln\left(\frac{J_{sc}}{J_0} + 1\right) \quad (2.2)$$

$$J_{sc} = q \int (I(E) EQE(E)) dE \quad (2.3)$$

$$\eta = \frac{V_m J_m}{P_{in}} = \frac{V_{oc} J_{sc} FF}{P_{in}} \quad (2.4)$$

$$FF = \frac{V_m J_m}{V_{oc} J_{sc}} \quad (2.5)$$

where q is the elementary charge, E is the photon energy, $I(E)$ is the solar irradiance spectrum.

2.2 Si Solar Cells

As mentioned in the overview, crystalline silicon solar cells are recognized as the first generation photovoltaic technology and dominate over 85% of the market. During the

past years, Si solar cells have evolved considerably by incorporating sophisticated designs such as anti-reflection coating and surface texturing, surface passivations for recombination suppression, to improve the light absorption and carrier extraction [57]. A remarkable efficiency of 25% was achieved by a Si solar cell design incorporated with passivated emitter and local diffusion in rear of the cell (PERL) [58]. This represents a milestone in the silicon solar cell development, and is very close to the theoretical efficiency limit for a single junction cell [59]. Fig. 2.5 shows the structure of a 25% efficiency cell [60]. In parallel with the high efficiency achieved, it is important that the cost of Si solar cells be lowered to render it competitive against other forms of energy. However, for the current wafer-based crystalline silicon solar cells, there is limit to further reduce the cost, due to the use of expensive bulk silicon wafers. It is possible to achieve high efficiency solar cell using thinner layer of Si, instead of bulk wafer, if optical confinement is introduced to increase the absorption of solar energy in the material. Therefore thin film Si is a promising candidate to achieve high efficiency solar cell at lower cost.

Figure 2. 5 : Structure of a 25% efficient silicon solar cell [60].

Amorphous silicon (a-Si) has drawn much interest owing to its relatively higher light absorption compared to crystalline Si in the visible light range [61] as well as its lower production cost by using the plasma enhanced chemical vapor deposition (PECVD) [22] or electron beam evaporation (Ebeam) deposition process [23]. In 1976, solar cell based on hydrogenated amorphous silicon (a-Si) was first reported with an efficiency below 3% [61]. Since then, there has been fast progress in the study of amorphous Si solar cells. A-Si PV modules based on the monolithic concept have demonstrated 5 to 7% efficiency. Its device configuration is shown in Fig. 2.6 [20]. However, the amorphous Si has much lower charge mobility than the crystalline Si, and cannot absorb light in the infrared region due to its high bandgap of ~ 1.7 to 1.9 eV. Thus amorphous Si based single junction solar cells are normally made in superstrate or substrate p-i-n structure to make use of the strong drift field for charge separation and collection. An optimal thickness of ~ 300 nm is preferred for the a-Si cells, and light trapping techniques are needed [20].

Figure 2. 6 : Schematic of amorphous Si monolithic modules in superstrate configuration [20].

Another promising thin film Si technology for PV application is polycrystalline silicon (pc-Si or poly-Si on glass). The fabrication process of the poly-Si film involves the use of solid phase crystallization (SPC) of amorphous silicon for the film formation, and

followed by rapid thermal anneal and hydrogen plasma passivation. Moreover, in an effort to obtain high crystallographic quality, seed layer approaches are also proposed combining with laser crystallization and aluminium-induced crystallization [62]. Recently, mini PV modules based on SPC poly-Si on glass made from PECVD deposited a-Si have achieved 10% efficiency, with a V_{oc} of ~ 500 mV and a J_{sc} of ~ 30 mA/cm² [63]. Thin-film SPC poly-Si solar cells made from e-beam deposited a-Si has been demonstrated to have the capability of achieving efficiencies over 5% on planar glass substrate [21], and the device structure is shown in Fig. 2.7. Thin-film poly-Si cells can be either p-type or n-type based devices without the use of a p-i-n structure. Substrate as well as superstrate configurations have been demonstrated [20]. Since the active layer of the thin-film poly-Si cells is very thin, light trapping schemes are very important to obtain high efficiency [19, 24, 64, 65].

Figure 2. 7 : Schematic of a thin-film SPC poly-Si solar cell in the superstrate configuration [21].

2.3 Organic Solar Cells

Although the current commercial PV market is dominated by inorganic Si solar cells, a large number of studies have been done on organic solar cells [25, 27-31]. Steady

progress in the performance of organic solar cells has been made since the first realization of photovoltaic effect in organic semiconductors [66]. In 1986, a solar cell based on bilayer donor-acceptor heterojunction concept was reported with a power conversion efficiency of 1% [67]. The structure of this cell is shown in Fig. 2.8, where a p-type (electron donor) organic semiconductor with a HOMO (highest occupied molecular orbital) and a n-type (electron acceptor) organic semiconductor with a LOMO (lowest occupied molecular orbital) form the heterojunction. By applying two electrodes that match the HOMO and LOMO levels, the incident light is absorbed and thus electron-hole pairs are generated and then separated due to the difference in the ionization potential and electron affinity of the adjacent materials [27]. A thick layer of active material ($> \sim 80$ nm) is needed for sufficient light absorption. However, the poor charge separation ability limits the efficiency of this type of organic solar cells due to its short exciton diffusion length (~ 10 nm) [25].

Figure 2. 8 : Bilayer heterojunction organic solar cells a) device structure and b) band diagram.

Further improvement in the efficiency has been achieved by introducing inter-mixing of donor-acceptor materials in a single layer (bulk heterojunctions (BHJ)) for efficient

photon harvesting [67-73]. As shown in Fig. 2.9, this bulk heterojunction structure has a phase-separated interpenetrating network inside the active layer, and thus enhances the charge separation ability [74] and allows the use of thick active layer to achieve high power conversion efficiency.

Figure 2. 9 : Bulk heterojunction organic solar cells a) device structure and b) band diagram.

Organic solar cells have been fabricated based on many materials with different structures, such as polymer/polymer [68, 75, 76], polymer/small molecule [77-80] and small molecule/small molecule [81, 82] blends. Recently, an efficiency of over 9% has been achieved for thieno[3,4-b]-thiophene/benzodithiophene/fullerene derivative [6,6]-phenyl- C_{61} -butyric acid methyl ester (PTB7/PCBM) cell [83].

2.4 Hybrid Solar Cells

In consideration of the high efficiency and good stability of inorganic solar cells and the relative low cost of the organic solar cells, the idea of fabricating more cost-effective hybrid solar cells by combining inorganic and organic materials was introduced since 2002 [37]. Semiconductor nanocrystals of lead sulfide (PbS) [84], lead selenide (PbSe)

[85], titanium diode (TiO₂) [86], and zinc oxide (ZnO) [87] have been used to fabricate hybrid solar devices in combination with polymers. In order to address the inefficient carrier transport problem in the inorganic nanocrystals due to hopping mechanism, the inorganic nanowires were utilized to improve the carrier transportation and collection. The nanowires that have been used include Si, CdS, CdSe [37, 88], GaAs [89], and ZnO [90] nanowires. Among them, SiNWs have attracted great attention as an environmentally friendly and abundant material. Moreover, the light-trapping characteristics of the SiNWs are excellent [38-40, 91-94], and the nanoscale carrier extraction inside the SiNWs [95] allows the realization of solar cells fabricated on low-cost low-quality silicon.

So far, hybrid cells based on Si/poly (3-hexylthiophene) (P3HT) [96] or Si/2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD) [47, 97] heterojunction have obtained ~10% PCE. Recently, Poly(3,4-ethylene-dioxythiophene):polystyrenesulfonate (PEDOT:PSS), which is a transparent P-type conductive polymer, has been used to fabricate hybrid solar cells [98] with Si, and a record efficiency of 13.01% has been reported [42]. Our group has also reported the highest PCE for planar, SiNWs based and synergistic surface textured Si/PEDOT:PSS hybrid cells, of 10.6% [43], 9.9% [99] and 9.9% [100], respectively.

2.5 Si Nanostructures Based Solar Cells

As we reduce the Si film thickness or use organic material to lower the material and fabrication cost of the solar cells, the light absorption and carrier collection are

compromised substantially due to lack of light absorbing material and inefficient carrier transport mechanism. In order to reduce the cost and concurrently achieve high efficiency solar cells, surface texturing especially with the use of nanostructures, have been widely exploited to address the light trapping and carrier extraction issues. Nanostructures including nanowires [101], nanocones [102-104], nanoholes [105] and nanodome [106] have demonstrated excellent capabilities in light trapping as well as carrier separation and collection [91]. And among them, Si nanowires (SiNWs) are the mostly well studied [101, 107, 108].

SiNWs can be fabricated by both “bottom up” or “top down” methods [109], and they exhibit quite different electrical properties. The “bottom up” SiNWs are commonly fabricated by using chemical vapor deposition and require additional doping process to control the conductivity [110]. Whereas the fabrication of “top down” SiNWs using typically Si substrates involves various patterning and etching techniques such as lithography, nanoimprinting, deep reactive ion etching and wet chemical solution etching [101]. The top-down SiNWs inherit the electrical property from the mother bulk material [109]. It is found that the surface properties of the SiNWs have large impact on their electrical property due to the large surface area. Therefore there is a necessity of surface passivation to improve the electrical properties of the SiNWs [111].

To lower the fabrication cost of the SiNWs, the electroless chemical etching method has been proposed and widely used to fabricate “top down” SiNWs, which have demonstrated excellent antireflection property over the entire solar spectrum [39]. The SiNWs fabricated on Si thin film on glass substrate by Sivakov et al demonstrated great

light absorption enhancement compared to the bulk Si thin film of the same thickness, with an increase of over 90% at 500 nm [92]. The reflectance was reduced to below 10% in the wavelength range from 300 to 800 nm. The SiNWs were found to have increased the optical path length of the incident light by 73 times under AM 1.5 illumination owing to the photonic crystal effects [108].

Si nanocones (SiNCs) with controllable dimensions have also been developed for light absorption and were found to reveal even higher light trapping capability than the SiNWs [112]. The SiNCs were found to increase the light absorption by 90% which is attributed to their more gradual effective refractive index change as compared to the SiNWs [113]. To lower the cost of fabrication of the Si nanostructures, patterning techniques using assembled monolayer of nanospheres such as SiO₂ and polystyrene (PS) nanospheres as mask have been proposed to bypass the expensive lithography approach [103, 112, 114]. Nanostructures with controllable dimensions could then be achieved by the following RIE etching or wet chemical etching using catalyst.

2.5.1 Si Nanostructured Inorganic Solar Cells

The incorporation of Si nanostructures into conventional inorganic solar cells substantially boost the power efficiency and allow the use of absorbing material of lower quality. In addition to their excellent light trapping capability, the cell in radial junction design has shorter path for carrier transport and thus has higher defect tolerance [101, 115]. Peng et al. have fabricated solar cells by incorporating metal-catalyzed electroless etching (MCEE) SiNWs structure to the conventional planar Si solar cell [39]. Fig. 2.10 shows the fabrication process of this cell, where the etched SiNWs served as anti-

reflection coating to enhance the light absorption and were doped by thermal phosphorus diffusion to form the p-n junction. Bulk Si solar cells have achieved power efficiency of 9.31% and 11.37% respectively for the vertically aligned and slanted SiNWs [116].

Figure 2. 10 : Fabrication of SiNWs solar cell with p-n junction formed via phosphorus dopant diffusion [39].

The fabrication of SiNWs by using the MCEE method has also been transferred onto deposited thin-film Si materials. A p+-n-n+ axial junction SiNWs solar cell of 0.64 mm² has been reported by Sivakov et al with an efficiency of 4.4% [92]. As shown in Fig. 2.11, mc-Si layer with different doping were formed on the glass substrate using electron beam evaporation and laser crystallization and were then etched by the MCEE method to form the SiNWs.

Figure 2. 11 : Fabrication process of the mc-Si axial p-n junction SiNWs solar cell [92].

S. Wong et al reported SiNWs axial junction solar cells with back surface field (BSF) and well-controlled SiNWs length and periodicity, which achieved a PCE of 9% [115]. The device surface was textured with rationally designed periodic Si nanopillars fabricated by photolithography and DRIE technique, which is unfortunately still not cost-effective. The fabrication process and device structure are shown in Fig. 2.12.

Figure 2. 12 : (a-e) Schematic of fabrication process of Si nanopillar array solar cell. (f) Cross-sectional image of the cell [115].

J. Zhu et al have demonstrated hydrogenated amorphous silicon (a-Si:H) nanodome solar cells with periodic nanostructures in both the active absorber and top contact layers [106]. Fig. 2.13 shows the schematic structure of the nanodome solar cells. Firstly, nanocone glass was fabricated by RIE etch using Langmuir-Blodgett assembly of close packed monodispersed SiO_2 nanoparticles as mask. The solar cell layers were then deposited on top of the nanocone substrate leading to the formation of nanodome top surface. With only an a-Si:H layer of 280 nm thick, the light absorption in the wavelengths range 400-800 nm was enhanced from 65% to 94% compared to the planar device. An efficiency of 5.9% is achieved with a very large J_{sc} of 17.5 mA/cm^2 .

Figure 2. 13 : Nanodome a-Si:H solar cell structure. SEM images of (a) nanocone quartz substrate and (b) a-Si:H nanodome solar cells after deposition of multilayers of materials on nanocones. (c) Schematic of cross-sectional view of the nanodome solar cell structure [106].

2.5.2 Si Nanostructured Hybrid Solar Cell

SiNWs have been used to fabricate SiNWs/organic hybrid solar cells by combining with various organic materials, such as poly (3-octylthiophene) (PO3T) [117], poly (3-hexylthiophene) (P3HT) blended with [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) [118], 2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD) [97], and poly (3,4-ethylenedioxy-thiophene): poly (styrenesulfonate) (PEDOT:PSS) [119]. The use of SiNWs in these cells has substantially enhanced light trapping and increased optical absorption in the solar cells. Huang et al. have demonstrated a 1.93% efficiency hybrid solar cell fabricated by embedding SiNWs arrays into P3HT/PCBM blends [118]. The device structure is shown in Fig. 2.14. In addition to the enhancement in light absorption in the near-infrared region, the incorporation of SiNWs has created new SiNWs/P3HT heterojunction for exciton dissociation and efficient carrier transport, and improved the efficiency.

Figure 2. 14 : Schematic diagram of SiNW and P3HT:PCBM hybrid solar cells [118].

He et al have successfully achieved a 10.3% efficiency for hybrid solar cell based on bulk SiNWs and a small molecule organic semiconductor Spiro-OMeTAD [47]. Fig. 2.15 shows the device structure. The SiNWs were fabricated on bulk N-type Si wafer using

MCEE method with HF-AgNO_3 solution. The Spiro-OMeTAD material was spin coated and filtrated into the SiNWs to form core-sheath heterojunction.

Figure 2. 15 : Schematic structure of SiNW and Spiro-OMeTAD hybrid solar cell [47].

In addition, He et al. have successfully fabricated MCEE SiNWs/PEDOT:PSS hybrid solar cell with an high efficiency of 9% by using a simple spin coating technique at room temperature [98]. It should be noted that, these SiNWs and SiNWs/PEDOT:PSS hybrid solar cell were fabricated using low cost and low temperature solution based fabrication process. The efficiency of Si/PEDOT:PSS hybrid cell was further increased to 9.9% by incorporating a synergistic surface texturing of MCEE SiNWs on the pyramids etched by KOH solution [100]. A high power conversion efficiency of 9.9% was achieved. The device structures for the SiNWs/pyramids/PEDOT:PSS cells is shown in Fig. 2.16.

Figure 2. 16 : Schematic structure of SiNWs/pyramids/PEDOT:PSS hybrid solar cell [100].

P. Yu et al. have successfully fabricated hybrid SiNWs/PEDOT:PSS cells with introduction of an intermediate 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) layer, and reported a record efficiency of 13.01% [42]. The device structure is shown in Fig. 2.17. The SiNWs were fabricated on N-type Si (100) substrate using MCEE etching method. The insertion of the TAPC layer improved the surface morphology of PEDOT:PSS coverage on top of SiNWs and suppressed the interface recombination, resulting enhancement in the V_{oc} and FF .

Figure 2. 17 : Device schematic of hybrid cell based on SiNWs and PEDOT:PSS with an intermediate TAPC layer. [42].

Jeong et al. have fabricated a hybrid solar cell composed of Si nanocones and PEDOT:PSS material and achieved a power conversion efficiency of 11.1% as shown in Fig. 2.18 [103]. The Si nanocones were fabricated by nanosphere lithography using Langmuir-Blodgett assembled SiO_2 nanoparticles as mask, followed by chlorine (Cl_2) and hydrogen bromide (HBr) plasma etch. The incorporation of nanocones improved the light absorption and resulted in a J_{sc} of 35.6 mA/cm^2 , which is only 17% less than that achieved for monocrystalline Si cell [103, 120].

Figure 2. 18 : Schematic illustration of the fabrication of Si nanocone hybrid solar cell [103].

2.6 Simulation of Optical Characteristics of Nanostructures

In addition to experimental works, there have been extensive simulation studies done to investigate the optical properties of Si nanostructures [91, 94, 107, 121, 122] for solar cell applications. These studies aimed to optimize the dimensional parameters of the nanostructures to give rise to maximum light harvesting. The simulations of optical properties of the nanostructures have been performed using various numerical methods including the finite element method (FEM) [123], finite-difference frequency-domain (FDFD) [124], finite difference time domain (FDTD) [125] and transfer matrix method (TMM) [126] to investigate the interaction of electromagnetic wave of light with the simulated structures by solving the full wave vector Maxwell equations.

Hu and Chen carried out numerical study of the light absorption in periodic vertically aligned SiNW arrays with diameters between 50 to 80 nm, as a function of the SiNWs length, diameter and filling ratio by using the TMM method [91]. The SiNW arrays revealed lower reflectance compared to planar thin film when the filling ratio is moderate.

Li et al. have further investigated in detail the effects of structural dimensions, including the array periodicity, diameter, and diameter to periodicity ratio, on light absorption of the SiNW arrays by using the FEM method [94, 107, 127]. It was found that changes in these structural parameters have large impact on the light absorption behavior of the simulated structures. The light absorption of photons at a given energy is largely enhanced owing to the strong scattering when the structural dimension is comparable to its respective wavelength. In addition, Li et al. have further studied the light absorption behavior in the low-aspect ratio semi-sphere structure [128], nanopore structure [129] and the nanocone arrays [130] on thin Si film. The optical studies of Si nanohole structures with various designs have also been carried out to analyze the effects of the structural parameters on the light trapping by L. Hong et al [105, 131, 132].

In summary, during the past few years extensive studies have been done on Si/organic hybrid solar cells. Several groups have reported various types of efficient Si/organic hybrid cells incorporated with different organic materials and Si nanostructures. Si nanostructured hybrid solar cells are expected to achieve improvement in efficiency owing to the excellent light trapping and carrier collection capabilities of the Si nanostructures. In particular, the SiNWs/PEDOT:PSS hybrid cells have shown great potential to achieve high efficiency and cost effective solar cells, attributed to the low cost and low temperature solution based fabrication process for the SiNWs and the hybrid cells. Concurrently with the experimental demonstration of nanostructure based solar cells, theoretical simulation studies have also been widely pursued to investigate and optimize the nanostructures to give rise to optimal light harvesting and guide the design of the solar cells.

Chapter 3 Planar Si/PEDOT:PSS Hybrid Solar Cells

In this chapter, high efficiency planar hybrid solar cells are fabricated and characterized based on N-type Si and a p-type polymer poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate) (PEDOT:PSS). Firstly, the motivation behind fabricating and studying the performance of planar hybrid Si/PEDOT:PSS cells is introduced. Following that, the fabrication process and characterization tools will be presented. Finally, the effect of the thickness of PEDOT:PSS as well as Si layer on the performance of the planar hybrid cells will be investigated experimentally. In addition, optical simulations are carried out to better understand the light absorption characteristics of the planar hybrid cells as a function of the PEDOT:PSS and Si absorber layer thickness.

3.1 Introduction and Motivation

As demand for energy grows rapidly, there has been significant interest in solar energy as an alternative to conventional fossil fuels. Among the various types of emerging solar cells, hybrid solar cells fabricated using silicon and organic materials have attracted much attention recently owing to their simple solution based low cost fabrication process, as compared to the more costly conventional Si solar cells [47, 133, 134]. To date, hybrid solar cells have been demonstrated on Si and organic materials such as poly (3-hexylthiophene) (P3HT) [96], Si/2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD) [47, 97] or poly (3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) [42, 47, 135, 136], and power efficiencies of over 10% have been reported. Si nanostructures such as Si nanowires [91, 108, 137, 138], Si nanocones [17, 139], Si nanoholes [140] are commonly incorporated into such cells owing to their excellent capabilities in light trapping, and carrier

separation and collection, which give rise to high photocurrent and high power conversion efficiency (PCE). More importantly, the use of nanostructures allows thinner Si to be employed so that the cost can be further reduced. Despite the advantages brought about by the use of nanostructures, there are a number of drawbacks. Additional steps are involved in the fabrication process, which will increase the fabrication complexity and cost. Besides, the Si nanostructures generally lead to higher carriers recombination, due to their surface defects and contamination introduced by the nanostructures fabrication process [100, 140, 141], and additional steps are required for defects removal and surface passivation. On the other hand, simple planar Si/PEDOT:PSS hybrid solar cells without the use of nanostructures have been fabricated with high efficiency, and we have reported maximum PCE of 9.4 % and 10.6 % respectively for planar Si/PEDOT:PSS hybrid cells based on Si (100) and Si (111) bulk wafers [44]. This demonstrates that high efficiency hybrid solar cells can be readily realized using just a simple, solution based and low temperature process of spin coating PEDOT:PSS on planar Si, followed by the formation of electrodes. To lower the material cost, we have also studied Si/PEDOT:PSS hybrid cells based on thin film planar Si, and achieved an average PCE of 5.3% using a 2.2 μm thick Si film [44]. Recently, a high PCE of 10.3% has been reported for planar multicrystalline Si/PEDOT:PSS solar cell, using a Si absorber thickness of only 5 μm passivated with Al_2O_3 [142]. However, so far the effects of structural parameters on the performance of the planar hybrid cells have not been investigated systematically.

In this chapter, we present simple low cost planar Si/PEDOT:PSS hybrid cells and study the effects of the thickness of PEDOT:PSS and Si layer on their performance. Planar

Si/PEDOT:PSS hybrid cells are fabricated based on N-type Si(100) wafer with different thicknesses of PEDOT:PSS layer using a simple spin coating technique. An optimum PEDOT:PSS thickness of ~78 nm has been found to give rise to the highest J_{sc} and EQE of 27.0 mA/cm² and 63.6%, respectively. Planar Si/PEDOT:PSS hybrid cells using thin film Si with different thicknesses of 2.2, 5.5, 10.6 and 15.5 μm are also fabricated, and their photovoltaic performance are investigated as a function of the Si film thickness. High average PCE of 8.2% and maximum PCE of 8.7% have been achieved for the cell with Si thickness of 15.5 μm . It exhibits a short circuit current density (J_{sc}) of 20.4 mA/cm², which is about 78% of that measured for a reference bulk Si cell fabricated using the same process. To better understand the light harvesting characteristics of the planar cells, we have performed optical simulations for the planar hybrid cell structure and studied the effects of both the PEDOT:PSS thickness and the Si thickness on the cell performance.

3.2 Fabrication and Characterization of Planar Si/PEDOT:PSS Hybrid Solar Cell

3.2.1 Fabrication of Planar Si/PEDOT:PSS Hybrid Cells

Fig. 3.1 shows the entire fabrication process of the planar Si/PEDOT:PSS hybrid solar cell. The planar Si samples were first cleaned in acetone, ethanol and deionized (DI) water for 10 min each and dipped into 5% hydrofluoric (HF) acid for 1 min to remove the native Si oxide. The cleaned planar Si samples were exposed to air for about 2 hr to allow the growth of a thin layer of native Si oxide which promotes a favorable band alignment

and an internal electric field at the junction interface for efficient charge separation. Ti/Pd/Ag metal films were deposited on backside of the Si wafer by electron-beam evaporation as the back electrode. A layer of conductive PEDOT:PSS mixed with 5-wt% dimethyl sulfoxide (DMSO) and 1-wt% Triton X-100 was then spin coated on top of the Si to form the heterojunction, followed by a 10 min annealing at 105°C in atmosphere. Finally, the cells were completed by depositing Ag grids on the PEDOT:PSS layer as the top electrode. The area of each cell is 0.95 cm² while the fraction of the Ag grid shading is 12%.

Figure 3. 1 : Fabrication process of planar Si/PEDOT:PSS hybrid solar cells.

3.2.2 Major Characterization tools

Several characterization tools were used in this work to investigate the properties of the solar cells, including the material properties and cell performance. LEO 1550 Gemini field emission scanning electron microscopy (FESEM) was used to characterize the structural morphology of the hybrid cells. Tenor P-10 surface profiler was used to measure the thickness of thin films such as the PEDOT:PSS material coated and the

deposited metal electrodes. The reflection spectra of different samples were measured using a PerkinElmer Lambda 950 UV/Vis/NIR spectrophotometer system. The current density-voltage (J - V) characteristics of the cells were examined using a Keithley 2400 electrometer. A solar simulator San-EI electric with an air mass (AM) 1.5 filter at a power density of 100 mW/cm^2 was used to illuminate the devices to determine the power conversion efficiency (PCE). The system was calibrated using a standard Si reference cell. A stainless steel mask with an opening area of 0.95 cm^2 , as shown in Fig.3.2 (a), was used in the measurement to shield the outskirt region to ensure an effective cell area of 0.95 cm^2 . A photograph of the device and a schematic of the device architecture is shown in Fig. 3.2 (b), where grid shading is 12%. A characterization system consisting of a 300 W Newport Xenon lamp, a chopper controller (Stanford Research Systems, Model SR540), a monochromator (Model Oriel Cornerstone 130) and a lock-in amplifier (Stanford Research Systems, Model SR830) was used to examine the external quantum efficiency (EQE) spectra of the cells. The incident light intensity of the system was calibrated using a standard Si photodiode, which has been calibrated by National Institute of Standards and Technology (NIST).

Figure 3. 2 : (a) Photo of the stainless mask used in I - V measurement, (b) photo of the real device and a schematic of the device structure.

3.2.3 Energy Band Diagram and Morphology of Si/PEDOT:PSS hybrid cell

Figure 3. 3 : Energy band diagram of Si/PEDOT:PSS hybrid solar cells.

The energy band diagram of the Si/PEDOT:PSS hybrid cell is shown in Fig. 3.3 with the illustration of carrier transport. In this hybrid solar cell, light photons are primarily absorbed in the Si material to generate electrons and holes, which are then separated at the Si/PEDOT:PSS heterojunction and transported to Si/Ti/Pd/Ag and PEDOT:PSS/Ag terminals respectively. The PEDOT:PSS (PH1000) has a highest occupied molecular orbital (HOMO) energy of about 5.0 eV, which can form ohmic contact with metal and is well matched to Si valence band of 5.17 eV for efficient hole collection.

Figure 3. 4 : Cross-sectional view SEM images of the planar Si coated with PEDOT:PSS layer with thickness of ~56 nm.

The morphology of a planar Si film coated with a layer of PEDOT:PSS (~56nm) is shown in Fig. 3.4. It is seen that the PEDOT:PSS forms a continuous uniform layer on top of the Si.

3.3 Optical Simulation Methodology

In our study, the simulation of light absorption characteristics of the Si/PEDOT:PSS hybrid solar cells are carried out using the High Frequency Structure Simulator (HFSS) software [143]. It performs simulations based on the finite element method (FEM), which is a numerical method by converting the partial differential equations into a set of linear algebraic equations to provide approximate solutions to boundary-value problems [123].

For our three dimensional structures to be simulated, FEM first divides them into many smaller tetrahedral finite elements, the entire collection of which is called a mesh [123]. A solution of interrelated EM fields is found to satisfy the Maxwell's equations across inter-element boundaries, and thus the whole spatial distribution of electric fields can be obtained.

Figure 3. 5 : Finite element mesh with tetrahedral elements for three dimensional structures [123].

Fig. 3.6 illustrates the steps involved in the HFSS numerical calculation. Firstly, HFSS generates initial tetrahedral mesh on the structure and calculate the corresponding electromagnetic field. The HFSS will then identify the region with a high degree of error and generate new mesh with smaller tetrahedral. HFSS will calculate new solution based on the updated mesh and repeat this process until the solution satisfies the convergence criteria.

Figure 3. 6 : Flow chart of HFSS during the adaptive analysis [137].

3.4 Effects of PEDOT:PSS Thickness on Planar Si/PEDOT:PSS Hybrid Cell Performance

In this section, planar Si/PEDOT:PSS hybrid cells are fabricated based on N-type Si(100) bulk wafer with different thicknesses of PEDOT:PSS layer to study their effects on the cell performance. An optimum PEDOT:PSS thickness of ~78 nm has been found to give

rise to the highest J_{sc} and EQE of 27.0 mA/cm² and 63.6%, respectively. We have also performed optical simulation for the thin film planar hybrid cell structure based on 10 μ m Si film, and the light absorption characteristics are studied in terms of the PEDOT:PSS film thickness. It is found that a high photocurrent density of ~ 24 mA/cm² is achievable for the thin film hybrid cell using PEDOT:PSS with a thickness of 80~90 nm.

3.4.1 Planar Si/PEDOT:PSS Hybrid Cell with Different Thicknesses of PEDOT:PSS Layer

In this study, 575 μ m thick single crystal silicon wafers with a phosphorous doping concentration of $\sim 5 \times 10^{15}$ cm⁻³ were used as the absorber layer to form heterojunction hybrid solar cell with PEDOT:PSS (Clevios PH500). The fabrication process and device structure have been shown in Fig. 3.1. The spin-coating speed was varied to obtain PEDOT:PSS layers with different thicknesses.

Figure 3. 7 : Current- voltage (J - V) characteristics the planar thin -film Si/PEDOT:PSS cells with different PEDOT:PSS T of 64, 78, 98, 117 and 135nm.

Table 3. 1 : Comparison of the photovoltaic data of planar Si/PEDOT:PSS hybrid cells with different PEDOT:PSS thickness.

PEDOT:PSS Thickness (nm)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
64	26.1	0.61	62.2	9.9
78	27.0	0.61	58.2	9.6
98	26.4	0.61	57.2	9.2
117	24.8	0.60	53.8	8.0
135	24.4	0.60	55.1	8.1

The current density-voltage (J - V) characteristics of the planar Si/PEDOT:PSS cells under AM 1.5G irradiation (100 mW/cm²) from a solar simulator (San-EI electric) are shown in Fig. 3.7. Table 3.1 summarizes the average photovoltaic data of the planar Si/PEDOT:PSS hybrid cells with different PEDOT:PSS thicknesses from 64 to 135 nm. Three samples were fabricated and characterized for each thickness of the PEDOT:PSS layer. It is seen that the V_{oc} that ranges from 0.60 ~ 0.61 V is comparable among the planar Si/PEDOT:PSS hybrid cells with different PEDOT:PSS thicknesses, and is comparable with previous reported results [44, 47]. This is expected as all the cells have the same heterojunction of the same interface properties and quality. There is a decrease in the fill factor (FF) when the thickness of PEDOT:PSS layer is increased. This could be attributed to the poor current collection efficiency associated with the increased series resistance for the thicker PEDOT:PSS layer. The series resistances (R_s) of the planar cells with different T are extracted from the the J - V curves and summarized in Table 3.2. The R_s is 5.16 Ωcm^2 for the cell with $T = 64$ nm. As T increases to 78, 98, 117, and 135 nm, the R_s is increased monotonically to 6.57, 7.48, 9.76, and 10.93 Ωcm^2 respectively. Overall the highest power conversion efficiency (PCE) occurs for the cells with the thinnest PEDOT:PSS of 64 nm, attributed to its largest FF .

Table 3. 2 : Series Resistance (R_s) of the planar Si/PEDOT:PSS hybrid cells with different PEDOT:PSS thicknesses.

	Series Resistance ($\Omega\cdot\text{cm}^2$)				
PEDOT:PSS thickness	64 nm	78 nm	98 nm	117 nm	135 nm
R_s (nm)	5.16	6.57	7.48	9.76	10.93

Fig. 3.8 shows the variation in the short circuit current density (J_{sc}) with respect to the PEDOT:PSS thickness. The highest J_{sc} of 27.0 mA/cm² occurs when the PEDOT:PSS thickness is ~78 nm. It is found that increasing or decreasing the polymer thickness reduces the J_{sc} . For the thickest PEDOT:PSS of 135 nm, the J_{sc} drops to 24.4 mA/cm², which is 9.6% lower than that of the cells with ~78 nm PEDOT:PSS.

Figure 3. 8 : The average short circuit current density (J_{sc}) of the planar Si/PEDOT:PSS hybrid cells with different PEDOT:PSS thicknesses.

Fig. 3.9 shows the external quantum efficiency (EQE) spectra of the planar Si/PEDOT:PSS hybrid cells. The EQE is nearly the same for all the cells in the infrared range with wavelength greater than 800 nm. Whereas for shorter wavelength, the EQE is

enhanced for the cells with a PEDOT:PSS thickness of ~78 nm, with a peak value of 63.6%. The light absorption enhancement is strongest in the visible range (400 nm~700 nm), owing to the low reflectance as shown in Fig. 3.10, which thus accounts for the highest J_{sc} observed at the thickness of 78 nm.

Figure 3. 9 : *EQE* spectra of the planar Si/PEDOT:PSS hybrid solar cells with different PEDOT:PSS thicknesses.

Fig. 3.10 shows the reflectance of the planar Si/PEDOT:PSS hybrid cells with different PEDOT:PSS thicknesses. Since the silicon wafer of 575 μm is sufficiently thick to totally absorb incident light, the light transmission through the wafer can be neglected. Therefore, the *EQE* is directly determined by the reflectance of the cells [98, 100]. It is noted that the cells with a PEDOT:PSS thickness of ~78 nm exhibit the lowest reflectance in the wavelength range where the peak of the solar spectrum exists and hence account for the highest *EQE* observed [98, 100]. As the polymer thickness increases, the reflectance peak shifts from ~350 nm to ~450 nm for the cells with PEDOT:PSS

thickness of 98nm, 117nm and 135nm. This results in an increase in the reflectance over the visible range and accounts for the decrease in the *EQE* shown in Fig. 3.9.

Figure 3. 10 : Reflectance of planar Si/PEDOT:PSS hybrid cells with different PEDOT:PSS thicknesses.

3.4.2 Simulation of Optical Characteristics of Planar Si/PEDOT:PSS Cell with Different PEDOT:PSS thicknesses

In the previous section, we have fabricated and studied the performance of planar hybrid cell based on thick Si wafer. To fully understand the effect of the PEDOT:PSS thickness on the light harvesting behavior of the cell, in this section, we perform optical simulation to investigate light absorption in the hybrid cell as a function of the PEDOT:PSS thickness. The simulation is based on a thin film planar hybrid cell structure with a fixed Si film thickness of 10 μm . Note that a simulation based on bulk wafer is not possible due to the enormous computing resources needed for a very thick Si absorber layer. Moreover, for practical realization of low cost Si/PEDOT:PSS hybrid cells, they have to

be fabricated on thin films Si, and hence it is meaningful to simulate such cells. It is found that a high photocurrent density of $\sim 24 \text{ mA/cm}^2$ is achievable for a hybrid cell using layer of PEDOT:PSS with thickness of 80~90 nm.

3.4.2.1 Simulation Structure

Figure 3. 11 : Schematic illustration of the planar Si/PEDOT:PSS hybrid structure.

Fig. 3.11 shows the schematic illustration of the planar Si/PEDOT:PSS hybrid structure simulated in this study. The planar hybrid structure consists of a planar Si thin film and a layer of PEDOT:PSS on top of it. The thickness of the Si film is fixed at $10 \mu\text{m}$, whereas the thickness of the PEDOT:PSS layer (T) is varied from 10 nm to 180 nm to investigate the effect of the PEDOT:PSS thickness on the light absorption behavior in the Si/PEDOT:PSS hybrid solar cells. The optical simulation was performed using a full wave finite element method (FEM) [144] and the optical constants of Si and PEDOT:PSS were obtained from the literature [145, 146]. The incident light with wavelength range from 300 to 1100 nm is incident normal onto the PEDOT:PSS top layer of the hybrid structure. Periodical boundary conditions are applied to the unit cell and the optical characteristics are extracted from the simulated spatial distribution of energy flux in the hybrid structure.

3.4.2.2 Results and Discussion of Effects of PEDOT:PSS Thickness on Light Absorption
in Planar Si/PEDOT:PSS Cell

Figure 3. 12 : Simulated light absorption in the (a) Si layer and (b) PEDOT:PSS layer. (c) Reflectance and (d) transmittance spectra of the planar hybrid structure consisting of 75 nm PEDOT:PSS top layer and Si film of different thicknesses.

Fig. 3.12 (a) and (b) depict the light absorption in the Si and PEDOT:PSS materials respectively, whereas Fig. 3.12 (c) and (d) show the overall reflectance and transmittance spectra of the planar hybrid structures respectively, with $T = 25, 50, 75, 100, 125,$ and 150 nm. At the thinnest T of 25 nm, the cell exhibits a low light absorption over the broad

wavelength range due to its high light reflection. As T is increased to 50 nm, there is a significant increase in light absorption for light photons of wavelength range $300 \text{ nm} < \lambda < 800 \text{ nm}$, with a light absorption peak of $\sim 83.0\%$ at $\sim 420 \text{ nm}$, attributed to the strong reduction in the light reflection in this region. As T is increased to 75 and 100 nm, the light absorption peak shifts to $\sim 510 \text{ nm}$ and $\sim 610 \text{ nm}$, with a value of $\sim 91.8\%$ and $\sim 92.7\%$, respectively. When T is further increase to 125 and 150 nm, the light absorption peak further shifts to the longer wavelengths, but there is decrease in light absorption in the broad wavelength range, which is mainly due to the shift of the reflection peak. It is noted that, in the longer wavelength region, although the reflection is further reduced, the light absorption is enhanced in the PEDOT:PSS material instead of Si, as the light absorption coefficient of PEDOT:PSS is relative higher and hence absorb more photons, as can be seen in Fig. 3.12 (b).

To evaluate the sunlight harvesting capability of the hybrid cells, we calculated the ideal short circuit current density (J_{sc}) using the equation [136, 147]:

$$J_{sc} = q \int_{300nm}^{1100nm} \alpha(\lambda) \frac{I_{AM1.5G}(\lambda)}{(hc/\lambda)} d(\lambda) \quad (3.1)$$

where q is the elementary charge, λ is the photon wavelength, $\alpha(\lambda)$ is the simulated light absorption, and $I(\lambda)$ is Air Mass 1.5 direct normal and circumsolar spectrum [148]. It should be noted that in this calculation only light absorption in the Si material is considered. This is because that the carriers generated in PEDOT:PSS layer have very short diffusion length [149] and are not easily extracted as electric current. Fig. 3.13 summarizes J_{sc} as a function of PEDOT:PSS thickness T from 10 to 180 nm.

Figure 3. 13 : Simulated photocurrent density (J_{sc}) of the hybrid cell as a function of the PEDOT:PSS thickness.

It is seen that the planar thin film Si/PEDOT:PSS hybrid structure reveals a J_{sc} of 17.84 mA/cm² at a thickness of 10 nm. As T increases, J_{sc} increases sublinearly and reaches its highest values of ~23.93 mA/cm² at $T = 80$ nm and ~24.05 mA/cm² at $T = 90$ nm, which is increased by ~ 34.8% compared to that of $T = 10$ nm. It is noted that when T is further increased, J_{sc} decreases sublinearly. This is due to the fact that as T is beyond 90 nm, the light absorption of the planar hybrid structure is reduced especially in the visible light region where the sunlight irradiation is high, due to the increase in reflection.

As we compare the simulated result with the experimental result shown in Fig. 3.8 and 3.13, it can be seen that their photocurrent density exhibit similar trend with increasing PEDOT:PSS thickness, where an optimum thickness exists that gives rise to the highest J_{sc} . It suggests that a layer of PEDOT:PSS of thickness of 70 ~ 100 nm is preferred for optimum light harvesting in Si/PEDOT:PSS hybrid solar cell. In addition to the optical

properties, it should also be noted that, in practical device, there is a larger parasitic resistance when a thicker PEDOT:PSS is used, resulting in poorer current collection efficiency and thus lower current density. Therefore, our experimental and simulation results suggest that the optimum PEDOT:PSS thickness to be considered for thin film hybrid cells fabrication will be around 70~80 nm. In conclusion, it is found that by adjusting the thickness of the PEDOT:PSS layer during spin coating process, the photocurrent density can be varied over a very wide range. Therefore, it is important in the fabrication of the hybrid cells to carefully tune and optimize the thickness of PEDOT:PSS spin coated on Si.

3.5 Effects of Si Thickness on Planar Si/PEDOT:PSS Hybrid Cell Performance

In the previous section, we studied the effect of PEDOT:PSS thickness on the performance of the hybrid Si/PEDOT:PSS solar cells. To further lower the cost, the hybrid Si/PEDOT:PSS solar cells should be fabricated on Si thin films grown on low cost substrates to bypass the use of bulk Si wafer [150]. In this section, we study experimentally planar Si/PEDOT:PSS hybrid cells using thin film Si with different thicknesses of $T = 2.2, 5.5, 10.6$ and $15.5 \mu\text{m}$ and investigate their photovoltaic performance as a function of the Si film thickness. In the absence of back reflectance, average power conversion efficiencies (PCE) of 5.0%, 6.2%, 7.7% and 8.2% have been achieved for T of 2.2, 5.5, 10.6 and $15.5 \mu\text{m}$, respectively. It is found that the hybrid cell with $T = 15.5 \mu\text{m}$ is able to generate a large short circuit current density (J_{sc}) of 20.4

mA/cm², which is about 78% of that measured for a reference bulk Si cell fabricated using the same process. Optical simulation is also performed to theoretically investigate the light harvesting characteristics of the hybrid cells. It is found that the J_{sc} increases with T and saturates at about $T = 15 \mu\text{m}$. With a reflector incorporated at the back of the thin film Si to increase the optical path length, a remarkable short circuit current density as high as 27.5 mA/cm² can be achieved. By adopting the recently proposed backPEDOT cell structure to minimize optical loss in PEDOT:PSS, our simulation results show that the J_{sc} can be further improved to 30.3 mA/cm². It is estimated that the simple planar Si/PEDOT:PSS cell using only 15 μm thick of Si thin film, without the incorporation of nanostructures for light trapping, can deliver a PCE of over 13%.

3.5.1 Planar Si/PEDOT:PSS Hybrid Cell with Different Thicknesses of Si Absorber Layer

Figure 3. 14 : Device structure of the planar thin film Si/PEDOT:PSS hybrid solar cells.

Fig. 3.14 shows the architecture of the fabricated planar thin film Si/PEDOT:PSS hybrid solar cell. Single crystalline Si thin films were grown epitaxially on n^{++} Si (100) substrates using dichlorosilane precursor and phosphine (PH_3) dopant gas at 1000°C in a

rapid thermal chemical vapor deposition (RTCVD) reactor. The Si layer grown has a phosphorus doping concentration of $1.5 \times 10^{16} \text{ cm}^{-3}$ while the n^{++} Si (100) substrate has an arsenic doping concentration of $\sim 1 \times 10^{20} \text{ cm}^{-3}$. The doping and thicknesses (T) of the epitaxial layers are confirmed by dynamic secondary ion mass spectrometry (DSIMS) as shown in Fig. 3.15 (a), and the crystallinity is confirmed by x-ray diffraction (XRD) spectrum shown in Fig. 3.15 (b). Note that as the heavily doped Si substrate has very short minority-carrier diffusion length, absorption leads to generation of carriers that recombine readily and do not contribute to photocurrent. Therefore, only the thin Si epilayer is responsible for the generation of photocurrent in the structure. It should also be emphasized that the CVD technique used in this work for the growth of thin film Si is not a practical approach as it is not a low cost and low temperature process. We applied it mainly with a focus to fabricate high quality thin film Si/PEDOT:PSS cells and investigate the performance of the cells as a function of the Si thickness. Ultimately, lower cost methods would have to be explored to realize Si thin films grown at low temperature and on low cost substrates to form the hybrid cells [142, 150].

Figure 3. 15 : (a) DSIMS profile and (b) XRD spectrum of the epitaxial Si thin film.

After cleaning in acetone, ethanol and deionized water, and dipping in 5 % hydrofluoric (HF) acid to remove the native Si oxide, the samples were exposed to air for about 2 hr to allow the growth of a thin layer of native Si oxide. This has been shown to promote a favorable band alignment and an internal electric field at the junction interface for efficient charge separation [43]. A layer of conductive PEDOT:PSS (PH1000) mixed with 5-wt% dimethyl sulfoxide (DMSO) was then spin coated on top of the Si films at 1800 r/min to form the heterojunction, followed by a 10 min annealing at 105°C in atmosphere. The thickness of the PEDOT:PSS layer is ~75 nm, which has been optimized to minimize reflectance of incident light. Finally, the cells were completed by depositing Ag grids and Ti/Pd/Ag film using E-beam evaporation on the PEDOT:PSS layer and backside of the Si substrate respectively to form electrodes. The area of each cell is 0.95 cm² while the Ag grid shading is 12% of the cell area. Planar hybrid cells based on bulk Si were also fabricated using same process for comparison. The bulk Si used is single crystalline N-type Si (100) wafer with phosphorus doping concentration of $\sim 3 \times 10^{15} \text{ cm}^{-3}$ and thickness of 575 μm .

Figure 3. 16 : Current-voltage (J - V) characteristics the planar thin -film Si/PEDOT:PSS cells with different T of 2.2, 5.5, 10.6 and 15.5 μm .

The current density-voltage (J - V) characteristics of the planar Si/PEDOT:PSS cells under AM 1.5G irradiation (100 mW/cm^2) from a solar simulator (San-EI electric) are shown in Fig. 3.16. The photovoltaic parameters of short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and PCE are summarized in Table 3.3. Four cells were fabricated for each thickness of Si films and the cell parameters listed are the average values. It is seen that average PCE of 5.0%, 6.2%, 7.7% and 8.2% and maximum PCE of 5.4%, 6.6%, 8.3% and 8.7% are obtained for cells with $T = 2.2, 5.5, 10.6$, and $15.5 \text{ }\mu\text{m}$, respectively. In comparison, the reference bulk cell reveals average and maximum PCE of 9.8% and 10.4 % respectively, mainly attributed to its higher J_{sc} as a result of a much thicker absorber layer.

Table 3. 3 : Photovoltaic parameters of planar thin film Si/PEDOT:PSS cells with different Si thicknesses.

Sample	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)	Max PCE
2.2 μm Si	12.7	0.61	65.4	5.0	5.4
5.5 μm Si	16.0	0.60	65.1	6.2	6.6
10.6 μm Si	19.2	0.60	66.6	7.7	8.3
15.5 μm Si	20.4	0.60	66.8	8.2	8.7
Bulk Si	26.2	0.59	63.2	9.8	10.4

As the Si thin films have the same optical properties as the thick Si substrates underneath, all the structures with different T exhibit the same reflectance characteristics. Fig. 3.17 plots the reflectance spectra of the cells with and without the PEDOT:PSS layer coated. It is seen that the reflectance is reduced with the PEDOT:PSS layer coated, as PEDOT:PSS layer also serves as an antireflective coating. This results in a very simple structure for

the Si/PEDOT:PSS hybrid solar cells, which is an inherent advantage as compared to conventional thin film Si solar cell where an antireflective coating is needed.

Figure 3. 17 : Reflectance spectra of the planar thin film Si/PEDOT:PSS cells with different T of 2.2, 5.5, 10.6 and 15.5 μm .

As seen from Table 3.3, J_{sc} increases monotonically from 12.7 mA/cm^2 at $T = 2.2 \mu\text{m}$ to 20.4 mA/cm^2 at $T = 15.5 \mu\text{m}$. As there is no change in the reflectance, this increase is a direct consequence of increased absorption as a result of a thicker absorber layer, particularly at longer wavelength light due to its weaker absorption and shallower absorption depth. This is confirmed from the *EQE* spectra of the cells shown in Fig. 3.18, where it can be seen that as T increases, the *EQE* spectra of the cells progressively broaden over the longer wavelength range of $\lambda > 500 \text{ nm}$. It is also noted that the *EQE* of the thickest cell with $T = 15.5 \mu\text{m}$ is similar with that of the reference bulk cell for $\lambda < 700 \text{ nm}$. This suggests that most of the photons in this wavelength range are already fully absorbed within the Si thin film of 15.5 μm . For photons over the longer wavelength range from 700 to 1100 nm, they are mainly absorbed in the heavily doped Si substrate,

and with the carriers mostly recombined due to the short minority carrier diffusion length [44]. As the range of full absorption of $\lambda < 700$ nm covers a substantial portion of the solar spectrum, it is noted that the $J_{sc} = 20.4$ mA/cm² achieved for the thickest cell with $T = 15.5$ μ m has already reached 78% of the 26.2 mA/cm² obtained for the reference bulk cell. For practical cells, a reflector should be incorporated at the back of the thin film Si to increase the optical path length and absorption, and enhance the short circuit current density. This can simply come in the form of the back metallic electrode and does not require additional layers or processes.

Figure 3. 18 : *EQE* spectra of the planar thin film Si/PEDOT:PSS cells with different T of 2.2, 5.5, 10.6 and 15.5 μ m.

From Table 3.3, it is seen that the FF of the thin film cells are higher than that of the reference bulk cell, mainly attributed to the highly doped n^{++} Si substrate below the epitaxial Si film which results in lower series resistance and better ohmic contact with the back electrode.

3.5.2 Simulation of Optical Characteristics of Planar Si/PEDOT:PSS Cell with Different Si Thicknesses

In this section, the effect of the Si absorber thickness on the light absorption characteristics of planar thin film Si/PEDOT:PSS hybrid solar cells will be theoretically investigated. The optical simulation was performed using a full wave finite element method (FEM) [144].

3.5.2.1 Simulation Structure

Figure 3. 19 : Schematic diagram of the simulated planar Si/PEDOT:PSS hybrid structure with a rear metal reflector.

Fig. 3.19 shows the schematic illustration of the planar Si/PEDOT:PSS hybrid structure simulated in this study. The hybrid structure simulated comprises PEDOT:PSS on top of a planar Si thin film and with a metallic electrode at the back. The metallic film serves as the electrode and concurrently a good back reflector to reflect light back into the Si thin film. Such a structure is closer to an actual cell compared to the epitaxial Si layer on Si substrate cells that we have fabricated. The thickness of the PEDOT:PSS layer is assumed to be 75 nm to correspond to that of the experimental cells, while the thickness of the planar Si thin film is varied from $T = 1$ to 25 μm . Light with wavelength ranging from 300 to 1100 nm is incident normal to the PEDOT:PSS top layer of the hybrid

structure. The metallic layer at the back is modeled as a perfect reflector such that light is fully reflected when it is incident on the thin film Si-metallic layer interface. The optical characteristics are extracted from the simulated spatial distribution of energy flux in the hybrid structure simulated. The optical constants of Si and PEDOT:PSS were obtained from the literature [145, 146].

3.5.2.2 Results and Discussion of Effects of Si Thickness on Light Absorption in Planar Si/PEDOT:PSS Cell

Figure 3. 20 : Simulated light absorption in the (a) Si layer and (b) PEDOT:PSS layer. (c) Reflectance spectra of the planar hybrid structure consisting of 75 nm PEDOT:PSS top layer and Si film of different thicknesses.

Fig. 3.20 (a) and (b) depict the light absorption in the Si and PEDOT:PSS materials respectively, whereas Fig. 3.20 (c) shows the overall reflectance spectra of the planar hybrid structures. It is seen from Fig. 3.20 (a) that the light absorption is nearly identical for all the structures over the shorter wavelength of $\lambda < 500$ nm, which is consistent with our experimental results that suggest light over this wavelength range is fully absorbed, even for the thinnest Si layer of ~ 2 μm . As T is increased, there is a broadening of the absorption spectra over the wavelength range $500 \text{ nm} < \lambda < 1100$ nm, attributed to the increased absorption by the thicker absorber layer. It is also noted that as T increases, the oscillations in the simulated light absorption and reflection spectra are weakened due to stronger absorption and hence weaker light interference.

To evaluate the sunlight harvesting capability of the hybrid cells, we calculated the ideal short circuit current density (J_{sc}) [136, 147] considering only the light absorption in the Si material. We also assume a quantum efficiency of 100% such that all absorbed photons will result in the generation and collection of carriers.

Figure 3. 21 : Simulated and experimental short circuit current density (J_{sc}) of the hybrid cell as a function of the Si film thickness.

Fig. 3.21 plots the simulated J_{sc} as a function of Si film thickness T from 1 to 25 μm , as well as the measured J_{sc} of the experimental devices. It is noted from the simulation results that J_{sc} increases with the Si film thickness due to the enhanced absorption arising from the thicker absorber layer. Comparing the simulated and experimental results, it is seen that the J_{sc} exhibit similar increasing trend with Si thickness. The experimental J_{sc} is lower due to carriers recombination, parasitic resistances and top Ag grid shading loss in the actual devices that are not considered in the simulation. Besides, the experimental cells do not have back reflection into the Si thin film, as the structure comprises Si epilayer on Si substrate having the same optical constants. This is in contrast to the simulated structure where there is back reflection which enhances the optical path length and absorption, particularly for longer wavelength light. It is also seen in Fig. 3.21 that there is a larger deviation between the experimental and simulated J_{sc} with increasing Si thickness, which is mainly attributed to the increased series resistance and recombination for the experimental cells.

It is observed from Fig. 3.21 that the simulated J_{sc} nearly saturates at around $T = 10 \mu\text{m}$ with a remarkable value of 26.4 mA/cm^2 . Recently planar multicrystalline Si/PEDOT:PSS solar cell with a Si absorber thickness of $5 \mu\text{m}$ has been reported with a J_{sc} of 20.6 mA/cm^2 when a SiO_x interface layer is added between Si and PEDOT:PSS for passivation. The J_{sc} is further increased to 25.4 mA/cm^2 when Al_2O_3 is introduced in place of SiO_x , attributed to the lower interface recombination and improved adhesion of PEDOT:PSS on the mc-Si thin film [142]. Note that the J_{sc} reported of 25.4 mA/cm^2 is slightly better than the 23.3 mA/cm^2 observed in our simulated results for Si film of the

same thickness of 5 μm . The slightly better result may be attributed to the structure adopted where PEDOT:PSS is placed behind instead of in front of the Si layer [142]. Such a back junction cell structure, or backPEDOT cell, will reduce parasitic optical absorption in PEDOT:PSS that does not contribute to the photocurrent [142]. Indeed, from our simulated absorption in PEDOT:PSS shown in Fig. 3.20 (b), it is found that this absorption can reach more than 10% especially at longer wavelength of light. We have further simulated the backPEDOT cell as shown in Fig. 3.22 where a PEDOT:PSS layer of 75 nm is placed behind a thin film Si layer, and a layer of Si_3N_4 is added on top of the Si film to serve as an anti-reflective coating. The simulated results are also plotted in Fig. 3.21 for comparison. It is seen that the J_{sc} obtained is the highest among the structures considered, attributed to the substantially reduced optical absorption in PEDOT:PSS when it is placed behind the Si film. Indeed the J_{sc} observed for a 5 μm Si film is comparable to that reported experimentally [142].

Figure 3. 22 : Schematic diagram of the simulated planar backPEDOT hybrid structure with a front anti-reflection Si_3N_4 layer of 70 nm and a rear metal reflector.

From Fig. 3.21, it is seen that the increase in J_{sc} with thickness diminishes when T reaches about 10 to 15 μm . This suggests that for practical devices such a thickness is

sufficient to harness most of the incident light. A further increase in the Si absorber thickness is not cost-effective consider that there is only incremental improvement in J_{sc} . Based on the backPEDOT cell structure that delivers a J_{sc} of 30.3 mA/cm² at $T = 15 \mu\text{m}$, and assuming the photovoltaic parameters of such backPEDOT hybrid cells of $V_{oc} = 0.66$ V and $FF = 66\%$ [142], we predict an ideal PCE of 13.2%. This is remarkable given that it is a planar thin film cell that can be fabricated at low temperature using solution based processes. To further improve the J_{sc} and PCE, besides adopting the backPEDOT cell structure, introduction of nanostructures for light trapping can also be considered. However, there is a challenge faced to properly treat and passivate the nanostructure surface to eliminate surface defects and contamination [151]. Otherwise any gain from the enhanced light trapping arising from the use of nanostructures may be negated by the increased carriers recombination.

3.6 Conclusion

In conclusion, we have demonstrated highly efficient planar thin-film Si/PEDOT:PSS hybrid cell using a very simple low temperature solution fabrication technique and studied the effects of the PEDOT:PSS thickness and Si thickness on the cell performance, both experimentally and theoretically. An optimum PEDOT:PSS thickness of ~ 78 nm has been found for the practical device to gives rise to the highest J_{sc} and EQE of 27.0 mA/cm² and 63.6%, respectively. Optical simulation for the thin film planar hybrid cell structure based on 10 μm Si film has also been performed to study the light absorption characteristics in terms of the PEDOT:PSS film thickness. It is found that a high photocurrent density of ~ 24 mA/cm² is achievable for a hybrid cell using layer of

PEDOT:PSS with thickness of 80~90 nm. Taken into account a larger resistance when a thicker PEDOT:PSS is used, our experimental and simulation results suggest that the optimum PEDOT:PSS thickness for thin film hybrid cells is around 70~80 nm.

Planar Si/PEDOT:PSS hybrid solar cells have also been fabricated using epitaxial thin-film Si absorber of various thicknesses. An average PCE of 8.2% was achieved for 15.5 μm thick Si cells. The light absorption behaviors in the planar thin-film Si/PEDOT:PSS hybrid solar cells are also studied theoretically using optical simulation. It is found that with only a layer of 15 μm thick Si film, the planar hybrid cell based on the backPEDOT structure is able to achieve a high photocurrent density of 30.3 mA/cm^2 and a PCE of 13.2%. This promising efficiency obtained demonstrates the feasibility of realizing efficient planar thin film Si/PEDOT:PSS hybrid solar cells fabricated using low temperature and solution based processes.

Chapter 4 Two-step Surface Treatment of SiNWs/PEDOT:PSS

Hybrid Solar Cells

This chapter demonstrates a surface treatment approach to improve the performance of SiNWs/PEDOT:PSS hybrid solar cells. Firstly, the fabrication of SiNWs using the metal-catalyzed electroless etching (MCEE) method will be presented. This is followed by the two step surface treatment of the SiNWs and the fabrication of the hybrid solar cells. The effects of the surface treatment on the performance of the hybrid cells based on SiNWs with and without the surface treatment will then be analyzed and discussed.

4.1 Introduction and Motivation

In Chapter 3, we have demonstrated high efficiency planar Si/PEDOT:PSS hybrid cells with a maximum power conversion efficiency (PCE) of ~10%. By varying the thickness of the PEDOT:PSS layer, the short circuit current density (J_{sc}) has been improved for the planar hybrid cells from 24.4 to ~27.0 mA/cm². To further increase optical absorption and hence J_{sc} , there has been significant interests in incorporating Si nanostructures such as Si nanowires (SiNWs) [99], nanocones [17, 139] and nanoholes [152] into solar cells in the past few years. Such nanostructures offer not only excellent light trapping but also efficient carrier extraction characteristics. Among the Si nanostructures, SiNWs prepared by the MCEE technique have been the most widely studied and commonly applied to fabricate the hybrid solar cells owing to their simple, fast and scalable process as compared to other approaches. Currently, hybrid SiNWs/PEDOT:PSS cells have been reported to have PCEs of over 11%, demonstrating promising potential for practical application [42, 153]. Despite the progress made, there still remain some challenges

facing the SiNWs hybrid solar cells. The SiNWs fabricated using the solution based MCEE technique [43, 100] suffer from severe surface recombination caused by the residual impurity and defective surfaces, and consequently compromise the performance of the SiNWs hybrid solar cells [43]. Many efforts have been directed to address the severe defective surface problem for the nanostructures fabricated using MCEE technique. For example, Chen et.al fabricated the inverted pyramid nanostructures to reduce the recombination rate by shrinking the surface area of the nanostructures, but not sacrificing their light absorption [154]. Other measures include attaching some chemical molecules to the surface to change its surface state as well as the energy band alignment, with an aim to suppress the surface recombination [45, 155]. However, these methods either introduce complicated fabricated processes, or use some unstable organic materials, which hamper their practical use. To date, there still lacks a simple and reliable method to address this problem. For conventional Si solar cells, a SiO_x layer is commonly used for effective surface passivation due to their excellent stability and the simple fabrication process involved [156]. Though this concept can also be applied to SiNWs, however, it is not suitable for the hybrid cell due to the high temperature thermal oxidation process and the very small dimensions of the nanostructures.

In this study, we propose a simple two-step surface treatment method to improve the surface quality of SiNWs in SiNWs/PEDOT:PSS hybrid cells. The SiNWs surface is first treated with ozone gas at low temperature to form a surface layer of sacrificial oxide. The oxidized surface is then partially etched by dilute HF solution to leave behind a thin residual SiO_x layer. A high efficiency of 12.4% with a high V_{oc} of 0.58 V has been achieved due to the suppression of recombination loss arising from the removal of Ag

nanoparticles and passivation of the SiNWs surface. These are 29.8% and 13.7% enhanced respectively as compared to similar SiNWs hybrid cells without the surface treatment. To the best of our knowledge, the V_{oc} of 0.58 V is the highest ever reported for hybrid SiNW/PEDOT:PSS solar cells.

4.2 Fabrication of SiNWs Using MCEE

The SiNWs were fabricated using the MCEE method [40, 137]. The silicon wafer was first cleaned in acetone, ethanol (IPA) and deionized (DI) water and then dipped into aqueous solution consisting of 4.6 M hydrofluoric (HF) acid and 0.02 M silver nitrate (AgNO_3). The SiNWs were then formed due to galvanic displacement reaction. The reaction processes involved the reduction of Ag^+ and oxidation of Si, as illustrated by the chemical equations below:

The schematic representation of the etching process of SiNWs is shown in Fig. 4.1. The Ag^+ ions capture electrons from the valence bands of Si when they are in contact with the silicon surface and thus oxidize the Si atoms into SiO_2 . The SiO_2 formed will then be etched away by HF acid. The reduction and oxidation process is repeated continuously and lead to the formation of vertical SiNWs aligned perpendicular to the wafer surface [157]. After the etching process, concentrated nitric acid was used to dissolve the silver

dendrites on the SiNWs and the SiO₂ formed on the SiNWs surface will be cleaned away by the following dilute HF solution etching.

Figure 4. 1 : Schematic diagram of the formation of SiNWs arrays [158].

4.3 Fabrication of SiNWs/PEDOT:PSS Hybrid Solar Cells with Surface Treatment

Fig. 4.2 shows the schematic illustration of the complete fabrication process for SiNWs/PEDOT:PSS hybrid solar cells with the two-step surface treatment.

Figure 4. 2 : Fabrication process of the SiNWs/PEDOT:PSS hybrid solar cells with surface treatment.

Fabrication of SiNWs on Si: The SiNWs were fabricated from a single crystal (100) Si wafer with a phosphorous doping concentration of $\sim 5 \times 10^{15} \text{ cm}^{-3}$ by using the MCEE method. The wafers were ultrasonically cleaned in acetone, IPA and DI water for 10 min each. The Si substrates were then dipped into an etching solution that contained 4.6 M HF and 0.02 M AgNO_3 at room temperature to fabricate the SiNWs. SiNWs with length of 500 nm were obtained by controlling the etching time at ~ 5 min. The samples were then rinsed in DI water for 5 min and put into concentrated nitric acid to remove the silver particles on the surface of the SiNWs. Subsequently, the etched samples were rinsed in DI water and then immersed into a 5% aqueous HF solution for 90s to remove the oxide.

Two-Step Surface Treatment of SiNWs: The as-prepared SiNWs samples were treated in an ozone environment at 50 °C for 10 min with a flow rate of 80 sccm. After the ozone treatment, the SiNWs were etched again in a 5% HF solution for an etching time of nominally 70 s, to reduce the thickness of the surface oxide and obtain a cleaner surface.

Fabrication of SiNWs/PEDOT:PSS Hybrid Cells: After the preparation of SiNWs, Ti/Pd/Ag metal films with thickness of 50/50/1000 nm were deposited on the backside of the Si wafer by electron-beam evaporation to form the back electrode. A thin conductive PEDOT:PSS layer was formed by spin coating the PEDOT: PSS solution (Clevios PH1000) on top of the SiNWs [100]. The PEDOT:PSS layer was then dried at 105°C for 10 min. Finally, the front silver grids electrode with a thickness of 800 nm was deposited on the PEDOT:PSS layer through a shadow mask by electron-beam evaporation. The fraction of the silver grid shading area is 12%. The hybrid cells have the active area of

0.95 cm². In addition, hybrid cells based on SiNWs without the surface treatment were fabricated under same condition for comparison.

4.4 Effect of Two Step Surface Treatment on the SiNWs Using Ozone

Transmission electron microcopy (TEM) investigation was carried out to investigate the changes to the SiNWs arising from the two-step surface treatment.

Figure 4. 3 : TEM images of the SiNWs (a) before and (b) after the two-step surface treatment. HRTEM images of (c) a silver particle attached on the SiNW surface before the ozone treatment and (d) silver particles/Si interface after the ozone treatment

Fig. 4.3 (a) and (b) show the bright field TEM images of the SiNWs before and after surface treatment respectively. As seen from Fig. 4.3 (a), some residual particles are attached on the SiNWs surface, especially at the tip of the SiNWs. These nanoparticles are identified to be silver based, as deduced from the electron energy loss spectroscopy

(EELS) results, as shown in Fig. 4.4. The residual Ag particles, yielded during the MCEE process, are hard to remove completely even though nitric acid has been used to dissolve them with exposure time of up to 3 or 4 hours. It may be due to the small size of the particles of several nanometers to several tens of nanometers, and that they are imbedded in the SiNWs, or the presence of an impurity layer (e.g. SiO_x or silicide) covers the particles and prevents them from coming in contact with the nitric acid. However, after the ozone treatment and HF etching process, most of the silver nanoparticles are removed from the SiNWs, as shown in Fig. 4.3 (b).

Figure 4. 4 : (a) Scanning transmission electron microscope (STEM) image of a Si nanowire fabricated using the MCEE method. The EELS mapping images based on (b) L edge of Si element and (c) M edge of Ag element. The EELS results clearly indicate that the particle on the top of the nanowires is silver.

High resolution transmission electron microscopy (HRTEM) study further provides insight into how the silver nanoparticles are removed by the two steps surface treatment. Fig. 4.3 (c) presents the HRTEM image of a silver particle on the SiNWs without the surface treatment. Clear parallel fringes of crystal plans indicate the single crystalline

nature of the SiNWs. No apparent amorphous SiO_x layer is found between the silver particles and the SiNWs. The HRTEM image shown in Fig. 4.3 (d) indicates that after the ozone treatment, an amorphous SiO_x layer is formed on the side wall of the SiNWs, as deduced from EELS study which reveals the presence of the elements Si and O. This SiO_x layer can be easily dissolved by the following HF etching process, resulting in the concurrent removal of the silver particles and thus a cleaner surface.

Figure 4. 5 : HRTEM images of the SiNWs (a) before and (b) after the ozone treatment. (c) SiNWs after surface treatment and subjected to HF etching time of 70s. A residual thin SiO_x layer is seen on the SiNWs surface.

Besides the residual particles on the surface of SiNWs, defects on the surface such as dangling bonds produced from the MCEE process will also be removed by the two-step treatment process. This arises because of the oxidation of the defective surface to form sacrificial oxide and the passivation of the Si surface by the residual thin oxide layer. The thickness of the residual SiO_x layer can be adjusted by controlling the etching time in the dilute HF solution. HRTEM was used to identify the SiO_x layer on the SiNWs, and the images of the SiNWs at different steps of the surface treatment process are presented in Fig. 4.5. The pristine SiNWs fabricated by the MCEE technique have a H^+ terminated surface, which can effectively prevent formation of native oxide on the Si surface.

Consequently, the SiNWs without the ozone treatment have only a very thin SiO_x layer on the SiNWs, as seen in Fig. 4.5 (a). After the ozone treatment, a thicker SiO_x layer with a thickness of 4 to 5 nm is formed on the SiNWs as shown in Fig. 4.5 (b). Shown in Fig. 4.5 (c) is the HRTEM image of a SiNWs subjected to an HF etching time of 70 s after the ozone treatment, where a thin residual SiO_x layer of about 1 to 2 nm is seen passivating the SiNW. It is noted that the SiO_x layer is fully removed when the HF etching time is extended to 150s.

Figure 4. 6 : Contact angle of the SiNW substrate (a) before oxygen treatment, (b) after oxygen treatment and (c) after HF etching.

The SiO_x layer on the SiNWs surface will change their wettability and this can be observed using contact angle measurement. Fig. 4.6 shows the contact angle measurement results of the SiNWs substrate before the ozone treatment, after ozone treatment and after the HF etching. The pictures clearly indicate that the oxygen treatment changes the wettability from hydrophobic (contact angle $\theta = 130.1^\circ$) to hydrophilic ($\theta = 67.3^\circ$). After the HF etching of 70 s, the wettability is still hydrophilic ($\theta = 85.8^\circ$) with a slightly increased contact angle, which clearly indicates the presence of the SiO_x layer. The hydrophilic surface is advantageous for the penetration of the

PEDOT:PSS aqueous solution to the gaps between the SiNWs, and results in better coverage of the PEDOT:PSS onto the SiNWs surface [159].

The two-step surface treatment process has been shown to result in cleaner and better passivated SiNWs surface. As will be presented in the following sections, this has led to improved *J-V* characteristics of the treated SiNWs cells.

4.5 Surface Morphology of SiNWs/PEDOT:PSS Hybrid Cells

Fig. 4.7 displays SEM images showing the morphologies of planar Si and SiNWs fabricated using the MCEE technique, and coated with PEDOT:PSS layers on top. Presented in Fig. 4.7 (a) is the SEM picture of a planar Si substrate spin coated with a PEDOT:PSS layer, which forms a thin uniform layer of about 80 nm thick. Fig. 4.7 (b) shows the cross-sectional SEM image of the SiNWs fabricated by the MCEE technique. The SiNWs are dense and have length of about 500 nm, diameters ranging from 20 - 100 nm, and gaps in between the SiNWs of less than 50 nm. Fig. 4.7 (c) and (e) present the top view of the PEDOT:PSS layer spin coated on SiNWs without and with surface treatment, respectively, while the corresponding cross-sectional pictures are shown in Fig. 4.7 (d) and (f). Continuous PEDOT:PSS films are formed on the top of the SiNWs array for both samples, though with rougher surfaces as compared to the planar cell shown in Fig. 4.7 (a). Moreover, due to the long molecular chain and the fast drying process, the PEDOT:PSS layer is not fully penetrated into the gaps between the SiNWs, resulting in exposed SiNWs surface between the bulk Si substrate and the PEDOT:PSS

film [98, 99]. These etched surfaces, without the coverage of the polymer, are most likely to lead to recombination of carriers. The PEDOT:PSS layer deposited on SiNWs subjected to surface treatment displays a smoother surface, as shown in the Fig. 4.7 (e) and (f). This may be due to the ozone treatment that has resulted in a more hydrophilic surface, which facilitates the better coverage of the PEDOT:PSS layer on the surface of the SiNWs [159].

Figure 4. 7 : Cross-sectional SEM images of (a) PEDOT:PSS layer coated on planar Si substrate, (b) SiNWs fabricated using the MCEE technique, (c) top view and (d) cross-section view of PEDOT:PSS layer coated on pristine SiNWs, (e) top view and (f) cross-section view of PEDOT:PSS layer coated on SiNWs with the surface treatment. (The scale bar is 500 nm.)

4.6 Performance of SiNWs/PEDOT:PSS Cells With/Without Surface Treatment

Figure 4. 8 : The AM 1.5 G illuminated J - V characteristics of the planar and SiNWs/PEDOT:PSS hybrid cells with and without surface treatment.

Table 4. 1 : Summary of photovoltaic parameters of the hybrid cells based on planar Si, untreated SiNWs and treated SiNWs.

Device	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
Planar Si	0.59 ± 0.01	26.1 ± 0.3	66.8 ± 2.1	10.3 ± 0.2
Pristine SiNWs	0.51 ± 0.02	30.1 ± 0.8	60.8 ± 3.4	9.4 ± 0.5
SiNWs with treatment	0.58 ± 0.01	30.8 ± 0.7	67.7 ± 1.4	12.2 ± 0.2

Fig. 4.8 shows typical illuminated current density-voltage (J - V) characteristics of the hybrid solar cells with and without the two-step surface treatment process. The curves were recorded under simulated AM 1.5 G irradiation at 100 mW/cm^2 derived from a solar simulator. For comparison, the J - V characteristic of a planar hybrid cell is also shown. The photovoltaic parameters of the hybrid cells, including short-circuit current density

(J_{sc}), V_{oc} , fill factor (FF), and PCE are summarized in Table 4.1, which shows the mean values and the standard deviations obtained by averaging ten hybrid cells per cell structure.

Compared to the planar cell, the pristine SiNWs cell exhibits an improved J_{sc} from 26.1 to 30.1 mA/cm². This is mainly ascribed to light trapping by the SiNWs. However, the V_{oc} of the pristine SiNWs cell is dropped to 0.51 V compared to the 0.59 V of the planar cell. This can be attributed to the higher carrier recombination loss associated with the defective surface and increased surface area of the Si nanostructures [43, 47, 100]. The increased recombination also reduces the FF . As a result, the PCE of the pristine SiNWs cell is even slightly lower than that of the planar cell, despite the improvement in its J_{sc} . In contrast, the SiNWs hybrid cell with surface treatment reveals recovered V_{oc} of 0.58 V, which is almost the same as that of the planar cell of 0.59 V, and is improved by 13.7% relative to that of the pristine SiNWs cell. Likewise, the FF has recovered to 67.7% which is slightly above that of the planar cell of 66.8%. The improved V_{oc} suggests the recombination loss of the SiNWs hybrid cell is suppressed after the surface treatment. With the higher V_{oc} and FF , and slightly improved J_{sc} , the SiNWs cell with surface treatment exhibits a high PCE of 12.2%, which is improved by about 29.8% as compared to that of the pristine SiNWs cell.

The improvement in V_{oc} observed for the hybrid cells with surface treatment is corroborated by the reduced reverse saturation current density (J_0) of the dark J - V curve shown in Fig. 4.9. The J_0 of the SiNWs cell with surface treatment is one order of

magnitude lower than that of the pristine SiNWs cell, and comparable to that of the planar cell. The series resistance (R_s) of different cells are extracted from the dark current by the plot of $dV/d(\ln J)$ versus J [160]. The average R_s extracted from ten hybrid cells per sample are found to be 3.04 ± 0.56 , 1.22 ± 0.40 and $2.08 \pm 0.68 \Omega \text{ cm}^2$ for the planar, pristine and surface treated SiNWs cells respectively. The pristine SiNWs cell has a smaller R_s than the planar cell, that is attributed to the nanoscale geometry of the SiNWs and the increased junction area, which facilitate carrier transportation and collection. The R_s of the surface treated SiNWs cell increases slightly after the surface treatment, which is attributed to the presence of the thin SiO_x layer on the surface of the SiNWs. The diode ideality factors (n) are also extracted through the fitting of the $\ln(J)$ - V curve under forward bias from 0.1 - 0.4 V [161]. The average n deduced for the planar cell, pristine and surface treated SiNWs cells are 1.27 ± 0.09 , 2.02 ± 0.45 and 1.59 ± 0.29 respectively. Compared to the planar cell, both the SiNWs cells possess larger n , which indicates that the incorporation of SiNWs has a negative effect on the Si/PEDOT:PSS junction characteristics. The defective surface of the SiNWs and the incomplete coverage of the PEDOT:PSS layer on the SiNWs may be the two reasons that account for the degradation of the junction. After the surface treatment, the ideality factor of the surface treated cell has improved, which indicates improved junction properties and lower recombination at the SiNWs/PEDOT:PSS interface. This is consistent with the improved V_{oc} , FF and J_{sc} , as presented earlier. In addition, the SiNWs subjected to an HF etching time of 70 s after the ozone treatment have a thin residual SiO_x layer of about 1 to 2 nm passivating their surface. The formation of this thin SiO_x layer can increase the effective electron affinity

at the Si surface, and result in favorable band alignment and an internal electric field that is beneficial for the charge separation [43, 162, 163].

Figure 4. 9 : The semilogarithmic scale dark J - V characteristics of the planar and SiNWs/PEDOT:PSS hybrid cells with and without surface treatment

The external quantum efficiency (EQE) spectra of the hybrid cells were measured and shown in Fig. 4.10. The results are in agreement with the variation of J_{sc} shown in Fig. 4.8. The two SiNWs samples present larger EQE than that of the planar cell over a wide wavelength range from 370 to 1000 nm, which is ascribed to the anti-reflective property of the SiNWs [17]. The EQE of the surface treated cell is slightly higher than that of the pristine SiNWs cell, which is attributed to its improved carrier collection efficiency associated with the reduced surface recombination.

Figure 4. 10 : *EQE* spectra of the planar and SiNWs/PEDOT:PSS hybrid cells with and without surface treatment.

4.7 Comparison of the SiNWs Hybrid Cells with Different Surface Treatments

Besides the removal of residual particles and surface defects, the enhanced photovoltaic performance of the treated cells is also contributed by the residual SiO_x layer on the SiNWs surface. The SiO_x layer has been demonstrated to be an effective surface passivation material and has long been used in standard Si solar cell process [156]. Low temperature UV ozone treatment has been used to introduce surface oxide to the SiNWs hybrid cell for wetting purpose [159], rather than for the formation of sacrificial oxide, and worse performance has been reported due to the increased series resistance. In our experiments, we found that the performance of the hybrid cells is dependent on the thickness of the residual SiO_x layer, which can be adjusted by controlling the etching time in the dilute HF solution. It was previously reported that improvement in performance of planar Si/PEDOT:PSS hybrid cells could be attributed to the presence of

native oxide [43]. In this study, we have also fabricated hybrid cells based on exposing pristine SiNWs to air for a day to form native oxide on their surface.

Figure 4. 11 : J - V characteristics of the hybrid cells based on the SiNWs etched with HF solution for 0 s and 150 s after ozone treatment, as well as SiNWs directly exposed to air for 1 day.

Fig. 4.11 shows the J - V characteristics of the hybrid cells based on the SiNWs etched with HF solution for 0 s and 150 s after ozone treatment, as well as SiNWs directly exposed to air for 1 day. Without the HF etching process (HF etch time is 0 s), the SiNWs hybrid cell treated with ozone exhibits a degraded V_{oc} of 0.39 V and FF of 29.5%. The SiNWs hybrid cell after 150 s HF etching shows PCE of 10.9% with a J_{sc} of 30.5 mA/cm² and V_{oc} of 0.54 V. As presented in section 4.4, a thick SiO_x layer with a thickness of 4 to 5 nm is formed on the SiNWs surface after the ozone treatment. For cells not subjected to the following HF etching process, the thick insulating SiO_x layer formed blocks carrier transportation, and results in dramatically increased R_s and deteriorated cell performance. This result is consistent with a previous report on Si/PEDOT:PSS hybrid cell [159]. As for the SiNWs hybrid cells with two step surface

treatment presented in section 4.6, at HF etching time of 70s, only a thin residual SiO_x layer of about 1 to 2 nm is formed, which can be easily tunneled through by the carriers. Therefore, the cell can benefit from better carrier separation due to the favorable band alignment and internal electric field arising from the SiO_x layer [43, 162, 163], without compromising its carrier transport property. When the HF etching time is extended to 150 s, the SiO_x layer is found to be completely removed, resulting in a lower V_{oc} of only about 0.54 V. This suggests that the residual SiO_x layer after the surface treatment is important in improving the V_{oc} .

For the hybrid cells based on exposing pristine SiNWs to air for a day to form native oxide on their surface, the cells exhibit a V_{oc} of about 0.54 V which is improved compared to the untreated cells, but however it is not as large as that achieved using the two-step treatment method, as Ag nanoparticles are expected to be presence on the surface of the SiNWs. In addition, as the formation of native oxide is not a well-controlled process that depends on many factors such as the temperature, humidity, and the original state of the surface, it is hence not feasible for practical applications in comparison to the two-step treatment method. This uncontrollable surface condition of the SiNWs of untreated cells also explains the larger variation in the performance of the cells observed relative to the treated cells, as evident from the larger standard deviations of the photovoltaic parameters seen in Table 4.1.

4.8 Conclusion

In conclusion, we have demonstrated a two-step surface treatment process to obtain high efficiency SiNWs/PEDOT:PSS hybrid cells. The surface treatment can help remove residual impurities and defects near the SiNWs surface, and effectively passivate the SiNWs to reduce the recombination loss at the surface. The SiNWs/PEDOT:PSS hybrid solar cell with surface treatment shows the highest ever reported V_{oc} of 0.58 V, which is almost the same as that of a planar hybrid cell. As a result, a PCE of 12.4% has been achieved for the hybrid cell, which is up to 14.1% if the silver grid covered area is not considered. The effect of the SiO_x thickness on the performance of the SiNWs hybrid cells with the two step surface treatment has also been investigated. It is found that that the thickness of residual SiO_x layer after the surface treatment has large impact on the improvement of V_{oc} . The improved PCE indicates that this simple approach of surface treatment is promising in boosting the efficiency of SiNWs/PEDOT:PSS hybrid cell and will potentially lead to their practical use.

Chapter 5 Thin Film SiNWs/PEDOT:PSS Hybrid Solar Cells

This chapter studies SiNWs/PEDOT:PSS hybrid solar cells that are based on epitaxial thin Si films, instead of bulk Si wafers. A two-step surface treatment process using oxygen plasma is proposed and applied to treat the SiNWs to remove defects and improve their surface quality, as well as to passivate the surface. The performance of the thin film SiNWs/PEDOT:PSS cells with and without the surface treatment is compared. The effects of the SiNWs length on the performance of the cells are also investigated. The performance of the cells with different thicknesses of Si thin film is also examined.

5.1 Introduction and Motivation

Currently, promising power conversion efficiency (PCE) of over 10% has been demonstrated for hybrid solar cells based on Si nanowires (SiNWs) and poly(3,4-ethylene-dioxythiophene):polystyrenesulfonate (PEDOT:PSS), with the SiNWs prepared by the metal-catalyzed electroless etching (MCEE) technique [42]. Despite the outstanding efficiency achieved, it should be noted that the hybrid cells demonstrated using expensive bulk Si wafer is not a feasible practical option for low cost applications. It is imperative that low cost thin film Si should be explored instead for the fabrication of hybrid solar cells. SiNWs/PEDOT:PSS hybrid solar cells based on a 2.2 μm thin film Si epitaxial layer that achieved a maximum PCE of 5.6% [44] have been previously reported. The PCE was found to be limited by the lower shunt resistance, as well as higher recombination rate associated with the SiNWs prepared by the MCEE technique that generally leads to defective surface contaminated with Ag nanoparticles [45, 164].

To further improve the performance of thin film SiNWs/PEDOT:PSS solar cells, in this work we fabricate such cells using thicker Si epitaxial layers to increase their optical absorption. In chapter 4, we have proposed a two-step surface treatment method to treat the SiNWs using ozone, which revealed a significant improvement in the open circuit voltage (V_{oc}) and overall performance of the hybrid SiNWs/PEDOT:PSS cells. However, the ozone treatment was found to be sensitive to the exposure time of the SiNWs in the ozone environment, leading to variation in the performance of the cell. In this work, we further improve the two step surface treatment process by using oxygen (O_2) plasma instead of ozone, and apply it to the thin film SiNWs/PEDOT:PSS hybrid cells. It is found that similar improvements in the surface quality can also be achieved with the use of oxygen plasma treatment. The performance of the hybrid thin film SiNWs/PEDOT:PSS cells with different Si thin film thickness are investigated in terms of the effects of the surface treatment and the wire length. For the cells with Si thickness of 5.5 and 10.6 μm , average PCEs of 6.20% and 7.27%, and maximum PCEs of 6.53% and 7.83% have been obtained respectively, under the optimized SiNWs length of 0.7 μm . For the case of a thicker Si thin film of 15.5 μm , an average PCE of 7.88% and a maximum PCE of 8.01% have been achieved with an optimized SiNWs length of 0.95 μm with the surface treatment. Given that only Si thin films have been used, the high PCEs obtained demonstrate the great potential of the thin film SiNWs/PEDOT:PSS hybrid structure to realize low cost and high efficiency solar cells.

5.2 Fabrication of Thin Film SiNWs/PEDOT:PSS Hybrid Solar Cells

Figure 5. 1 : Fabrication process of the SiNWs/PEDOT:PSS hybrid solar cells with surface treatment.

Fig. 5.1 illustrates the entire fabrication process for the thin film SiNWs/PEDOT:PSS hybrid solar cells with the two-step surface treatment using O_2 plasma.

Growth of Epitaxial Si Film: The Si films used in this work are the same as those used to fabricate planar thin film Si/PEDOT:PSS hybrid cells and their growth details and characterizations have been presented in chapter 3. Si layers of 5.5, 10.6 and 15.5 μm thickness were obtained by controlling the growth time.

Fabrication of SiNWs on Si Films: The SiNWs were fabricated on the thin film Si layers by using the MCEE method. The Si films were ultrasonically cleaned in acetone, ethanol (IPA) and deionized (DI) for 10 min each, and then dipped into an etching solution that contained 4.6 M hydrofluoric (HF) acid and 0.02 M AgNO_3 to fabricate the SiNWs.

SiNWs with different lengths of 0.4, 0.7, 0.95, 1.5, and 2.7 μm were obtained by controlling the etching time. Concentrated nitric acid and 5% dilute HF solution were then used to remove the silver particles and oxide on the surface of the SiNWs.

Two-Step Surface Treatment of SiNWs: The as-prepared SiNWs were first treated in a RF 13.56 MHz inductively coupled oxygen plasma, generated with an O_2 gas flow of 30 sccm, RF power of 30 watts and pressure of 200 mTorr, for 480 s to form a layer of sacrificial oxide. The SiNWs were then etched in 5% dilute HF acid normally for 80 ~ 90 s to partially remove the oxide layer and obtain a cleaner surface.

Fabrication of SiNWs/PEDOT:PSS Hybrid Cells: The SiNWs were spin coated with highly conductive PEDOT:PSS (PH1000) mixed with 5-wt% dimethyl sulfoxide (DMSO) at 2800 r/min, and then annealed at 105 $^{\circ}\text{C}$ for 10 min in atmosphere. The cells were completed by depositing electrodes that comprised a layer of Ag grids (1200 nm thick) on the PEDOT:PSS layer and Ti/Pd/Ag (50/50/1000 nm) metal films on the backside of the Si substrate using e-beam evaporation. The cell has a size of 0.95 cm^2 and a 12% incident light power loss due to the Ag grid shadowing. In addition, hybrid cells based on thin film SiNWs without the surface treatment were fabricated under same condition for comparison. For each type of sample of a given SiNWs length, about 4 cells were fabricated and characterized.

5.3 Two-Step Surface treatment of SiNWs Using O₂ Plasma

Figure 5. 2 : (a) TEM image and (b) HRTEM image of a silver particle attached on the SiNW tip.

Transmission electron microscopy (TEM) measurement was used to investigate the changes to the SiNWs arising from the two-step surface treatment. Some residual Ag nanoparticles are generally found on the SiNWs surface, especially at the tips of the SiNWs. Fig. 5.2 (a) and (b) show the bright field TEM image and the high resolution transmission electron microscopy (HRTEM) image of a Ag nanoparticle on the tip of a SiNW after the MCEE etching process. These residual Ag nanoparticles, yielded during the MCEE process, are hard to remove completely due to their small size and the fact that they are normally imbedded in the SiNWs [151]. In our surface treatment process, O₂ plasma was used to oxidize the SiNWs surface and capture the Ag nanoparticles. This SiO_x layer formed was then dissolved by the following HF etching process, leading to the concurrent removal of the Ag nanoparticles, and resulting in a cleaner surface [151].

The two step surface treatment process also removes the defects on the surface such as dangling bonds produced from the MCEE process. The O₂ plasma oxidizes the defective surface to form sacrificial oxide, which is partially removed by the following HF etching,

leaving only a thin layer of residual oxide to passivate the SiNWs surface. The thickness of the residual SiO_x layer can be adjusted by controlling the etching time in the dilute HF solution. Fig. 5.3 (a) and (b) show the HRTEM images of a SiNW before and after the oxygen plasma treatment, respectively. As seen in Fig. 5.3 (a), the as-prepared SiNW has only a very thin SiO_x layer on the surface due to its H^+ terminated surface arising from the MCEE process, which effectively prevents formation of native oxide on the Si surface. From Fig. 5.3 (b), it is seen that a thicker SiO_x layer of 4 to 5 nm thickness was formed after the oxygen plasma treatment. Fig. 5.3 (c) shows the SiNW after the 5% HF etch for ~ 85 s, where a thin layer of 1 to 2 nm SiO_x is seen to remain on the surface for passivation purpose.

Figure 5. 3 : HRTEM images of the SiNWs (a) before and (b) after the O_2 plasma treatment. (c) SiNWs after surface treatment and subjected to HF etching time of 85s. A residual thin SiO_x layer is seen on the SiNWs surface.

Moreover, the SiO_x layer on the SiNWs surface will change their wettability and lead to hydrophilic surface. This is advantageous for the PEDOT:PSS aqueous solution to penetrate into the gaps between the SiNWs, resulting in better coverage of the PEDOT:PSS onto the SiNWs surface [159]. We believe the two-step surface treatment

process that effectively removes the surface defects and passivate the SiNWs surface, accounts for the improvement in J - V characteristic of the treated SiNWs cell which will be presented in the following sections.

5.4 Effects of Surface Treatment on Thin Film SiNWs/PEDOT:PSS Cell

In this section, we examine the effects of the two step surface treatment using O_2 plasma on the performance of SiNWs/PEDOT:PSS hybrid cells. We will compare the performance using cells that were fabricated with a wire length (L) of $0.4\ \mu\text{m}$ and on a $10.6\ \mu\text{m}$ Si film.

5.4.1 Morphology of Thin Film SiNWs/PEDOT:PSS Cell With/Without Surface Treatment

Fig. 5.4 (a) and (b) show the top view SEM images of the SiNWs coated with PEDOT:PSS with wire length of $0.4\ \mu\text{m}$ without and with surface treatment, respectively; their corresponding cross-sectional view SEM images are shown in Fig. 5.4 (c) and (d). It can be seen that PEDOT:PSS does not penetrate well into the SiNWs gaps due to its long polymer chain [98]. For shorter SiNWs with $L = 0.4\ \mu\text{m}$ that are more vertically aligned, PEDOT:PSS forms a continuous canopy coverage on top of the SiNWs. It can be seen that the SiNWs subjected to the surface treatment have a smoother surface coverage of PEDOT:PSS layer compared to the untreated SiNWs. This could be attributed to the hydrophilic surface of the SiNWs after the oxygen plasma treatment, which improves PEDOT:PSS coverage in the spin coating process [159].

Figure 5. 4 : (a) and (b) show the top view SEM images of the SiNWs coated with PEDOT:PSS with wire length of $0.4 \mu\text{m}$ without and with surface treatment, respectively; (c) and (d) show the corresponding cross-sectional view SEM images of these samples.

5.4.2 Performance of Thin Film SiNWs/PEDOT:PSS Cell With/Without Surface Treatment

Fig. 5.5 shows the illuminated (AM 1.5G, 100 mW/cm^2) J - V characteristics of the SiNWs/PEDOT:PSS hybrid cells with wire length of $0.4 \mu\text{m}$ based on a $10.6 \mu\text{m}$ Si film, without and with the two-step surface treatment. The photovoltaic data are presented in Table 5.1, including the open circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and power conversion efficiency (PCE). The photovoltaic data for planar cell based on the same Si film are also presented for comparison. The PCE of the $0.4 \mu\text{m}$ SiNWs cell after surface treatment is increased from 7.0% to 7.7%, as a result of the

recovery in V_{oc} from 0.496 to 0.572 V. The J_{sc} is increased to 20.5 mA/cm² for SiNWs cells compared to the 19.1 mA/cm² for the planar counterpart.

Figure 5. 5 : The illuminated J - V characteristics of 0.4 μ m SiNWs cell based on 10.6 μ m Si film. The results of treated and untreated cells are presented. The results of planar cell without the SiNWs are also included for comparison.

Table 5. 1 : Photovoltaic parameters of the planar and SiNWs/PEDOT:PSS hybrid cells with 0.4 μ m SiNWs, without and with surface treatment. The cells are based on thin Si film of 10.6 μ m thickness.

<i>SiNW Length</i>	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
Planar	0.582	19.1	59.7	6.6
0.4μm (Not	0.496	20.8	67.3	7.0
0.4μm (Treated)	0.572	20.5	65.7	7.7

The improved V_{oc} is indicative of the suppression of recombination loss in the SiNWs hybrid cells after the surface treatment process. The O₂ plasma oxidizes the surface of the SiNWs where there are abundance of residual silver nanoparticles and surface defects resulting from the MCEE process [164, 165]. The subsequent HF etching process

effectively removes the SiO_x layer concurrently with the embedded impurities, leaving behind only a thin residual oxide layer to passivate the SiNWs surface [15, 156]. The oxide layer also facilitates a favorable band alignment and leads to an internal electric field at the junction interface, leading to better charge separation [160]. Moreover, the SiNWs with SiO_x surface layer are observed to be more hydrophilic compared to the H^+ terminated pristine SiNWs, leading to a smoother surface coverage of PEDOT:PSS layer on top of the SiNWs as seen in Fig. 5.4. This avoids local shunting across the cells due to protrusion of the SiNWs tips as discussed previously. The increase in shunt resistance is evidenced from the dark condition J - V curves shown in Fig. 5.6, where it can be seen that the untreated cell suffers from early turn-on which is not seen in the case of the treated cell. The cleaner SiNWs surface and better coverage of PEDOT:PSS layer also leads to the enhancement in carrier separation and thus the improvement in FF .

Figure 5. 6 : The dark J - V characteristics of 0.4 μm SiNWs cell based on 10.6 μm Si film. The results of the treated and untreated cells are presented. The results of planar cell without the SiNWs are also included for comparison.

The series resistances (R_s) are also extracted from the J - V curve of hybrid cells ($dJ/dV|_{V=V_{oc}}$), and their values are presented in Table 5.2. It is seen that, the SiNWs cell with wire length of 0.4 μm have smaller R_s than the planar counterpart. This is attributed to the enhanced carrier transport and collection of the SiNWs cells owing to the nanoscale geometry of the SiNWs and the increased junction area. The R_s of the surface treated SiNWs cell increases slightly after the surface treatment, which is attributed to the presence of the thin SiO_x layer on the surface of the SiNWs.

Table 5. 2 : Series Resistance of the hybrid cells based on planar Si, untreated SiNWs and treated SiNWs fabricated on thin Si film of 10.6 μm thickness.

Series Resistance R_s ($\Omega.\text{cm}^2$)			
Si film	Planar	0.4 μm NW (Not Treated)	0.4 μm NW (Treated)
10.6 μm Si	6.13	2.83	4.27

As seen from Table 5.1, the J_{sc} of SiNWs with wire length of 0.4 μm is decreased slightly after the surface treatment as compared to the untreated cells. Fig. 5.7 shows the corresponding external quantum efficiency (EQE) spectra of the cells presented above. It is seen that the EQE for the 0.4 μm SiNWs cells exhibit higher value than the planar cell over broad wavelength range. With surface treatment, the EQE of the treated SiNWs cell decreases as compared to the untreated cell. The change in the EQE is consistent with the variation in J_{sc} of the 0.4 μm SiNWs cells shown in Table 5.1.

Figure 5. 7 : The *EQE* spectra of the planar and 0.4 μm SiNWs cell based on 10.6 μm Si film. The results of the treated and untreated cells are presented.

To understand the variation in J_{sc} , the reflectance of the SiNWs coated with PEDOT:PSS layer without and with the surface treatment were measured and shown in Fig. 5.8. It is seen that the reflectance of the 0.4 μm SiNWs after surface treatment is higher compared to the untreated SiNWs with same wire length. This change in the reflectance is attributed to the change in the PEDOT:PSS coverage morphology due to the more hydrophilic SiNWs surface after the surface treatment, as seen from Fig. 5.4. This is because of the fact that the PEDOT:PSS layer acts as antireflection coating and reduces the reflection of incident light. For shorter SiNWs, aside from the light trapping effect arising from the SiNWs, this antireflection coating of PEDOT:PSS also has large impact on the light reflection characteristics. This change in the reflectance could account for the decrease in *EQE* and J_{sc} in the shorter SiNWs cells. However, it is noted that in the case of longer SiNWs, the light trapping effect of SiNWs is so strong that it dominates, thus the effect of PEDOT:PSS coating morphology on the reflectance is insignificantly small.

Figure 5. 8 : The reflectance spectra of SiNWs coated with PEDOT:PSS layer without and with surface treatment.

5.5 Effects of Wire Length on the Performance of Thin Film SiNWs/PEDOT:PSS Cell

In section 5.4, we have presented the planar and 0.4 μm SiNWs/PEDOT:PSS cells, and investigated the effect of surface treatment on the SiNWs cell performance. In this section, we will study the performance of the SiNWs/PEDOT:PSS cells as a function of the wire length. All the SiNWs cells were fabricated on 10.6 μm Si thin film and subject to the surface treatment using O_2 plasma.

5.5.1 Morphology of Thin Film SiNWs/PEDOT:PSS Cell with different Wire Lengths

Figure 5.9 : (a) - (e) shows the top view SEM images of the SiNWs coated with PEDOT:PSS with different L of 0.4, 0.7, 0.95, 1.5 and 2.7 μm with surface treatment, respectively; (f) - (j) show the corresponding cross-sectional view SEM images of these samples.

Fig.5.9 (a)-(e), and (f)-(j) show the top and cross-sectional views of the SiNWs with different L of 0.4, 0.7, 0.95, 1.5 and 2.7 μm coated with PEDOT:PSS, respectively. Fig. 5.9 (a) and (f) show PEDOT:PSS forms a continuous canopy coverage on top of the more vertically aligned shorter SiNWs with $L = 0.4 \mu\text{m}$. As L increases to 0.7 and 0.95 μm , the SiNWs suffer from agglomeration at the top resulting in the formation of small bundles of SiNWs and consequently small gaps between the bundles of SiNWs due to the Van Der Waals and attractive capillary forces [17, 166, 167]. For these wire lengths, there are only a few SiNWs inside each bundle. As a result, the PEDOT:PSS layer starts to infiltrate into the gaps of the small SiNWs bundles but only at the top portion, leading to a bumpy surface contour on top of the SiNWs bundles, as shown in Fig. 5.9 (b-c) and (g-h). The SiNWs at the outer side of the bundles have PEDOT:PSS coated on their tips as

well as their top portion of the sidewalls, while the SiNWs within each bundle are coated only at the tips with sidewalls uncoated with PEDOT:PSS. As L is further increased to 1.5 and 2.7 μm , the aggregations of SiNWs are further enhanced, leading to larger SiNWs bundles and larger gaps between these bundles. This leads to the poor infiltration of the PEDOT:PSS into the top portion of the SiNWs, as more SiNWs are encapsulated inside the large bundles. Meanwhile, the enhanced aggregation and large gaps also result in poor coverage of PEDOT:PSS, leading to more protrusions of SiNWs, as can be seen from Fig. 5.9 (d-e) and (i-j).

5.5.2 Performance of Thin Film SiNWs/PEDOT:PSS Cell with different Wire Lengths

Figure 5. 10 : Average photovoltaic parameters of (a) PCE and V_{oc} , and (b) J_{sc} and FF of the SiNWs/PEDOT:PSS solar cells based on 10.6 μm Si absorber, as a function of wire length L .

Fig.5.10 and Table 5.3 summarize the statistical distributions of the PCE, V_{oc} , J_{sc} and FF of the cells with different wire lengths. The parameters listed for every cell are the average values based on the four cells fabricated. The current density-voltage (J - V) characteristics of SiNWs/PEDOT:PSS cells of different L with surface treatment were

measured under 100 mW/cm² illumination (AM 1.5G) from a solar simulator and under dark condition, and are presented in Fig. 5.11 (a) and (b), respectively.

Table 5. 3 : Photovoltaic parameters of the SiNWs/PEDOT:PSS hybrid cells with different wire lengths based on thin Si film of 10.6 μm thick. The parameters listed are based on the average value except for the last column.

Si Films	SiNW Length	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]	MAX
10.6 μm Si	0.4 μm	0.565	20.33	62.8	7.22	7.74
	0.7 μm	0.562	20.67	62.6	7.27	7.83
	0.95 μm	0.543	20.88	62.4	7.08	7.24
	1.5 μm	0.475	19.81	53.2	5.02	5.26
	2.7 μm	0.435	17.35	47.0	3.55	3.67

All of the SiNWs have been subject to surface treatment and fabricated on Si absorber of 10.6 μm . The average PCE of the SiNWs/PEDOT:PSS cells exhibits a maximum value of 7.27% at $L = 0.7 \mu\text{m}$. Further increase in L leads to continuous decreases in PCE to 3.55% when L is increased to 2.7 μm . The average V_{oc} and FF exhibit their maximum values of 0.565 V and 62.8% at $L = 0.4 \mu\text{m}$, and decreases monotonically to 0.435 V and 47.0% respectively at $L = 2.7 \mu\text{m}$. The average J_{sc} increases with L and reaches the maximum value of 20.88 mA/cm² at $L = 0.95 \mu\text{m}$, beyond which it decreases to 17.35 mA/cm² as L is increased to 2.7 μm .

Figure 5. 11 : (a) The illuminated and (b) dark *J-V* characteristics of the SiNWs/PEDOT:PSS solar cells based on 10.6 μm Si absorber, as a function of wire length L .

As shown in Fig. 5.10, V_{oc} generally decreases monotonically as L increases from 0.4 to 2.7 μm . This could be due to the enhanced carrier recombination loss associated with the defective SiNWs surface and increased surface area of the SiNWs [99, 100, 104]. SiNWs prepared by the MCEE technique have been reported to have more surface defects for longer SiNWs, leading to a shorter carrier lifetime and higher recombination rate [164,

165]. With the surface treatment, the surface of the shorter vertically aligned SiNWs can be effectively improved by removing the impurity particles and defects on the SiNWs surface owing to their effective exposure to the surface treatment. However, for longer SiNWs, the enhanced aggregations lead to the formation of large bundles of SiNWs. While the SiNWs locate at the outer layer of the bundles can have cleaner surface at both wire tips and their sidewalls, those SiNWs inside the bundles are prevented from the surface treatment with many impurities and defects remaining on their sidewall surface. Thus the surface treatment has limited effect on the performance improvement for the very long SiNWs.

The drop in V_{oc} could also be attributed to the lower shunt resistance for longer SiNWs/PEDOT:PSS cell [17, 168, 169]. As shown in Fig. 5.9, longer SiNWs will result in a bumpy coverage of PEDOT:PSS which could possibly lead to local shunting across the cells if the protrusion of the SiNWs tips penetrate the PEDOT:PSS layer and are in close contact with the front silver electrode. The lower shunt resistance for longer SiNWs leads to the increase in the reverse saturation current and an early turn-on of the diode in the dark condition [17, 136], as shown in Fig. 5.11 (b). This lower shunt resistance also leads to poor FF .

In addition, the increased series resistance associated with the rough PEDOT:PSS contour for the longer SiNWs accounts for the decrease in FF [17, 98]. The series resistances (R_s) of SiNWs cells with different L are extracted from the the J - V curves and summarized in Table 5.4. The R_s is $4.27 \Omega\text{cm}^2$ for the cell with $L = 0.4 \mu\text{m}$, and is decreased to $3.92 \Omega\text{cm}^2$ for the cells with $L = 0.7 \mu\text{m}$. As L further increases to 0.95 , 1.5 and $2.7 \mu\text{m}$, the R_s is increased to 4.54 , 6.17 and $7.97 \Omega\text{cm}^2$ respectively. It is noted that, for the shorter

SiNWs, the series resistance decreases with the increased wire length, which is attributed to the enhanced carrier separation. The junction area formed between SiNWs and PEDOT:PSS material is increased with the increasing wire length, and thus facilitates the photogenerated minority carriers separation and extraction [109, 170, 171]. However, for the very long SiNWs, the bundling due to aggregation of SiNWs is enhanced, resulting in inefficient charge separation. Moreover, the rougher surface of coverage of PEDOT:PSS layer for the longer SiNWs cells lead to the increase in the series resistance [98]. As a result, the FF generally decreases with the increase of L , which is consistent with the trend shown in Fig. 5.10.

Table 5. 4 : Series Resistance (R_s) of the SiNWs/PEDOT:PSS hybrid cells with different wire lengths based on thin Si film of $10.6 \mu\text{m}$ thickness.

Series Resistance ($\Omega.\text{cm}^2$)					
Si films	$0.4\mu\text{m}$ NW	$0.7\mu\text{m}$ NW	$0.95\mu\text{m}$ NW	$1.5\mu\text{m}$ NW	$2.7\mu\text{m}$ NW
$10.6 \mu\text{m}$ Si	4.27	3.92	4.54	6.17	7.97

Figure 5. 12 : EQE of the SiNWs/PEDOT:PSS solar cells based on $10.6 \mu\text{m}$ Si film, as a function of wire length L .

The J_{sc} firstly increases with L , and reaches a maximum value at SiNWs length of 0.95 μm for the 10.6 μm Si film used, and then decreases continuously with a further increase in L . Fig. 5.12 shows the *EQE* spectra of the SiNWs/PEDOT:PSS cells with different L . The *EQE* peak increases with L up to $L = 0.95 \mu\text{m}$, with a maximum value of 69.7% at 625 nm. This is consistent with their reflectance spectra shown in Fig. 5.13 where the 0.95 μm SiNWs cell has lower reflectance compared to the shorter SiNWs cells. The high *EQE* is attributed to the enhanced light trapping and charge separation capabilities of the SiNWs, resulting in highest J_{sc} of 20.88 mA/cm^2 , as shown in Fig. 5.10 and Table 5.3. As L increases to 1.5 and 2.7 μm , though the reflectance is further reduced to below 5% owing to the more effective light trapping by the longer SiNWs, the *EQE* of the cells decrease monotonically, especially in the shorter wavelength range of 400 - 800 nm. This is indicative of higher recombination rate. For longer SiNWs, the SiNWs tips inside the aggregated SiNWs bundles are prevented from the surface treatment that can improve their surface quality, and they are poorly coated and do not form junction with PEDOT:PSS. This results in higher recombination rate, particularly for shorter wavelength photons [164] which are mostly absorbed near the tips of the SiNWs.

Figure 5. 13 : Reflectance spectra of the surface treated SiNWs/PEDOT:PSS solar cells with different SiNWs length.

5.6 Effects of Si Film Thicknesses on the Performance of SiNWs/PEDOT:PSS Cells

To study the effects of the thickness of the Si thin films on the performance of the SiNWs/PEDOT:PSS cell, cells with 0.95 μm wire length based on Si thin films of different thicknesses of 5.5, 10.6 and 15.5 μm were fabricated and characterized. The thin Si films were grown with same quality and with same phosphorus doping concentration of $1.5 \times 10^{16} \text{ cm}^{-3}$.

Figure 5. 14 : The illuminated J - V characteristics of the SiNWs/PEDOT:PSS solar cells based on different Si films of 5.5, 10.6 and 15.5 μm thickness.

Table 5. 5 : Photovoltaic parameters of the SiNWs/PEDOT:PSS hybrid cells with 0.95 μm wire length based on Si thin film of different thicknesses. The parameters listed are based on average value except for the last column.

SiNW	Si Thickness	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]	MAX
0.95 μm	5.5 μm	0.539	17.04	64.83	5.96	6.12
	10.6 μm	0.543	20.88	62.42	7.08	7.24
	15.5 μm	0.536	23.76	61.88	7.88	8.01

Fig.5.14 shows the illuminated (under AM 1.5G, 100 mW/cm^2) current density-voltage (J - V) characteristics of the surface treated SiNWs/PEDOT:PSS cells of $L = 0.95 \mu\text{m}$ based on thin Si films with different thicknesses. Table 5.5 summarizes the photovoltaic parameters of PCE , V_{oc} , J_{sc} and FF . It is seen that as the Si film thickness increases from 5.5 μm to 15.5 μm , the average PCE and maximum PCE of the SiNWs cell increases substantially from 5.96% and 6.12% to 7.88% and 8.01% respectively, attributed mainly to the enhancement in J_{sc} .

Figure 5. 15 : The *EQE* spectra of the SiNWs/PEDOT:PSS solar cells based on different Si films of 5.5, 10.6 and 15.5μm thickness.

Fig. 5.15 shows the *EQE* spectra of the SiNWs/PEDOT:PSS cells with different Si thicknesses. The *EQE* peak increases from 62.5% to 71.1% as the Si film thickness increases from 5.5 to 15.5 μm respectively. The increase in *EQE* is attributed to the enhanced light absorption with thicker Si absorber material, resulting in larger J_{sc} from 17.04 to 23.76 mA/cm², as shown in Fig. 5.14 and Table 5.5. It is noted that there is only a slight increment in the *EQE* at shorter wavelength region for the cells fabricated on 10.6 and 15.5 μm Si film comparing to the cell fabricated on 5.5 μm Si film. This is because that with the effective light trapping arises from the SiNWs, shorter wavelength photons [164] are mostly absorbed by the SiNWs and effectively separated and collected by the SiNWs/PEDOT:PSS junction, independent of the Si thin film thickness. The enhancement in *EQE* is more significant over the wavelength range from 600 to 1100 nm. The longer wavelength light is mainly absorbed in the bulk of the Si thin film, which is thus enhanced when the Si thin film thickness is increased. Note that even the thickest epitaxial Si absorber layer of 15.5 μm does not fully capture longer wavelength photons.

These photons are instead absorbed mainly in the heavily doped Si substrate, where the carriers generated are not extracted due to the short minority-carrier diffusion length and high carriers recombination rate [17]. As a result, all the cells have lower EQE in the infrared region from 700 to 1100 nm as compared to similar cells based on bulk Si [98].

5.7 Comparison of SiNWs/PEDOT:PSS Cell Performance for Si Film of Different Thicknesses With/Without Surface Treatment

Figure 5. 16 : Average (a) PCE, (b) V_{oc} , (c) J_{sc} and (d) FF for SiNWs/PEDOT:PSS cells based on 5.5, 10.6 and 15.5 μm thick Si films without (w/o) and with surface treatment as a function of SiNWs length.

Fig. 5.16 (a)-(d) summarize the average photovoltaic parameters of the SiNWs/PEDOT:PSS solar cells fabricated on different Si films without and with surface treatment as a function of L . In general, these parameters are seen to have similar trend for the three Si films with different thicknesses of 5.5, 10.6 and 15.5 μm . For example, the cells that are surface treated exhibit better performance compared to the untreated cells, and the peak PCE of the cells generally occur at shorter SiNWs. For the SiNWs cells based on 5.5 and 10.6 μm Si film, the PCE peaks at $L = 0.7 \mu\text{m}$, whereas for the 15.5 μm Si film, it peaks at $L = 0.95 \mu\text{m}$. It is also noted that for all the cells with different Si thin film thicknesses, the J_{sc} peaks at $L = 0.95 \mu\text{m}$.

For the case of SiNWs without the surface treatment, it is found that their PCE peaks at much shorter L compared to their corresponding treated counterparts. This is because that, although longer SiNWs have better light trapping, the higher recombination rate due to their poor surface results in less effective carrier extraction and thus lower cell performance. Their better performance is only realized when the surfaces have been treated.

5.8 Conclusion

In conclusion, we have demonstrated high efficiency SiNWs/PEDOT:PSS hybrid solar cells using thin Si absorbers. Thin film Si with different thickness of 5.5, 10.6 and 15.5 μm have been used to fabricate the hybrid cells with different SiNWs lengths. A two step surface treatment involving O_2 plasma and HF etching has been proposed and applied to treat the SiNWs. The performance of the thin film SiNWs/PEDOT:PSS hybrid cells have been studied in terms of the surface treatment effect, SiNWs length effect, and the Si film thickness. It is found that the V_{oc} and thus the PCE can be significantly improved by the surface treatment process. The SiNWs cells with relative shorter wire length of 0.7 ~ 0.95 μm are found to exhibit the highest average PCEs. Average PCEs of 6.20%, 7.28% and 7.88% have been achieved for the SiNWs/PEDOT:PSS cells based on the 5.5, 10.6 and 15.5 μm Si absorber, respectively, and the corresponding maximum values are 6.53%, 7.83% and 8.01%. This study demonstrates the potential of achieving high efficiency and low cost Si/PEDOT:PSS hybrid solar cells using thin film Si.

Chapter 6 SiNCs/PEDOT:PSS Hybrid Solar Cells

This chapter presents the study of silicon nanocones (SiNCs) and hybrid solar cells based on the SiNCs and PEDOT:PSS. The fabrication process of the SiNCs by dry etching of Si substrate patterned using monolayer polystyrene (PS) nanospheres as mask will be presented first. Hybrid Si/PEDOT:PSS solar cells based on the SiNCs will then be discussed and investigated in terms of their optical, electrical and photovoltaic properties. Finally, the optical properties of the SiNCs on thin film Si will be examined using theoretical simulation based on the finite element method.

6.1 Introduction and Motivation

In previous chapters, we have fabricated and investigated the hybrid poly(3,4-ethylene dioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) solar cells based on silicon nanowires (SiNWs) prepared by the metal-catalyzed electroless etching (MCEE) method to improve light harvesting of the hybrid solar cells. To date most of the hybrid SiNWs solar cells reported are typically based on SiNWs fabricated using the MCEE technique [99, 136]. However, such SiNWs are not periodic, and thus it is difficult to study and understand the detailed effects of the nanostructural parameters on the performance of the cells. Besides, there is limited control on the dimensions of the SiNWs, such as diameter and periodicity, to allow optimization of the cell performance. In addition, longer SiNWs fabricated from the solution based MCEE technique suffers from agglomeration due to the effect of surface tension [167]. To better understand the effects of the structural parameters on the cell performance and to optimize the cell efficiency, it is imperative that hybrid solar cells based on periodic nanostructures with controllable dimensions be studied. Many top-down approaches have been developed to fabricate periodic

nanostructures, which include deep-UV lithography [172], electronic beam lithography, focus ion beam (FIB) writing and nanoimprinting [173, 174]. However, these techniques either require the use of expensive equipment, or involve complicated and time-consuming processes. Moreover, methods such as the e-beam lithography, FIB also suffer from low throughput. Compared to these methods, nanosphere lithography (NSL) is a promising low cost approach that is capable of fabricating periodic and homogenous nanostructures of various sizes at the wafer scale [175].

In this chapter, we demonstrate the fabrication of periodic Si nanocones (SiNCs) by dry etching of Si substrate using assembled monolayer polystyrene (PS) nanospheres as mask. Compared with SiNWs, SiNCs are mechanically more robust due to the larger base. Besides, their structure presents a more gradual change in the effective refractive index and thus is expected to possess better antireflective property [176]. Hybrid Si/PEDOT:PSS solar cells have been fabricated based on periodic SiNCs with different periodicities (P) that range from 400 nm to 800 nm. The hybrid SiNCs/PEDOT:PSS solar cells are found to exhibit improved optical properties and short-circuit current density (J_{sc}) as compared to planar Si hybrid cells [43]. We found that the SiNCs/PEDOT:PSS solar cell with a periodicity of 400 nm presents the highest PCE of 7.1% due to its strong light trapping around the peak of the solar spectrum and better current collection efficiency. In addition to the experimental investigation of the SiNCs hybrid solar cells, their optical properties are also studied theoretically using simulation based on the finite element method.

6.2 Fabrication of SiNCs Using PS Nanospheres as Mask

6.2.1 Fabrication of SiNCs

Figure 6. 1 : Fabrication process of the Si nanocones by dry etching of Si substrate patterned using monolayer polystyrene (PS) nanospheres as mask.

Fig. 6.1 illustrates the fabrication process of the SiNCs using the nanosphere lithography technique.

Assembly of PS Nanospheres Mask: Polystyrene (PS) nanospheres were first deposited as a monolayer on an N-type Si (100) substrate. The PS nanospheres solution was first mixed with ethanol in a volume ratio of 1:1, and then dropped on the water surface in a petri dish. The nanospheres assembled into a monolayer and floated on the water, and were subsequently transferred to the Si substrate by the Langmuir–Blodgett assemble method [177-179].

O₂ Plasma Etching to Reduce the Size of PS Nanospheres: The PS nanospheres coated Si samples were first etched using O₂ plasma to reduce the diameters of the PS nanospheres. The O₂ plasma etching was conducted with an O₂ flow rate of 20 sccm under a RF power of 30 W and pressure of 200 mTorr. The reduction in the size of the PS nanospheres can be controlled by adjusting the etching time.

Cl₂ Plasma Etching to Fabricate SiNCs: Following that, chlorine (Cl₂) plasma was used to etch the Si substrate masked by the PS nanospheres to form SiNCs arrays. The Cl₂ plasma etching was conducted with a Cl₂ flow rate of 50 sccm under a RF power of 200 W and pressure of 160 mTorr. The etching depth of the SiNCs can be controlled by adjusting the etching time. It should be noted that the nanospheres were also etched in this process but with a relatively slower rate.

Removal of PS Nanospheres: After the etching process, the PS nanospheres were removed by ultrasonic cleaning for 20 min using organic solvent toluene.

Fig. 6.2 shows the scanning electron microscope (SEM) images of the SiNCs fabricated at various stages. Fig. 6.2 (a) presents a typical SEM image of the monolayer PS nanospheres deposited on Si substrate. The nanospheres with a diameter (D) of 400 nm are in contact with one another and form a hexagonal pattern. After the O₂ plasma etching, the diameter of the PS nanospheres was reduced to about 330 nm, as seen in the Fig. 6.2 (b). It is typically reduced to just slightly less than the originally diameter of the PS nanospheres. Fig. 6.2 (c) displays the SiNCs formed after the Cl₂ plasma etching process,

while Fig. 6.2 (d) and (e) show the top and side views respectively of the SiNCs after the removal of the nanospheres. From the images, it is noted that the SiNCs have a height of about 500 nm and the top diameter is about half the bottom diameter. The periodicity is about 400 nm for this sample.

Figure 6. 2 : The SEM images of the fabrication of the SiNCs at each step: (a) Monolayer PS nanospheres with diameter of 400 nm coated on Si substrate, (b) after O_2 plasma etching, (c) after Cl_2 plasma etching, (d) top view and (e) cross section view of the SiNCs after the removal of PS nanospheres.

6.2.2 SiNCs Structures with Controllable Dimensions

The dimension and shape of the SiNCs are determined by several factors, including the initial size of PS nanospheres, the O_2 plasma etching time, and the Cl_2 etching time. The periodicity is determined by the original size of the nanospheres, which is equal to the distance from center of one PS nanosphere to the center of an adjacent PS nanosphere. SiNCs with different periodicities can be obtained by using PS nanospheres with different

diameters. Fig. 6.3 shows the SEM images of the PS nanospheres coated on the Si substrates with different initial diameters of 400, 500, 600 and 800 nm, respectively.

Figure 6. 3 : The SEM images of initial PS nanospheres coated on Si with diameter of (a) 400 nm, (b) 500 nm, (c) 600 nm and (d) 800 nm.

As the PS nanospheres assembled on the Si are in close contact with each other, O₂ plasma is generally used to reduce their size in order to open a window for the Cl₂ plasma to reach the underlying Si material and thus facilitate the etching to form SiNCs. The reduction in the diameter of the PS nanospheres can be controlled by adjusting the etching time. Fig. 6.4 (a) and (b) show the SEM images of PS nanospheres with diameter of 400 nm after O₂ plasma etching for 100 and 200 s, respectively. The PS nanospheres were reduced respectively to have diameter of 330 and 210 nm, and can be completely etched away if the etching time is further increased. It is noted that the reduced diameter of PS nanospheres after the O₂ plasma process approximately defines the bottom diameter of SiNCs formed when the PS nanosphere mask is not fully etched away after the following SiNCs etching process.

Figure 6. 4 : The SEM images of PS nanospheres ($D = 400$ nm) after O_2 etching for (a) 100 s and (b) 200 s.

During the Cl_2 plasma process, the Si material exposed to the Cl_2 plasma is etched in vertical direction while Si beneath the PS nanosphere mask is not affected. The Cl_2 etching time determines the depth of the SiNCs. Fig. 6.5 (a)-(c) present the SiNCs fabricated with different depth of 200, 300 and 500 nm, by using PS nanospheres with diameter of 400 nm as mask. It is noted that the PS nanospheres can also be etched in the Cl_2 plasma but with a slower rate comparing to that in O_2 plasma. Note that the diameter of PS nanospheres after the Cl_2 plasma etching approximately defines the top diameter of the SiNCs formed.

Figure 6. 5 : The SEM images of SiNCs with different depths of (a) 200 nm, (b) 300 nm and (c) 500 nm, with PS nanosphere mask diameter of 400 nm.

Therefore, by controlling the etching process in O_2 plasma and Cl_2 plasma, SiNCs with different shapes can be obtained. Fig. 6.6 displays SiNCs of different shapes formed after the Cl_2 plasma etching process by using PS nanospheres with diameter of 400 nm as mask. Fig. 6.6 (a) shows the SiNCs formed when the sample was directly etched in Cl_2 plasma for 5 min without using O_2 plasma etching to reduce their diameters. Due to the close arrangement of the PS nanospheres and the slower etch rate of PS material in Cl_2 plasma, the PS nanospheres are reduced only by a small fraction. Thus the underlying Si material has an insufficient etching, resulting in SiNCs with larger top diameter and non-uniform morphology. Fig. 6.6 (b) shows the SiNCs formed when the sample was first etched in O_2 plasma for 100 s and then in Cl_2 plasma for 5 min. The O_2 plasma etching reduces the diameter of PS nanospheres to about 330 nm and opens a large window for effective Cl_2 plasma etching of Si. After being etched in Cl_2 plasma for 5 min, uniform SiNCs are formed with only small size PS nanospheres left on top of their tips which define their smaller top diameters. Under the same O_2 plasma etching condition, when the Cl_2 etching time is increased to 6 min, the PS nanospheres are just completed etched away, resulting in sharp SiNCs, as shown in Fig. 6.6 (c). As the Cl_2 etching time is further increased to 12 min, the SiNCs are being etched without any mask, resulting in an over-etch of the Si. As the top portion of the SiNCs has a higher etch rate than the bottom part, their shape changes into stepper cones. The morphology of this SiNCs is shown in Fig. 6.6 (d).

Figure 6. 6 : The SEM images of SiNCs with different shapes under different etching conditions. (a) Directly etched in Cl_2 plasma for 5 min, (b) O_2 plasma etch for 100 s, followed by Cl_2 etch for 5 min, (c) O_2 plasma etch for 100 s, followed by Cl_2 etch for 6 min, and (d) O_2 plasma etch for 100 s, followed by Cl_2 etch for 12 min.

6.3 SiNCs/PEDOT:PSS Hybrid Solar Cells

6.3.1 Fabrication of SiNCs for the Hybrid Cells

N-type Si (100) wafers with thickness of 575 μm and resistivity of 1-3 $\Omega\cdot\text{cm}$ were used as substrates for the SiNCs fabrication. To obtain SiNCs arrays with different periodicities, PS nanospheres with different diameters of 400, 500, 600 and 800 nm were used. PS nanospheres were deposited as a monolayer on the Si substrates using the method presented in section 6.2.1. The PS nanospheres with 400, 500, 600 and 800 nm diameter were first etched using O_2 plasma under the conditions of 30 W RF power, 20 sccm O_2 gas flow rate and 200 mTorr pressure for 100, 125, 150 and 200 s, respectively. Following that, Cl_2 plasma was used to etch the Si substrate masked by the PS nanospheres to form SiNCs arrays. The Cl_2 plasma etching was conducted for 5 min with

a Cl_2 flow rate of 50 sccm under a RF power of 200 W and pressure of 160 mTorr. Note that the nanospheres were also etched in the process of the Si etching. After the etching process, the nanospheres were removed by ultrasonic cleaning using the organic solvent toluene for 20 min. The SiNCs obtained have heights of about 500 ~ 600 nm and their dimensional details are summarized in Table 6.1.

Table 6. 1 : Dimensions of the SiNCs used for the hybrid solar cell fabrication.

Diameter of PS nanospheres (nm)	Periodicity of SiNCs (nm)	Bottom Diameter of SiNCs (nm)	Top Diameter of SiNCs (nm)	Ratio of Top to Bottom Diameter
400	400	320	150	0.47
500	500	430	200	0.47
600	600	560	270	0.48
800	800	760	400	0.53

6.3.2 Hybrid Cell Fabrication and Cell Morphology

Figure 6. 7 : Fabrication process of the SiNCs/PEDOT:PSS hybrid solar cell.

The fabrication process of the SiNCs/PEDOT:PSS hybrid solar cell is illustrated Fig. 6.7. The as-prepared SiNCs samples were first cleaned in acetone, ethanol (IPA) and deionized (DI) water for 10 min each, and then dipped into 5% dilute hydrofluoric (HF) acid for 1 min to remove the surface native oxide. Ti/Pd/Ag metal films with thickness of 50/50/1000 nm were deposited on the rear surface of the Si substrate by electron-beam evaporation to form the back electrode. PEDOT:PSS (PH1000 from Clevios) solution mixed with 5 wt % dimethyl sulfoxide and 1 wt % triton 100 was deposited on the SiNCs by spin coating at 3000 rpm for 50s. The PEDOT:PSS layer was then dried at 105°C for 10 min. The thickness of the PEDOT:PSS film coated is about 50 nm. Finally, silver grid electrode with a thickness of 800 nm was then deposited on top of the PEDOT:PSS layer to complete the hybrid solar cell structure. The fraction of the silver grid shading area is 12%. The hybrid cells have an active area of 0.95 cm².

Fig. 6.8 shows the surface morphology of the SiNCs/PEDOT:PSS hybrid solar cells having PEDOT:PSS layer on the top of the SiNCs with different periodicity. Due to its large molecular chain, PEDOT:PSS forms a layer on top and does not penetrate into the SiNCs. It is seen that the PEDOT:PSS layer is not well supported by the SiNCs tips at larger periodicity and sinks because of gravity, resulting in rougher surfaces.

Figure 6. 8 : Surface morphology of PEDOT:PSS layer on the top of the SiNCs with different periodicities of (a) 400 nm, (b) 500 nm, (c) 600 nm and (d) 800 nm.

6.3.3 Performance of the Hybrid SiNCs/PEDOT:PSS Cells

Figure 6. 9 : Reflectance spectra of SiNCs samples coated with PEDOT:PSS, with periodicity of 400nm, 500nm, 600nm and 800nm.

Fig. 6.9 shows the reflectance spectra of the SiNCs structures with periodicity (P) of 400 nm, 500 nm, 600 nm and 800 nm coated with PEDOT:PSS, together with that of a planar Si cell, recorded using an UV/Vis/NIR spectrophotometer system (Lambda 950). It is seen that the reflectance of all the SiNC samples is generally low, mostly in the range of 5–15% over a wide wavelength spectrum of 350 to 1100 nm. It is also much lower than that of the planar cell, reaffirming the light trapping enhancement by the SiNCs. The SiNCs structure with P of 400 nm exhibits the lowest reflectance in broad wavelength range whereas the structure with P of 800 nm exhibits the largest reflectance.

Figure 6. 10 : Current density–voltage (J - V) characteristics of the hybrid cells, with periodicity of 400 nm, 500 nm, 600 nm and 800 nm.

Fig. 6.10 shows the current density–voltage (J - V) characteristics of the SiNCs hybrid cells with different periodicities. The J - V curves were recorded under simulated AM 1.5G irradiation at 100 mW/cm². The photovoltaic parameters of short circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and PCE extracted from the J - V curves are summarized in Table 6.2. It is seen that the highest PCE of 7.1% is obtained for the

cell with $P = 400$ nm. With an increase in the periodicity, the V_{oc} is relatively stable whereas both the J_{sc} and FF decrease, resulting in a drop in the PCE. The PCE of the hybrid cell with $P = 800$ nm is decreased to only 3.6%.

Table 6. 2 : Photovoltaic parameters of the hybrid cells based on planar Si and the SiNCs with different periodicities (P).

Sample	$J_{sc}(\text{mA}/\text{cm}^2)$	$V_{oc}(\text{V})$	$FF(\%)$	PCE(%)
Planar	26.1	0.59	64.9	10.0
P 400	29.1	0.42	57.7	7.1
P 500	28.2	0.41	56.7	6.5
P 600	27.7	0.42	45.8	5.3
P 800	25.7	0.40	35.3	3.6

In terms of the photovoltaic parameters, the SiNCs cells of smaller periodicities exhibit better J_{sc} than the planar cell. For example, the one with $P = 400$ nm has a J_{sc} of 29.1 mA/cm^2 in comparison to that of planar cell of 26.1 mA/cm^2 . On the other hand, the V_{oc} of the SiNCs hybrid cells is only about 0.42 V, which is much lower than the V_{oc} of 0.59 V observed for the planar cell [43]. This is attributed to the high recombination rate of the SiNCs hybrid cells as compared to the planar cell. The Cl_2 plasma etching and the ion bombardment will introduce surface defects at the SiNCs that act as recombination sites and promote carriers recombination. This and the larger surface area of the SiNCs are responsible for the increased carrier recombination. The open circuit voltage is largely dependent on the light induced current and the saturation current of the solar cell devices. The saturation current is mainly determined by the recombination of the solar cell. Since the same material system of high quality Si and PEDOT:PSS have been used, the surface

quality of the SiNCs determines the recombination current. As the SiNCs with different periodicities all suffer from the surface defects resulting from the same dry plasma etching process, the surface recombination dominates which leads to low V_{oc} values range from 0.40 to 0.42 V for all the SiNCs hybrid cells. The degradation in V_{oc} observed for the SiNCs hybrid cells is also corroborated by the increased reversed saturation current density (J_0) of the dark J - V curve shown in Fig. 6.11, which is up to one order of magnitude higher than that of the planar cell. This issue can be addressed by proper surface treatment and passivation to minimize the defects [43, 180].

Figure 6. 11 : Current density–voltage (J - V) characteristics of the hybrid cells, with periodicity of 400 nm, 500 nm, 600 nm and 800 nm under dark condition.

The J_{sc} decreases with increasing periodicity, which is consistent with the trend of the reflectance for the SiNCs with different periodicity shown in Fig. 6.9. In addition to the light trapping, the change in J_{sc} may also be associated with the poorer current collection efficiency for the SiNCs cells at larger periodicity. As the PEDOT:PSS layer sits on top

of the SiNCs in contact with their sharp tips, some may pierce through the PEDOT:PSS layer and come in contact directly with the top silver grid to result in lower shunt resistance. This is more likely to occur for structures with larger P as there is more prominent protruding of the SiNCs on the PEDOT:PSS layer, as can be seen from Fig. 6.8. Such structures also have rougher surfaces which will render it harder to form continuous Ag grid on top, and also result in poorer contact between the Ag grid and the PEDOT:PSS layer. This will lead to higher series resistance of the cells. Therefore the irregular surface morphology of the structures with larger P will lead to degradation in J_{sc} and the FF as observed. Fig. 6.12 shows the external quantum efficiency (EQE) of the hybrid solar cells where it is seen that the cell with $P = 400$ nm exhibits the strongest spectral response, particularly at shorter wavelength range. Overall the EQE decreases slightly with increasing periodicity, which is consistent with the J_{sc} trend as observed in Table 6.2.

Figure 6. 12 : External quantum efficiency (EQE) of the hybrid cells, with periodicity of 400 nm, 500 nm, 600 nm and 800 nm.

6.4 Optical Simulation of Light Absorption in SiNCs/PEDOT:PSS Hybrid Cells

In the previous section, we have presented the fabrication of SiNCs and hybrid solar cells based on the SiNCs and PEDOT:PSS. To further understand the optical properties of the hybrid SiNCs/PEDOT:PSS cells, simulation study of their optical characteristics has been performed using the commercial software High Frequency Structural Simulator based on the finite element method [144].

6.4.1 Simulation Structure

Figure 6. 13 : (a) Cross-sectional and (b) top view schematic diagram of the simulated SiNCs/PEDOT:PSS structure.($T1 = 3 \mu\text{m}$, $T2 = 50 \text{ nm}$, $H = 500 \text{ nm}$, D/P ratio = 0.5.)

Fig. 6.13 shows the schematic of the simulated hybrid SiNCs/PEDOT:PSS structure. It consists of periodic SiNCs with a height (H) of 500 nm that is approximately the value observed experimentally for the SiNCs fabricated. There is an underlying Si thin film with a thickness ($T1$) of 3 μm and a top PEDOT:PSS layer with a thickness ($T2$) of 50 nm. The SiNCs are set to be in contact with each other. Thus the bottom diameter of the SiNCs is equal to their periodicity. The top diameter (D) to periodicity (P) ratio (D/P ratio) of the SiNCs is fixed at 0.5, similarly based on the experimental value, while P is

varied from 200 to 800 nm to find the optimal structure that maximizes sunlight absorption. A plane wave with wavelength λ ranging from 300 to 1100 nm is incident normally on top of the hybrid structure. The periodic structure is simulated by applying periodic boundary conditions to the unit cell. The refractive indices of Si and PEDOT:PSS are obtained from the literature [145, 146].

6.4.2 Light Absorption Behavior in SiNCs/PEDOT:PSS Hybrid Cell

Figure 6. 14 : Simulated light absorption in the (a) Si layer and (b) PEDOT:PSS layer. (c) Reflectance and (d) transmission spectra of the hybrid structure as a function of P at a fixed D/P ratio of 0.5.

Fig. 6.14 (a) and (b) depict the simulated light absorption in the Si and PEDOT:PSS materials respectively, whereas Fig. 6.14 (c) and (d) show the simulated overall reflectance and transmittance spectra of the hybrid structures respectively. At the smallest P of 200 nm, the light absorption is enhanced at shorter wavelength with $\lambda < 550$ nm, attributed to the strong scattering resulting from the comparable size of the structural dimension and the light wavelength [107]. As P is increased to 400 nm, the light absorption peak shifts to 550 nm and there is also a significant increase in light absorption for long wavelength light ($\lambda > 600$ nm) compared to the $P = 200$ nm structure. This is due to the increase in the structural dimension which correspondingly shifts the strong scattering to longer wavelengths. When P is 600 nm, though there is a slight drop in light absorption for shorter wavelength range below 600 nm, the light absorption is significantly enhanced for $\lambda > 600$ nm as compared to the structures with smaller P . The strong scattering in the longer wavelength range increases the optical path length and results in a low transmittance, as can be seen in Fig. 6.14 (d). This indicates that the light is strongly absorbed before it could penetrate through the structure. As P is further increased to 800 nm, the structure exhibits a slightly higher light absorption at longer wavelength as compared to $P = 600$ nm structure, but the absorption is generally lower for $\lambda < 800$ nm range, resulting in a degradation of its overall performance. It is noted that as P increases, the light absorption in the PEDOT:PSS layer is strong for the structures with $P = 600$ and 800 nm, as there is strong scattering at the longer wavelength range of $\lambda > 800$ nm where the absorption coefficients of PEDOT:PSS are higher.

Figure 6. 15 : Ultimate efficiency of the hybrid structure as a function of P at a fixed D/P ratio of 0.5.

Fig. 6.15 summarizes the ultimate efficiencies (η) for the simulated structures as a function of P at a fixed D/P ratio of 0.5. The ultimate efficiency is calculated from the absorption spectra under the standard Air Mass 1.5 spectrum [143] to determine the optimum structure for maximum sunlight harvesting. It is given by [16]

$$\eta = \frac{\int_{E_g}^{\infty} \frac{I(E) \times \alpha(E) \times E_g}{E} dE}{\int_0^{\infty} I(E) dE} \quad (6.1)$$

where $I(E)$ is the spectral solar intensity corresponding to the Air Mass 1.5 direct normal and circumsolar spectrum [143], E is the photon energy, E_g is the Si band gap energy of 1.1 eV, and $\alpha(E)$ is the absorption spectrum of the hybrid structure. This formula assumes that each photon with energy greater than the band gap will be absorbed in the solar cell to generate one electron-hole pair, which is then extracted as electric current without loss [16]. From Fig. 6.15, it is seen that the SiNCs/PEDOT:PSS hybrid structure reveals a highest ultimate efficiency of 33.7% at $P = 600$ nm, which is attributed to the

enhancement in light absorption over a broad wavelength range that includes the peak of the solar spectrum.

It is noted that the simulated result is not exactly consistent with the experimental result, as the highest efficiency for the latter is found to occur for the structure with a smaller P of 400 nm. The deviation can be attributed to the fact that our simulation was performed for a Si thin film of 3.5 μm thickness, whereas the actual devices were fabricated on thick Si substrates of 575 μm . Note that due to computing resource constraints, it is challenging to simulate structures with thick Si substrates. Due to the different Si absorbing layer thicknesses, the overall absorption characteristics and hence the optimum structural parameter will differ. Indeed as can be seen from Fig. 6.14 (d), the structures with smaller P of 200 nm and 400 nm have high transmittance at longer wavelength of $\lambda > 600$ nm, attributed to the lower absorption coefficients at these wavelengths and the thin Si absorbing layer. However, this is not the case when thick Si substrates are used as the light will be fully absorbed. Therefore, maximum absorption is expected to occur at larger P for the simulated Si thin film structure. Note that for low cost practical application, the hybrid cells should be fabricated using Si thin films instead of bulk Si wafers. Thus, our simulation results are relevant and reveal how the structures should be optimized when Si thin films are employed. Another factor that accounts for the variation between the experimental and simulated results is that the fabricated structures are not perfectly periodic or with uniform PEDOT:PSS coverage morphology as noted from Fig. 6.8, in contrast to the simulated structures.

Our experimental results indicate that J_{sc} decreases with increasing periodicity, whereas the simulation results reveal that the ultimate efficiency increases with periodicity up to $P = 600$ nm. The inconsistent trend in the change in J_{sc} and optical absorption may be associated with the poorer current collection efficiency for the experimental cells at larger periodicity. As the PEDOT:PSS layer sits on top of the SiNCs in contact with their sharp tips, some may pierce through the PEDOT:PSS layer and come in contact directly with the top silver grid to result in a lower shunt resistance. This is more likely to occur for structures with larger P as there is more prominent protruding of the SiNCs on the PEDOT:PSS layer, as can be seen from Fig. 6.8 that shows the surface morphology of the PEDOT:PSS layer on the top of the SiNCs with different P . Such structures also have rougher surfaces as the PEDOT:PSS layer is not well supported by the nanocone tips at larger P and sinks because of gravity. The rougher surface will render it harder to form continuous Ag grid on top, and also result in poorer contact between the Ag grid and the PEDOT:PSS layer. This will lead to higher series resistance of the cells. Therefore the irregular surface morphology of the structures with larger P will lead to degradation in J_{sc} and the FF as observed experimentally. This also explains why the optimum P for the experimental cells is observed at a lower value compared to that deduced from the optical simulation.

6.5 Conclusion

In conclusion, we have proposed an approach to fabricate periodic SiNCs using assembled monolayer polystyrene (PS) nanospheres as mask and dry etching process. Hybrid SiNCs/PEDOT:PSS solar cells with different SiNCs periodicity have been fabricated and characterized. Excellent light trapping ability of the SiNCs has been demonstrated by the experimental results. A highest PCE of 7.1% has been achieved for the hybrid cell with a periodicity of 400 nm, due to the strong light trapping near the peak of the solar spectrum and good current collected efficiency. With proper surface treatment and passivation to minimize the defects on the SiNCs surface, it is expected that the performance of the cells can be further improved. The fabrication process employed in this work can also be readily applied to Si thin film to realize low cost and highly efficient hybrid Si/PEDOT:PSS thin film cells based on SiNCs. In addition, we have also investigated the light absorption in a SiNCs/PEDOT:PSS hybrid solar cell structure based on a 3.5 μm thin Si layer. The SiNCs/PEDOT:PSS hybrid structure reveals a highest ultimate efficiency of 33.7% with a periodicity (P) is 600 nm when the top diameter to periodicity is fixed at 0.5. This also demonstrates the light absorption in thin film Si/PEDOT:PSS solar cell can be greatly enhanced with the incorporation of SiNCs.

Chapter 7 Conclusion and Future Work

7.1 Conclusion

In this project, we have systematically studied Si/PEDOT:PSS hybrid solar cells based on planar Si, as well as nanostructured Si that includes Si nanowires (SiNWs) and Si nanocones (SiNCs).

Simple planar Si/PEDOT:PSS hybrid heterojunction solar cells have been demonstrated using spin coating technique based on bulk Si wafers and Si thin films. The planar cells were fabricated and studied in terms of both the PEDOT:PSS thickness and Si thin film thickness. It is found that an optimum PEDOT:PSS thickness of ~78 nm gives rise to the highest short circuit current density (J_{sc}), external quantum efficiency (EQE) and power conversion efficiency (PCE) of 27.0 mA/cm², 63.6% and 10.4% respectively, for cells based on bulk Si. In comparison, a PCE of 8.7% has been achieved for cells based on Si thin films with a Si thickness of 15.5 μ m. It achieved a J_{sc} of 20.4 mA/cm², which is about 78% of that measured for the reference bulk Si cell, despite that thin film cell has only 15.5 μ m thick of Si absorber layer. Optical simulations have also been carried out for the planar thin film hybrid cell structure and the effects of both the PEDOT:PSS thickness and the Si thickness on their light harvesting characteristics studied. It is found that the light absorption is sensitive to the thickness of the PEDOT:PSS layer. An optimum thickness of 70~100 nm has been found, which is consistent with we have observed experimentally, that will lead to minimum light reflection and maximum light absorption. With increasing Si thin film thickness, the simulated J_{sc} is noted to nearly saturate at around a Si thickness of 10 μ m with a remarkable value of 26.4 mA/cm².

To enhance the light harvesting capability of the hybrid cells, Si nanowires (SiNWs)/PEDOT:PSS hybrid cells based on bulk Si wafers have been investigated. The SiNWs were prepared by the metal-catalyzed electroless etching (MCEE) technique. A simple two-step surface treatment method has been proposed to remove Ag nanoparticles surface contaminants and passivate the surface of SiNWs, and thus improve their surface quality. A high efficiency of 12.4% with a high J_{sc} of 30.8 mA/cm² and a high V_{oc} of 0.58 V have been achieved due to the enhancement of light absorption arising from the SiNWs and the suppression of recombination loss attributed to the surface treatment. Compared to similar SiNWs hybrid cells without the surface treatment, the efficiency and V_{oc} are 29.8% and 13.7% enhanced respectively.

SiNWs/PEDOT:PSS solar cells have also been demonstrated on thin film Si that is lower cost and hence more practical as compared to bulk Si wafers. The proposed two-step surface treatment has also been used to treat the SiNWs surface to improve the cell performance. In this study we have applied oxygen (O₂) plasma instead of ozone for the surface treatment. The performance of the hybrid thin film SiNWs/PEDOT:PSS cells have been investigated in terms of the effects of the surface treatment and the wire length. It is found that improvement in the surface quality can also be achieved with the use of oxygen plasma treatment, similar to that using ozone treatment. For a Si film of 10.6 μm thick, we have obtained an average PCE of 7.27% and a maximum PCE of 7.83%, under the optimized SiNWs length of 0.7 μm.

In addition to SiNWs prepared using the MCEE technique, we have studied Si/PEDOT:PSS hybrid cells based on Si nanocones (SiNCs). The periodic Si nanocones (SiNCs) were fabricated by dry etching of Si substrates using assembled monolayer polystyrene (PS) nanospheres as mask. The SiNCs cells have been fabricated with different periodicities (P), and the highest PCE of 7.1% have been measured for the cell with a periodicity of 400 nm, due to its strong light trapping around the peak of the solar spectrum and better current collection efficiency. Optical simulation based on the finite element method has also been carried out to study the optical properties of the SiNCs/PEDOT:PSS cell. For a SiNCs/PEDOT:PSS hybrid solar cell structure based on a 3.5 μm thin Si layer, the light absorption in the cell was found to have been greatly enhanced with the incorporation of SiNCs. It reveals a highest ultimate efficiency of 33.7% with a periodicity (P) is 600 nm when the top diameter to periodicity is fixed at 0.5.

In conclusion, we have studied the Si/PEDOT:PSS solar cells based on planar Si and nanostructured Si, as well as bulk Si wafers and thin film Si. For practical application, Si/PEDOT:PSS solar cells should be ultimately fabricated on thin film crystalline Si or polycrystalline Si grown on low-cost substrates instead of the costly bulk Si. Owing to the simple low temperature process and the low cost material, the Si/PEDOT:PSS hybrid cell is a promising cost-effective alternative to our current energy source.

7.2 Recommendation for future research

Despite the good light trapping capability of the SiNCs, the SiNCs/PEDOT:PSS hybrid cells have relatively lower V_{oc} and FF and thus poorer overall performance than the planar and SiNWs cells. This is believed to be caused by the high surface recombination arising from their surface defects due to the etching process. For our SiNWs cells, surface treatment has been shown to result in significant improvement on the cell performance. A future work would therefore be to apply the proposed two-step surface treatment process to the SiNCs for defects removal and surface passivation, and to improve the cell performance.

In our study both SiNWs and SiNCs structures have been fabricated and incorporated into the Si/PEDOT:PSS hybrid cells, and have shown good light trapping and carrier collection capabilities. For the SiNCs/PEDOT:PSS hybrid cells, only the effect of periodicity of the SiNCs have been studied at this stage. Other structural parameters, such as diameter to periodicity ratio and the height of SiNCs are also important and expected to affect the cell performance. Therefore a future work would be to investigate in detail the other structural parameters of the SiNCs on the performance of SiNCs/PEDOT:PSS hybrid cells.

In our project, SiNWs/PEDOT:PSS solar cells have been demonstrated with high efficiency based on both the single crystalline bulk Si wafer and epitaxially grown thin film Si. As for the SiNCs cells, they have so far been fabricated on bulk Si wafers. A future work would be to demonstrate SiNCs/PEDOT:PSS hybrid cells based on thin film Si, particularly microcrystalline and polycrystalline Si grown on low cost substrate.

In this project, the Si/PEDOT:PSS cells have been fabricated with the PEDOT:PSS layer coated on top of the Si material. It has been reported that [142] a backPEDOT cell with an inverted structure, that is to have the PEDOT:PSS layer below the Si film, can exhibit better light absorption behaviour. The improved performance has also been confirmed by our simulation results presented in Chapter 3. With the PEDOT:PSS layer underneath the Si absorber layer, the parasitic light photons absorbed in the PEDOT:PSS layer is reduced, resulting in more light being absorbed by the Si film. A future work will be to fabricate such backPEDOT cells and study their performance in relation to the conventional cells.

Author's publications

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2. **Hao Wang**, Jianxiong Wang, and Rusli, "Planar Thin-Film Si/PEDOT:PSS Hybrid Solar Cell", *BIT's 5th Annual World Congress of Nano Science & Technology*, Xi'an, China, 24 Sep 2015 (invited).
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