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Si Nanostructures Based Solar Cells

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ABSTRACT

To address the current problems of increasing energy shortages and serious environmental pollutions, clean energy option such as photovoltaic has been actively explored. Currently, the single crystalline silicon (Si) solar cell dominates the photovoltaic market. Unfortunately, its high cost has seriously impeded its competition with fossil fuels and prevented its wide-spread application. To address the cost issue, nanostructures based Si solar cells have been actively researched as the strong light trapping capability of the nanostructures will potentially allow a thinner layer of Si to be employed. In order to further reduce the cost of Si nanostructures based solar cells, hybrid Si/organic cells incorporating conductive polymers have been pursued, leveraging on the benefits of polymers which include low temperature, simple and solution based process capability, and low cost.

In this work we study high efficiency hybrid solar cells based on Si nanohole (SiNH) structures and poly (3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS). The SiNH structures are fabricated on Si substrates using the metal-catalyzed electroless etching (MCEE) method, and the cells are obtained by spin coating of PEDOT:PSS on top. The hybrid cells are optimized by varying the hole depth, and a maximum power conversion efficiency (PCE) of 8.3% is achieved at a hole depth of 1 μm . To better understand the experimental results, we have also simulated the optical characteristics of SiNH structures using the finite element method, and the results are discussed in the context of light trapping and scattering.

The SiNH structures fabricated using the MCEE technique are generally non-periodic. In this work we have also studied the fabrication of periodic SiNH structures with hexagonal unit cell, using a monolayer of patterned polystyrene (PS) spheres as a mask. Periodic SiNH structures with different structural dimensions have been fabricated and investigated in terms of their microstructures and optical reflectance. Compared with planar Si wafer, such structures exhibit much lower reflectance due to the enhanced scattering introduced by the SiNHs. Concurrently we have carried out optical simulation using the finite element method to optimize the structural periodicity and hole diameter for maximum light absorption. The optimum structure is found to have a periodicity of 693 nm and hole diameter of 560 nm, and it yields the highest ultimate efficiency of 28.8%.

Besides the vertical SiNH structures, we have investigated the light absorption characteristics of several other nanoholes structures to examine their potential applications in solar cells. These include (i) slanting SiNH structures where the longitudinal axis of the SiNHs is not aligned perpendicular to the surface of the Si film, (ii) random SiNH structures where randomness has been introduced to the radius, depth and position of the SiNHs, to simulate more realistic non-periodic structures that are achieved using low cost approaches such as the MCEE technique, and (iii) a hybrid solar cell structure that comprises nanopylramids and nanoholes. For the slanting SiNH structures, the optimal condition for maximum absorption of solar energy is achieved when the periodicity is 700 nm and diameter/periodicity ratio is 0.85. The highest ultimate efficiency achieved is 32.9%, which is higher than that of the vertical

counterpart of 29.7%. Therefore, the slanting SiNH structure is a potential approach to further improve the efficiency of Si solar cell. As for the random SiNH structures, it is found that when randomness is introduced to the hole radius, depth and position, the light absorption is significantly improved compared to the periodic nanohole array due to reduced reflectance, additional resonances induced and broadening of the existing resonance. Therefore, structural randomness in SiNH structures is beneficial for light absorption, and hence the use of high cost techniques to fabricate periodic SiNH structures for solar cell application may not be necessary. Lastly, we proposed a hybrid solar cell structure that comprises nanopyramids and nanoholes. The hybrid nanostructure is designed with the smaller NH structure to suppress light reflectance for short wavelength light and the larger NP structure to enhance light trapping for long wavelength light. The optimized structure has a periodicity of 800 nm and nanohole diameter of 560 nm. The hybrid nanostructure has light absorption that is substantially increased above the Lambertian limit, achieving an ultimate efficiency of 38.3%. The ultimate efficiency is maintained above the Lambertian limit even for incident angle up to 50 degree for TM polarized sunlight. The results suggest that the proposed hybrid nanostructure is very promising to achieve high performance solar cell.

To further reduce the cost of Si/organic hybrid solar cells, it is important that the cells are fabricated on Si thin films, rather than bulk Si wafers. In this work we also study the formation of poly-crystalline Si (poly-Si) based on laser annealing of amorphous silicon (a-Si) thin films. Besides achieving crystallization, our approach of using the laser annealing process has also resulted in the formation of nanostructures on the surface of

the poly-Si films, which is important for light trapping and enhancement of optical absorption. In the first study, a 400 nm thick a-Si film is crystallized using a diode-pumped solid-state neodymium doped yttrium orthvanadate (DPSS Nd:YVO₄) UV laser. It is found that with pulse energy of 380 mJ/cm², the a-Si is converted to poly-Si with concurrent nanodome texturing with periodicity of ~ 300 to ~ 500 nm. The absorption efficiency (ultimate efficiency) of the illuminated Si thin film is enhanced by ~ 200% as compared with the untreated a-Si. In our second set of experiments, a femtosecond laser is used to crystallize a-Si film with a thickness of 1.6 μ m, which simultaneously leads to the formation of micro/nanocone structures on the surface with diameters varying from ~ 160 nm to ~ 1.4 μ m. The micro/nanocone structures have resulted in significantly enhanced light absorption as compared with the untreated film. We have also used the same femtosecond laser to fabricate periodic ripple structure on crystalline Si wafer surface with a structural periodicity of 600 nm and ripple modulation height of 300 nm. Compared with planar Si substrate, the ripple structures have substantially suppressed light reflectance, leading to a ~ 41% improvement in light absorption.

Table of Contents

Acknowledgements	xiii
ABSTRACT.....	xv
Table of Contents	xix
List of Figures.....	xxii
List of Tables	xxvi
Abbreviations	xxvii
Chapter 1 Introduction.....	1
1.1 Background and Motivation.....	1
1.2 Objectives.....	5
1.3 Major Contribution of the Thesis	7
1.4 Report Organization	9
Chapter 2 Literature Review	12
2.1 Introduction and Fundamentals of Solar Cells	12
2.2 Organic Solar Cell Device.....	16
2.2.1 Single Junction OPV	17
2.2.2 Bilayer Junction OPV	19
2.2.3 Bulk Heterojunction OPV	20
2.3 Hybrid Solar Cell Device	20
2.4 Nanostructures for Light Trapping.....	22
2.4.1 Si Nanostructured Inorganic Solar Cells.....	27
2.4.2 Si Nanostructured Hybrid Solar Cells.....	30
2.5 Simulation of Nanostructures.....	34
Chapter 3 SiNH/PEDOT:PSS Hybrid Solar Cell.....	37
3.1 Silicon Nanohole PEDOT:PSS Hybrid Solar Cell	37
3.1.1 Introduction and Motivation	37
3.1.2 Experiments Details of Hybrid SiNH/PEDOT:PSS Solar Cell	38
3.1.3 Surface Morphology of SiNH Structures.....	40
3.1.4 Etching Mechanism of Forming SiNH	41
3.1.5 Optical and Electrical Characterizations of SiNH Structures	43
3.2 Simulation of Light Absorption in SiNH/PEDOT:PSS Structure.....	50
3.2.1 Introduction and Motivation	50
3.2.2 Simulation Methodology	50
3.2.3 Light Absorption of Hybrid SiNH Structure	52
3.2.4 Ultimate Efficiency of Hybrid SiNH Structure	55
3.3 Conclusion.....	60
Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application.....	61
4.1 Introduction and Motivation.....	61
4.2 Fabrication and Characterization of SiNHs	62

4.3	Simulation of Light Absorption of Hexagonally Arranged SiNH	67
4.3.1	Introduction and Motivation	67
4.3.2	Simulation Details.....	67
4.3.3	Light Absorption of Hexagonally Arranged SiNH.....	69
4.4	Conclusion.....	76
Chapter 5	Simulation Studies of SiNH Structures.....	78
5.1	Light Absorption of Slanting Nanoholes	79
5.1.1	Introduction and Motivation	79
5.1.2	Simulation Methodology of Slanting SiNH.....	80
5.1.3	Light Characteristic of the Slanting SiNH	81
5.1.4	Experimental Details of Fabrication of Slanting SiNH	89
5.2	Light Absorption of Random SiNH Structure.....	92
5.2.1	Motivation.....	92
5.2.2	Simulation of Random SiNH Structures.....	93
5.2.3	Light Characteristic of Random SiNH.....	95
5.3	Light Trapping in Hybrid Nanopyramid and Nanohole Structures.....	100
5.3.1	Motivation.....	100
5.3.2	Simulation Methodology	101
5.3.3	Lambertian Limit	103
5.3.4	Light Absorption of Hybrid SiNH and Pyramid Structure	103
5.4	Conclusion.....	107
Chapter 6	Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation.....	109
6.1	Introduction and Background.....	109
6.2	Review of Crystallization of Si Thin Films	110
6.2.1	Solid Phase Crystallization (SPC)	110
6.2.2	Metal Induced Crystallization (MIC).....	111
6.2.3	Laser Annealing Crystallization	111
6.3	UV Laser Crystallization of a-Si.....	115
6.3.1	Introduction.....	115
6.3.2	Experimental Details.....	116
6.3.3	Crystallization of a-Si and Formation of Nanodome Structure	118
6.3.4	Optical Characteristics of the Nanodome Structure.....	122
6.3.5	Comparison with Simulation	124
6.4	Femtosecond Laser Crystallization of a-Si	126
6.4.1	Motivation.....	126
6.4.2	Experimental Details.....	127
6.4.3	Formation of Nanocone Structures	128
6.4.4	Crystallization of 1.6 μm a-Si Film	131
6.4.5	Optical Characteristic of the Formed Conical Structures	133
6.5	FS Laser Fabrication of Ripple Structure.....	136
6.5.1	Motivation.....	136
6.5.2	Experiments	137
6.6	Ripple Structure Formation.....	138
6.7	Conclusion.....	145
Chapter 7	Conclusion and Future Work	147

7.1	Conclusion.....	147
7.2	Future Work	149
7.2.1	Removal of Silver Particle from the MCEE process	149
7.2.2	Structural Parameters Optimization.....	150
7.2.3	Surface Passivation for the SiNH Structure.....	150
7.2.4	Transfer to the Thin Film Technology.....	151
Lists of Publications.....		152
References.....		156

List of Figures

Figure 1-1: 2013 Percentage of the world energy supply [1].	2
Figure 1-2 :Forecast of the future energy use by the German Scientific Advisory Board [3, 4].	3
Figure 2-1 : Schematic illustration of a solar cell device [28].	12
Figure 2-2 : Cost and efficiency of three generations of solar cells [29].	13
Figure 2-3 : Photogeneration of carriers in a solar cell resulting in current flow [33].	14
Figure 2-4 : Equivalent circuit of a solar cell [34].	16
Figure 2-5 : Energy band diagram of a bulk heterojunction OPV.	17
Figure 2-6 : Device structure of a single junction OPV.	18
Figure 2-7 : Device structure of a bilayer junction OPV.	19
Figure 2-8 : Device structure of a bulk heterojunction OPV.	20
Figure 2-9 : Schematic of the hybrid solar cell using the nanowire structure and P3OT [46].	22
Figure 2-10 : Illustration of the formation of a nanowire structure [58].	24
Figure 2-11 : Illustration of the formation of the nanocone structure [13].	25
Figure 2-12 : Absorption spectrum of different structures [13].	26
Figure 2-13 : (a)-(e) Schematic of the fabrication process of Si nanowire solar cell. (f) Cross-sectional view of the cell [62].	28
Figure 2-14 : V_{oc} , J_{sc} and FF as a function of roughness for the fabricated SiNW solar cell [56].	28
Figure 2-15 : Illustration of the fabrication steps of the nanodome based solar cells devices[15].	30
Figure 2-16 : Schematical illustration of the fabricated Si nanocone based hybrid solar cell [25].	31
Figure 2-17 : Schematic description of the fabrication process for Si/Spiro hybrid solar cell [20].	32
Figure 2-18 : Schematic illustration for the hybrid solar cell with pyramid and nanowire structures[21].	33
Figure 2-19 : Finite element mesh with (a) triangular elements for two dimensional structure and (b) tetrahedral elements for three dimensional structures [63].	35
Figure 2-20 : Flow chart of HFSS during the adaptive analysis [67].	36
Figure 3-1 : (a) Ag nanosphere formed upon laser annealing, (b) top view SEM of the nanohole structure with H of 1 μm , (c-f) cross-sectional views SEM of the SiNH structure for the hole depth of 0.5 μm , 1 μm , 2 μm and 4 μm respectively and (g) tilted view of the SiNH structure with depth of 1 μm and with the PEDOT:PSS coated on top.	41
Figure 3-2 : Schematic description of the Si etching with Ag as catalyst to form SiNH [24].	42
Figure 3-3 : Reflectance spectra of the SiNH structures with different hole depths.	44
Figure 3-4 : SEM of the surface of the nanohole structure with H of 4 μm .	44

Figure 3-5 : Incident Photon-Electron Conversion Efficiency (IPCE) of the SiNH hybrid solar cells.	45
Figure 3-6 : Current-density-voltage (J-V) curves of the SiNH hybrid solar cells under the illumination of the standard AM 1.5 G irradiation.	48
Figure 3-7 : Schematics illustration of the SiNH hybrid structure with (a) three-dimensional view and (b) cross-sectional view.	51
Figure 3-8 : Optical characteristics of the SiNH hybrid structure with varying P at a fixed D/P ratio of 0.8. (a) Light absorption in Si, (b) absorption in PEDOT: PSS, (c) light reflectance and (d) light transmittance of the overall structure.	53
Figure 3-9 : Optical characteristics of the SiNH hybrid structure with varying D/P ratio at a fixed P of 600 nm. (a) Light absorption in Si, (b) absorption in PEDOT: PSS, (c) light reflectance and (d) light transmittance of the overall structure.	55
Figure 3-10 : Ultimate efficiency of the SiNH hybrid structures.	57
Figure 3-11(a) Unit cell of the hybrid SiNH/PEDOT:PSS structure. Normalized E-fields distribution for different wavelengths when (b) $\lambda = 400$ nm, (c) $\lambda = 750$ nm and (d) $\lambda = 960$ nm.	58
Figure 3-12 Angular dependence of optical absorption of hybrid SiNH/PEDOT:PSS structure.....	59
Figure 4-1 : The SEM images of the initial PS spheres formed on the Si surface. The diameters of the spheres are (a) 330 nm, (b) 476 nm, (c) 600 nm and (d) 800 nm.	63
Figure 4-2 : The SEM images of gold film after PS ball formation. (a) PS ball diameter 330 nm and O_2 plasma of 150 s, (b) PS ball diameter 476 nm and O_2 plasma of 200 s, (c) PS ball diameter 600 nm and O_2 plasma of 250 s, (d) PS ball diameter 800 nm and O_2 plasma of 350 s.	65
Figure 4-3 : The cross-sectional SEM images of gold film after the nanohole formation. (a) PS ball diameter 330 nm and O_2 plasma of 150 s, (b) PS ball diameter 476 nm and O_2 plasma of 200 s, (c) PS ball diameter 600 nm and O_2 plasma of 250 s, (d) PS ball diameter 800 nm and O_2 plasma of 350s.	66
Figure 4-4 : Light reflectance of the periodic nanohole structure fabricated.	66
Figure 4-5 : Schematics illustration of the hexagonally arranged SiNH structure with (a) 3-dimensional view and (b) top view.....	68
Figure 4-6: Light absorption spectra of the hexagonally arranged SiNH structures as a function of the periodicity and a fixed D/P ratio of 0.81.	70
Figure 4-7 : Light absorption spectra of the hexagonally arranged SiNH structures with a varying D/P ratio with a fixed P of 693 nm.	71
Figure 4-8 : Ultimate efficiency of the SiNH structures with different structural periodicity and D/P ratios.	72
Figure 4-9 : Angular dependence of optical absorption of hexagonally arranged SiNH structure and the planar $2\ \mu\text{m}$ thin film structure.....	75
Figure 4-10 : Light absorption spectra of both the hexagonally arranged and squarely arranged SiNH structure. The planar $2\ \mu\text{m}$ thin film serves as a reference.	76
Figure 5-1 : The simulated slanting SiNH structures. (a) 3D view (b) top view and (b) cross-sectional view of the slanting SiNH structure.	81
Figure 5-2 : Absorption spectra of the slanting SiNH structure (a) with different P at a fixed D/P ratio of 0.8 and (b) with different D/P ratios when P is 700 nm.	83

Figure 5-3 : The ultimate efficiency values of the slanting nanohole structure with different P and D/P ratios.	84
Figure 5-4 : (a) Reflectance, (b) transmittance and (c) absorption spectra of the planar 2 μm thin film and the optimal vertical (V-SiNH) and slanting (S-SiNH) SiNH structures.	86
Figure 5-5 : (a) Unit cell of the slanting SiNH. Normalized E-fields distribution for different wavelengths when (b) $\lambda = 400$ nm, (c) $\lambda = 750$ nm and (d) $\lambda = 990$ nm.	87
Figure 5-6 : The ultimate efficiency of the slanting SiNH structure at different incident angles for both TE/TM polarized light.	89
Figure 5-7 : The SEM images of the as-prepared slanting SiNH structure. (a) Top view of the deposited Ag nanoparticles, cross sectional view of the slanting SiNH with an etching concentration of (b) 4.6 M HF and 20 mM H_2O_2 and (c) 4.6 M HF and 2 mM H_2O_2	91
Figure 5-8 : Schematics illustration of (a) periodic SiNH structure, and random SiNH structures with variation in (b) hole radius, (c) hole depth and (d) hole position.	95
Figure 5-9 : (a) Light reflectance, (b) transmittance, and (c) absorption of the SiNH structures with random hole radius.	96
Figure 5-10 : (a) Light reflectance, (b) transmittance, and (c) absorption of the SiNH structure with random hole depth.	98
Figure 5-11: (a) Light reflectance, (b) transmittance, and (c) absorption of the SiNH structure with random hole position.	99
Figure 5-12 : The simulated hybrid structure of nanopyramid and nanohole thin film solar cell structure. (a) 3-dimensional schematic, (b) top view and (c) cross-sectional view of the hybrid structure. The blue color represents Si material while the yellow color refers the nonabsorbing Si_3N_4 that is on top of the hybrid structure. The red color represents the perfect electric conductor.	102
Figure 5-13 : Absorption spectra of the optimized hybrid structure, planar Si thin film cell of 2 μm thick, and Lambertian limit absorption for 1.33 μm thick Si thin film cell.	105
Figure 5-14 : The angular dependence of the ultimate efficiency of the hybrid cell for both TE and TM polarized light.	107
Figure 6-1 : Schematic of near-complete region and following crystallization process [119].	113
Figure 6-2 : Schematic of the layered laser crystallization cell [130].	114
Figure 6-3 : Schematic illustration of laser crystallization process on a-Si thin film: (a) as deposited 400 nm a-Si on 100 nm SiO_2 coated glass surface; (b) laser annealing of a-Si thin film; (c) nanodome structure formation after laser annealing; (d) Secco etch to reveal the grain boundaries.	116
Figure 6-4: SEM images of (a) as-deposited a-Si and 400 nm thick a-Si thin films irradiated under different laser energy densities: (b) 266 mJ/cm^2 , (d) 294 mJ/cm^2 , (e) 380 mJ/cm^2 , (f) 439 mJ/cm^2	118
Figure 6-5 : Raman spectra of 400 nm thick a-Si thin films irradiated with laser energy densities: 294 mJ/cm^2 , 380 mJ/cm^2 , 439 mJ/cm^2 and 507 mJ/cm^2 with intensity peak 520 cm^{-1} . The inset shows the Raman spectrum of the original as deposited a-Si film, with the peak at $\sim 480\text{cm}^{-1}$	120
Figure 6-6 : Surface morphologies of (a) original as deposited planar 400 nm thick a-Si thin film with a roughness of 3.4 nm and (b) UV laser irradiated film with laser energy density 380 mJ/cm^2 . The AFM scan area is 5 $\mu\text{m} \times 5\mu\text{m}$	121

Figure 6-7 : (a) Reflectance, (b) transmittance and (c) absorption spectra of laser treated 400 nm thick a-Si thin films with laser energy densities of 294 mJ/cm ² , 380 mJ/cm ² , 439 mJ/cm ² and 507mJ/cm ² . The original as-deposited planar 400 nm a-Si is used as a reference. (d) Absorption spectra of a-Si thin film with thickness of 100 nm.....	122
Figure 6-8 : Absorption spectra of: (i) experimental 400 nm thick a-Si thin film irradiated with laser pulse energy 380 mJ/cm ² and (ii) simulated Si nanodome structure with a periodicity of 300 nm and 400 nm. The dome height is 300 nm and the underlying film is 100 nm. The inset shows the simulated periodical nanodome structure.....	125
Figure 6-9 : AFM images of 1.6 μ m Si thin film treated with different laser fluences : (a) as-deposited, (b) 255 mJ/cm ² , (c) 333 mJ/cm ² , (d) 372 mJ/cm ² , (e) 490 mJ/cm ² , (f) 588 mJ/cm ² and (g) 784 mJ/cm ² . The AFM scan area is 5 μ m $\times$ 5 μ m.....	129
Figure 6-10 : SEM images of 1.6 μ m Si thin film treated with laser fluences : (a) 588 mJ/cm ² and (b) 784 mJ/cm ²	130
Figure 6-11 : Diameter and height of the as formed conical structures after laser irradiation under different laser fluences.	131
Figure 6-12 : (a) Raman spectra of 1.6 μ m a-Si thin films treated with different laser fluences. (b) Crystallization volume fraction of c-Si film under different laser fluences.	132
Figure 6-13 : (a) Reflectance, (b) transmittance, and (c) absorbance spectra of laser treated 1.6 μ m a-Si thin films with laser fluence of 294 mJ/cm ² , 372 mJ/cm ² , 490 mJ/cm ² , 588 mJ/cm ² and 784mJ/cm ²	134
Figure 6-14 : (a) Camera photo (b) optical microscope image of area labeled by “x” in (a) and (c) SEM image for the FS laser treated Si substrate.	139
Figure 6-15 : SEM images of laser processed Si wafer irradiated under different laser fluence (a) 411 mJ/cm ² , (c) 450 mJ/cm ² , (c) 490 mJ/cm ² , and (d) 676 mJ/cm ²	140
Figure 6-16 : (a) 3-dimentional (b) cross-sectional view of surface morphologies of sample irradiated with laser fluence of 490 mJ/cm ² . The AFM scan area is 5 μ m $\times$ 5 μ m.	141
Figure 6-17 : The excited quasifree carrier densities in the conduction band of Si as a function the FS laser fluence and the critical carrier density with Drude plasma resonance.....	143
Figure 6-18 : Reflectance spectra of original Si wafer and nano-ripple structure with P of 600 nm and D of 300 nm irradiated with laser fluence of 490 mJ/cm ²	144

List of Tables

Table 3.1 : Summary of the Photovoltaic Parameters.....	46
Table 5.1 : Ultimate Efficiencies of Different Random SiNH Structures.	97

Abbreviations

AFM	Atomic force microscopy
Ag	Silver
AM 1.5G	Air Mass 1.5 Global
a-Si	Amorphous silicon
CVD	Chemical vapor deposition
D	Diameter
DPSS Nd:YVO ₄	Diode-pumped solid-state neodymium doped yttrium orthovanadate
E-field	Electric field
F	Laser fluence
FDFD	Finite difference frequency domain
FDTD	Finite difference time domain
FEM	Finite element method
FESEM	Field-emission scanning electron microscopy
FF	Fill factor
H	Hole depth
HFSS	High frequency structure simulator
HOMO	Highest occupied molecular orbital
IPCE	Incident photon-to-electron conversion efficiency
ITO	Indium tin oxide
J _{sc}	Short-circuit current density
J-V	Current density voltage
LLC	Layered laser crystallization
LUMO	Lowest occupied molecular orbital
MCEE	Maskless metal-catalyzed electroless etching
MIC	Metal induced crystallization
NH	Nanohole
NP	Nanopyramid
OPV	Organic photovoltaic
P	Periodicity
PCE	Power conversion efficiency
PEC	Perfect electric conductor
PEDOT:PSS	Poly (3,4-ethylenedioxythiophene):polystyrene sulfonate
PNS	Periodic nanohole structure
Poly-Si	Polycrystalline silicon
PS	Polystyrene
PV	Photovoltaic
RIE	Reactive ion etching
RNS	Random nanohole structure
SEM	Scanning electron microscope
SiNH	Silicon nanohole
SiNW	Silicon nanowire
SPC	Solid phase crystallization
TE	Transverse-electric
TM	Transverse-magnetic

TMM	Transfer matrix method
UV	Ultraviolet
V_{oc}	Open circuit voltage
η_{UE}	Ultimate efficiency
λ	Wavelength

Chapter 1 Introduction

1.1 Background and Motivation

In the past decades, we have witnessed serious energy and environmental crisis caused by fossil fuels consumption. Fig. 1.1 compares the shares of the world primary energy supply in 1973 and 2011 [1], where it is clearly seen that energy consumption is still mainly powered by three conventional sources, which are gas, oil and coal. The rapid depletion of fossil fuels and the environmental issues resulting from their use, such as air pollution and global warming, have resulted in strong attention towards the use of renewable and clean energy. This is important not only to conserve and protect the environment, but also to sustain economic development. Among the various renewable and clean energy sources, photovoltaic (PV) is the most promising as it is clean, environment friendly and inexhaustible [2]. Although the cost is relatively high at present for PV devices, the increased environmental awareness and continuous progress made towards achieving higher efficiency and lower cost have made them an attractive option. Fig. 1.2 shows the prediction of the energy share for the next hundred years by the German scientific advisory board [3, 4]. By the year 2050, the production of oil, gas and coals will reduce, and correspondingly there will be a high demand for solar energy. By year 2100, as coals are depleted, the share world energy consumption will be completely changed and dominated by solar energy. Therefore, solar energy presents a bright future for renewable energy.

Currently, the world PV market has observed significant growth since 2000 with an annual growth rate of over 40% [5], which is dominated by commercial crystalline

Chapter 1 Introduction

silicon(Si) solar cell [6]. The high quality single crystalline Si has made it perfect for carrier transportation. In addition, it has the advantages of material abundance, mature technology and common process infrastructure with the developed CMOS industry. A high efficiency over 25% has been achieved by the University of New South Wales on single crystalline Si using a PERL cell [7, 8], approaching the theoretical efficiency limit predicted by Shockley [9]. On the other hand, because of the indirect band gap property of crystalline Si, it requires over 200 μm thick Si for efficient light absorption, which accounts for more than half of the solar cell module cost [2].

Figure 1-1: 2013 Percentage of the world energy supply [1].

To lower the cost, Si thin film based solar cells have been explored and gained extensive attention. When the thickness of the Si absorbing layer is only several micrometers, light absorption is significantly reduced and consequently light trapping mechanisms are needed to improve absorption. Different nanostructures have been actively researched to address this issue, which include Si nanowire [10, 11], nanocone [12], nanodome [13], and nanopillar [14] arrays. Typically the dimensions of the nanostructures are comparable

Chapter 1 Introduction

with the wavelength of the main solar spectrum to enhance scattering and extend the optical path length of sunlight, leading to significantly stronger light absorption.

Figure 1-2 :Forecast of the future energy use by the German Scientific Advisory Board [3, 4].

Complex equipment or lithography techniques are normally required to fabricate the ordered nanostructure [15, 16]. There exists a low cost maskless method of fabricating Si nanostructures based on metal-catalyzed electroless etching (MCEE). This has motivated strong research interest to consider applying such the nanostructures to improve the Si solar cell efficiency while reduce processing cost. The MCEE technique has been commonly used to fabricate Si nanowire (SiNW) structures. On the other hand, the use of the technique for the fabrication of Si nanohole (SiNH) structures is not common and not widely reported [17]. There are several advantages offered by SiNH structures over SiNW structures. Compared with free-standing nanowire based crystalline Si solar cells which are fragile and easily cracked, the nanohole structure is much more mechanically robust and has demonstrated a higher short circuit current density [16]. The light trapping ability of SiNH structure has also been proven to be higher than SiNW structure with the

Chapter 1 Introduction

same filling ratio [18]. Therefore, it is more effective in improving light absorption within the Si film. Besides, due to the interconnecting geometry of nanohole, it can enhance carrier transport as compared to the nanowire geometry. In addition, the geometry of nanohole would ease electrode fabrication and result in better contact as compared with nanowire structure [16]. Lastly, the nanohole fabrication depends less on the Si material quality than the nanowire, which provides the potential to further reduce the raw material cost by using cheaper Si, such as multi-crystalline Si.

Apart from the research on nanostructures based Si solar cells, there has been effort directed toward the study of hybrid solar cells built using a combination of inorganic semiconductors such as Si and organic materials [19-22] in the recent years to lower the cost of solar cells. Such solar cells offer the combined advantages of inorganic semiconductors, such as long diffusion length, high carrier mobility and mechanical strength, and organic materials that include low temperature and low cost process. Although the initial power conversion efficiency reported in 2002 for the hybrid CdSe nanorods solar cell with the conjugated polymer is low at only 1.7%, it has already demonstrated great potential to achieve higher efficiency solar cell with reduced cost[23]. Since then tremendous progress has been achieved for hybrid cells, particularly the hybrid Si/PEDOT:PSS solar cell with the introduction of nanostructures to improve light absorption [24, 25]. A world record efficiency of 13.01% has been recently achieved for Si nanowire based hybrid solar cells [26]. Therefore, hybrid solar cells are potentially efficient and low cost, and are promising in rendering solar cells affordable to encourage their widespread utilization.

Chapter 1 Introduction

In this project, we propose to study hybrid Si/PEDOT:PSS solar cell with the incorporation of SiNH structure for light trapping. In contrast to conventional crystalline Si solar cell, only simple and low cost solution based processes are required for the fabrication of hybrid SiNH solar cell. On the other hand, compared with organic solar cell, it has demonstrated great potential to achieve higher efficiency due to the use of higher mobility carrier Si and the incorporation of nanostructures. Therefore, the hybrid SiNH/PEDOT:PSS solar cell can substantially offer high efficiency at low cost, and is promising for practical applications in the future.

In this work we also conduct a systematic analysis of the optical characteristics of SiNH structures with different arrangements and configurations, to understand the physics behind the light absorption in the nanostructures. It is expected that due to the strong interaction between the nanostructures and the incident sunlight, the effective optic path length is significantly increased, leading to strong light absorption enhancement. The simulation studies can also help to identify the optimal structural parameters that give rise to the highest efficiency.

1.2 Objectives

In this project, silicon nanohole based hybrid Si/PEDOT:PSS solar cells are studied. The light absorption characteristics of the SiNH structure are also investigated. The scope of the work includes the design, fabrication and characterization of SiNH/PEDOT:PSS hybrid solar cells, and optical simulation of SiNH structures with different configurations using the finite element method. The objectives of this study are summarized as follows:

Chapter 1 Introduction

1. Study the fabrication of SiNH structures using the metal-catalyzed electroless etching (MCEE) method and characterize their surface morphology.
2. Fabricate SiNH/poly(3,4-ethylene-dioxythiophene): polystyrenesulfonate (PEDOT:PSS) hybrid solar cells and characterize their electrical, optical and photovoltaic properties. The impact of the hole depth on the hybrid solar cell efficiency will be investigated.
3. The SiNH structures fabricated using the MCEE method are non-periodic and non-uniform. In this work we also study the fabrication of periodic SiNH structure with a hexagonal unit cell using a layer of polystyrene spheres (PS) as a mask. The microstructures and optical reflectance of the structures are characterized.
4. Besides the conventional SiNH structures, other SiNH structures that include slanting SiNH, random SiNH and hybrid nanohole and nanopyramid structures are systematically investigated using optical simulation based on the finite element method. The structural parameters are varied to determine the optimum structures that give rise to maximum absorption of solar energy.
5. The fabrication of SiNH/PEDOT:PSS solar cells demonstrated in this work is based on bulk Si wafer which however is not a practical approach due to the high cost involved. To be practical, such hybrid solar cells should be fabricated on thin film Si. In this work we also study the realization of poly-crystalline Si thin film

Chapter 1 Introduction

from amorphous Si thin film using laser annealing, with concurrent formation of nanostructures on the surface.

1.3 Major Contribution of the Thesis

SiNH arrays with strong light absorption ability have been fabricated using the electroless chemical etching process, which is simple, solution based and scalable. Based on the SiNHs fabricated, we have successfully demonstrated hybrid SiNH/PEDOT:PSS solar cells. By varying the SiNH depth of the hybrid solar cells, the optimized structure has been identified with a hole depth of 1 μm , and it reveals the highest power conversion efficiency of 8.3%. In addition, we have simulated the light absorption of the SiNH/PEDOT:PSS hybrid solar cells using the finite element method. The optimal absorption condition is achieved when the structural periodicity is 600 nm and the diameter to periodicity ratio is 0.8, and it offers the highest ultimate efficiency of 30.5%.

Periodic SiNH structures with a hexagonal unit cell and different structural dimensions have been fabricated using a monolayer of polystyrene (PS) spheres patterned as mask. The SiNH structures fabricated have periodicity ranging from 330 nm to 800 nm, and exhibit a substantially reduced light reflectance due to their comparable dimensions with the wavelength of sunlight. A systematic simulation study of the light absorption has also been conducted for the periodic SiNH structures. It is found that maximum light absorption occurs for a structure with periodicity of 693 nm and hole diameter of 560 nm, yielding an ultimate efficiency of 28.8%. In addition, the light absorption of the periodic SiNH structures with the hexagonal unit cell has been compared with those having a

Chapter 1 Introduction

square unit cell. Both exhibit comparable light absorption and the result is slightly better for those with square unit cell due to the presence of fewer symmetric planes.

Apart from the periodic and vertically aligned SiNH structure, we have also studied light absorption for three other types of SiNH structures having different configurations. Firstly, slanting SiNH structure has been investigated using optical simulation and the optimal structure has been identified with the periodicity of 700 nm and diameter/periodicity ratio of 0.85. It exhibits the highest ultimate efficiency of 32.9%, which is higher than that of vertical SiNH structure of 29.7%. Concurrently, we have also demonstrated how slanting SiNH structures can be fabricated using a simple and low cost process. Secondly, randomness in the structural parameters of SiNH structure, which include the hole radius, depth and position, has been introduced and it is found from optical simulation that the light absorption is significantly improved compared to the periodic SiNH structure due to reduced reflectance, additional resonances induced and broadening of the existing resonance. Lastly, a hybrid structure comprising nanopylramids and nanoholes has been investigated using optical simulation. The optimized structure has been identified with the periodicity of 800 nm and nanohole diameter of 560 nm, and it is found to have an absorption that is above the Lambertian limit, achieving an ultimate efficiency of 38.3%. The high ultimate efficiency is maintained above the Lambertian limit even for incident angles up to 50° for TM polarized sunlight. The results suggest that the proposed hybrid nanostructure is very promising to achieve high performance solar cell.

Chapter 1 Introduction

We have also successfully crystallized amorphous thin film using laser annealing in two sets of experiments. In our first study, 355 nm DPSS Nd:YVO₄ laser was used to crystallize and texture 400 nm thick a-Si thin film in a one-step annealing process. The a-Si film was converted to poly-Si with nanodome texturing, with periodicity of around 300 to 500 nm. The absorption efficiency (ultimate efficiency) of the UV laser treated Si thin film was enhanced by ~ 200% compared with the original unannealed a-Si film. The improved material quality and enhanced light trapping capability render such films promising for applications in high efficiency Si thin film solar cells. In the second study, a thick 1.6 μm a-Si film was successfully crystallized with the formation of micro/nanocones structure using ultrafast femtosecond laser annealing. The micro/nanocones formed have diameters varying from ~ 160 nm to ~1.4 μm , leading to substantial light absorption enhancement. In addition, we have also studied the use of femtosecond laser on Si substrates to realize uniformly distributed periodic ripple structure over a large area, with the periodicity of 600 nm and modulation height of 300nm. Compared with planar Si substrate, the ripple structure has substantially suppressed light reflectance, and an absorption enhancement of ~ 41% has been demonstrated.

1.4 Report Organization

This thesis consists of seven chapters as follows:

Chapter 1: An introduction to the background, motivation and objectives of the project is presented. The organization of the report is also covered.

Chapter 1 Introduction

Chapter 2: The operating principle of a solar cell is presented. Following that we review the development of organic solar cells and the use of nanostructures for light trapping in solar cells. Next, the operating principle and the advantages of Si/organic hybrid solar cells are examined. Finally, the details of simulation of light absorption in nanostructures are discussed.

Chapter 3: The fabrication process for SiNH structures and hybrid SiNH/poly (3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) solar cells is presented. The characterization and simulation results of the hybrid cells are discussed and analyzed.

Chapter 4: The use of PS spheres for the fabrication of periodic SiNH structure having hexagonal unit cell and different structural periodicities and hole diameters is presented. A theoretical simulation of light absorption in the SiNH structure is also carried out to determine the optimized structure that will give rise to maximum solar energy absorption.

Chapter 5: Different SiNH structures, which include slanting SiNH structure, SiNH structure with randomness in its structural parameters and a hybrid nanostructure that comprises nanopyramids and nanoholes, are investigated using optical simulation based on the finite element method. The absorption results of these structures are analyzed and the optimized structures for maximum absorption are identified.

Chapter 6: Two methods to achieve poly-Si from a-Si thin films, using one-step laser annealing process with the concurrent formation of nanostructures are discussed. The microstructures and morphology of the poly-Si formed are analyzed in relation to the

Chapter 1 Introduction

energy density of the lasers used. The measured reflectance of the poly-Si films formed are also presented and discussed.

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

Chapter 2 Literature Review

This chapter gives a literature review on the fundamentals of solar cells, silicon nanohole structures, hybrid solar cells and simulation work related to solar cells. Firstly, an introduction to the fundamentals of solar cells will be presented and organic and hybrid solar cells will be discussed. Following that, a review of different methods of fabrication of nanostructures is examined. The simulation of optical characteristics of nanostructured based solar cells is then reviewed.

2.1 Introduction and Fundamentals of Solar Cells

Figure 2.1 shows the basic structure of a solar cell device which can directly convert sunlight into electricity. The steps involved in the operation of a solar cell are light absorption, charge transportation and charge collection [27, 28]. When light is incident on the cell and absorbed by the active material, charge carriers are generated in the form of electron-hole pairs. The separation, transportation and collection of these carriers at the electrodes will generate current and voltage, and hence electric power, at the external circuit [28].

Figure 2-1 : Schematic illustration of a solar cell device [28].

Chapter 2 Literature Review

Currently, solar cells can be classified into three generations as shown in Fig. 2.2 [29]. The first generation solar cells are based on crystalline bulk Si, which account for 80% of the commercial solar cell market. The group headed by Prof. Martin Green at University of New South Wales has made tremendous contribution to the development of first generation solar cells [2, 7, 30, 31]. The second generation solar cells are based on thin films instead of bulk materials, with an aim to reduce material usage and lower the cost. They include copper indium gallium selenide (CIGS), cadmium sulfide (CdS), cadmium telluride (CdTe), amorphous and polycrystalline Si. The third-generation solar cells focus on improving the cell efficiency while reducing the cost. Some examples include quantum dots/well, hot carrier, intermediate band, multi-junction and tandem solar cells[32].

Figure 2-2 : Cost and efficiency of three generations of solar cells [29].

Chapter 2 Literature Review

Although many materials are suitable for photovoltaic energy conversion, practically all inorganic photovoltaic devices are operating in the form of a p-n junction, which comprises n-type and p-type semiconductors putting together as shown in Fig. 2.3 [33]. The Fermi levels in both semiconductors are aligned under thermal equilibrium, resulting in a built-in electric field developed over the depletion region. When light is incident on the cell, photons with energy greater than the band gap of the material will excite electrons from the conduction band to the valence band, leading to generation of electron-hole pairs. The drift of the generated e-h pairs will produce electric current.

Figure 2-3 : Photogeneration of carriers in a solar cell resulting in current flow [33].

Figure 2.4 shows the equivalent circuit of a solar cell which consists of a current generator in parallel with a diode [34]. Two resistances are included to correctly model the cell. One is the series resistance and the other is shunt resistance. The series resistance is contributed by resistance to the carrier flow in the material and at the contact between the semiconductor and metal electrodes [34]. The shunt resistance is caused by leakage of

Chapter 2 Literature Review

current from one terminal to the other, bypassing the junction [34]. To achieve high power conversion efficiency (PCE), the shunt resistance should be high and the series resistance should be low. As the generated electrons and holes diffuse separately into its respective electrodes, they tend to recombine. Therefore, in order to achieve a high efficiency cell, the carrier recombination should be minimized.

The four most important parameters to measure the performance of a solar cell are the short circuit current density (J_{sc}) when the biased voltage is zero, open circuit voltage (V_{oc}) when the current is zero, fill factor (FF) and power conversion efficiency (η) which are given below [28]:

$$J_{sc} = q \int (P(E)\eta(EQE))dE \quad (2.1)$$

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

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \quad (2.3)$$

where $P(E)$ is the spectral irradiance of the standard AM1.5G solar spectrum for each photon energy, $\eta(EQE)$ is the external quantum efficiency, k is the Boltzmann constant, J_0 is the diode saturation current, P_{max} is the maximum power generated by the solar cell, P_{in} is the incident sunlight energy and the FF is the fill factor, which is a ratio of the P_{max} to the product of V_{oc} and I_{sc} [28].

Figure 2-4 : Equivalent circuit of a solar cell [34].

2.2 Organic Solar Cell Device

Solar cells based on inorganic materials are normally expensive since they usually involve high cost processes such as CVD deposition, high temperature furnace annealing, and low pressure deposition. To lower the fabrication cost, organic photovoltaic (OPV) has been actively pursued attracted due to its advantages of flexibility, low temperature and cheap solution based process [35-37]. Ever since the early low efficiency OPV of 1% reported in 1986 [38], the OPV has made many breakthroughs with power conversion efficiency crossing over 10% recently [39]. The operating mechanism of OPV is different from that of inorganic solar cells. Fig. 2.5 gives a schematic illustration of the band diagram of an OPV device. In the equilibrium state for the organic material, an orbit of HOMO (highest occupied molecular orbital) level and LUMO (lowest occupied molecular orbital) level will be formed, which is similar to the conduction band and covalent band respectively for an inorganic semiconductor material [40]. When the incident light shines on the material, excitons are generated, which are similar to e-h pairs

Chapter 2 Literature Review

in inorganic solar cell devices. The generated excitons are then separated into electrons and holes to generate the current.

Figure 2-5 : Energy band diagram of a bulk heterojunction OPV.

OPV can be divided into following categories. They are single junction OPV, bilayer junction OPV and bulk heterojunction OPV.

2.2.1 Single Junction OPV

For the single junction OPV, it is the simplest form of the OPV which is schematically illustrated in Fig. 2.6. A single layer of organic material is sandwiched between two electrodes. At one layer, a high work function material, such as indium tin oxide (ITO) is used. At the other layer, a low work function material is used. Therefore, there is an electric field established due to the difference in the electrode work function [41]. Upon the sunlight absorption, the electron is excited to the LUMO and the holes into the HOMO to form an exciton. The electric field difference induced by the electrodes will separate the generated excitons to result in electric current. The generated holes will travel to the high work function electrode while the electrons will travel to the low work

Chapter 2 Literature Review

function electrode. Therefore, the work function of the high work function material should be sufficiently high to match the energy level of the polymer's HOMO level. Similarly, the low work function material on the other electrode should match the energy level of the LUMO [42]. Hence, the difference between the work functions of the two electrodes leads to an electric field that separates the generated carriers. In addition, in the original Metal-Insulator-Metal model, the maximum V_{oc} that can be achieved for the solar cells is determined by the work function difference [43]. Hence, it has a critical effect on the final cell efficiency of organic solar cells. The work functions of commonly used metal electrode materials are listed as follows: In (4.2 eV), Al (4.4 eV), Ag (4.6 eV), Cu (4.7 eV), Au (5.2 eV), ITO(4.1-5.3 eV), Ca (2.9 eV), Li (2.9 eV), Mg (3.66 eV) [44]. Although such an OPV device is simple, its quantum efficiency and power conversion efficiency are very low [38] , due to the high recombination of the generated excitons before reaching the electrodes.

Figure 2-6 : Device structure of a single junction OPV.

Chapter 2 Literature Review

2.2.2 Bilayer Junction OPV

For the bilayer junction OPV, there are two layers sandwiched between the electrodes as shown in Fig. 2.7, with one labeled as electron donor and the other electron acceptor. Once the two organic materials are put together, the electrostatic forces will be induced at the interface between the two materials due to the differences in their electron affinity and ionization energy [19]. Upon sunlight absorption, excitons are generated at the interface of the two organic materials and separated due to the established electrostatic force. Due to the strong local field induced by the organic materials, it can break up the excitons more efficiently than the single junction OPV [19]. However, one critical disadvantage of the bilayer junction OPV is that it needs an active absorbing layer over 100 nm to efficiently absorb the sunlight. Therefore, for such OPV device, the generated exciton separation is only effective near the interface between the two organic materials. For the exciton generated far away from the interface, it will recombine before reaching the junction interface because its diffusion length is only in the order of 10 nm [45].

Figure 2-7 : Device structure of a bilayer junction OPV.

Chapter 2 Literature Review

2.2.3 Bulk Heterojunction OPV

To overcome the problem with the bilayer junction OPV, bulk heterojunction OPV has been developed. Instead of separating the electron donor and acceptor as in the bilayer junction, they are mixed together for the bulk heterojunction OPV to form a polymer blend as shown in Fig. 2.8. By controlling the blend length to be comparable with the exciton diffusion length, the generated excitons can easily diffuse to the interface to be separated instead of recombined [19].

Figure 2-8 : Device structure of a bulk heterojunction OPV.

2.3 Hybrid Solar Cell Device

Although there has been tremendous progress and breakthrough achieved for organic solar cells, some disadvantages of organic solar cells have impeded their commercialization. Compared with the inorganic solar cells, organic solar cells have lower power conversion efficiency, and the cells stability is also low as they will easily degrade in ambient environment. To leverage on the advantages of organic solar cells such as their flexibility, lightweight, and low-cost production, and advantages of inorganic solar cell such as their high carrier mobility, long diffusion length and

Chapter 2 Literature Review

mechanical strength, the idea of hybrid solar cells has been developed. Polymer materials based on poly (3-octylthiophene) (PO3T) [46], poly (3-hexylthiophene) (P3HT) blended with [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) [47], and poly (3,4-ethylenedioxy-thiophene): poly (styrenesulfonate) (PEDOT:PSS) [21] have been actively investigated. For the inorganic material, in the early stage, lead sulfide (PbS) [48], cadmium sulfide (CdS) [49], titanium dioxide (TiO₂) [50], and zinc oxide (ZnO) [51] have been actively researched. However, hybrid solar device made from PbS or CdS will result in serious environmental issues, which impede their further development. For the hybrid solar devices based on TiO₂ or ZnO, their high bandgap makes it difficult to absorb the sunlight spectrum with low energy, leading to lower efficiency. To address the environmental compatibility issue and improve the power conversion efficiency for hybrid solar cells, Si based hybrid solar cells have been actively researched and made a significant progress in terms of the power conversion efficiency [24-26, 52].

Figure 2.9 plots the schematic of a hybrid solar cell based on Si nanowire structure and P-type poly (3-octylthiophene) (P3OT) as reported by Kalita et al. [46]. Carbon nanotubes (CNTs) have been added into the P3OT solution to improve the carrier transportation and exciton dissociation. The gold electrode was evaporated on the top layer of the cell. The efficiency has improved from 0.09% for planar cells to 0.61% for Si nanowire cells. Although the absolute power conversion efficiency is low, the work has open up a new frontier of research on hybrid solar cells. Since then tremendous progress has been made in the development of hybrid solar cells based on Si, with the highest power conversion efficiency of 13.01% reported [26].

Figure 2-9 : Schematic of the hybrid solar cell using the nanowire structure and P3OT [46].

2.4 Nanostructures for Light Trapping

As Si thin film thickness is reduced down to several micrometers for cost saving in solar cells, the light absorption is compromised substantially because of the low absorption coefficient of Si, especially in the long wavelength region. Therefore, surface texturing techniques have been actively applied in the thin film solar cell technology for light trapping and absorption enhancement. Conventionally KOH has been used to etch Si to form pyramid structure for light trapping. This approach, however, is not suitable for solar cells based on thin films since the typical dimension of the pyramid formed is larger than the film thickness [53]. There has been research focusing on the use of nano-scale structures to boost light absorption and increase the short circuit current for thin film solar cells. Nanowire [10], nanodome [54], and nanocone[12] structures based solar cells have been demonstrated and revealed great potential to yield high power conversion efficiency owing to their strong light trapping capability. Those nanostructures can effectively scatter light into the active absorbing layer, extend the effective optical path

Chapter 2 Literature Review

length and increase light absorption [11]. Currently, the most widely researched structure is Si nanowire based devices [10, 55, 56].

For the synthesis of Si nanowires, it is generally categorized into bottom up and top down approaches. For the bottom up approach, the chemical vapor deposition is used, among which the vapor liquid solid method is the most commonly utilized [57]. The nanowires are synthesized in a furnace with the flowing chemical precursor vapors react on a substrate with the assistance of some metal catalyst particles. The metal particles will form a liquid eutectic with the Si material. When the flowing chemicals decompose in the liquid eutectic, the Si will precipitate because of the super saturation of the solution [57]. As for the top down method, it involves lithography processes using e-beam or nanoimprinting to form a layer of mask with the dimension the same as the nanowire structure. It is then followed by deep reactive ion etching (RIE) to etch away unwanted Si to form the desired nanowires. The above those processes require special equipment setup and are costly [10].

To reduce the process cost for the fabrication of Si nanostructures, metal assisted chemical etching has been developed to offer a solution based and low cost approach, which also provides the flexibility to control the nanowire diameter and periodicity. Fig.2.10 shows the schematic description for the formation of Si nanowires using this approach [58]. Firstly, a single layer of polystyrene (PS) spheres is spin coated or dip coated on the Si substrate. After that the diameter of the PS balls is reduced using RIE process. Next, a thin layer of silver film is deposited to cover the whole surface. The

Chapter 2 Literature Review

sample is then dipped into a solution with a mixture of HF and H₂O₂. The patterned PS ball monolayer functions as a mask as in the lithographic process and the silver layer acts as the catalyst for etching to form the nanowire structure. The PS balls are then removed using CHCl₃ solution and the silver film dissolved in boiling aqua regia. Using this method, the diameter and periodicity of the Si nanowires formed can be exactly controlled by the PS ball size and the RIE time.

Figure 2-10 : Illustration of the formation of a nanowire structure [58].

In the presence of the nanowire structure, the reflectance of Si is substantially reduced and the light absorption is much higher compared to planar Si [10, 11]. However, because of the abrupt variation in the effective refractive indices between air and nanowire structure, there is still a significant amount of light being reflected [59]. To address this issue, other structures such as nanodome, nanopyramid and nanocone ones have also been developed for light trapping. Fig. 2.11 shows the scanning electron microscope

Chapter 2 Literature Review

pictures of the nanocone structure reported by Jia et al. [13]. The nanowires were developed using the Cl_2 based anisotropic RIE etching. After the formation of the nanowire structure, it was sharpened by $\text{C}_2\text{ClF}_5/\text{SF}_6$ gas through further isotropic etching, resulting in undercut generated. The PS ball layer also functioned as the etching mask for the development of the nanocone structure. In addition, the tip radius and aspect ratio of the nanocone structure can be precisely controlled by the etching conditions.

Figure 2-11 : Illustration of the formation of the nanocone structure [13].

The nanocone structure demonstrates much stronger light absorption ability compared to the nanowire structure. Fig. 2.12 shows the absorption spectra of planar Si thin film, Si nanowire and Si nanocone structures at the normal incidence [13]. The absorption of the nanowire structure is improved from ~65% of planar thin film to ~80%. It is further increased to 90% for the nanocone structure, indicating that the incident sunlight is

Chapter 2 Literature Review

strongly absorbed by the nanocone structure, due to the more gradual variation of the effective refractive index compared with the nanowire structure [59].

Figure 2-12 : Absorption spectrum of different structures [13].

Therefore, by the introduction of the nanostructure, the light absorption can be substantially improved. Firstly, the light reflection is sufficiently suppressed by the nanostructure due to the better index matching. Secondly, the light trapping properties provided by the nanostructure can effectively improve the light absorption and reduce the amount of light transmission [10]. Therefore, the reduced light reflection and transmission leads to the significantly enhanced light absorption for nanostructure based solar cell. It has been shown that the nanowire and nanocone structures have demonstrated high light absorption over a broad range of the solar spectrum and incident angles as compared with the planar film due to the gradual change of the refractive index of the nanostructure [12]. Another common factor for the light absorption enhancement is

Chapter 2 Literature Review

due to the random surface texturing. Hence, the sunlight can effectively scatter around the nanostructure, extending the effective path length. Yoblonovitch has derived the limit for this kind of light absorption enhancement. It is shown that the optical path length can be effectively increased by $4n^2$ after angle averaging is taken into consideration, where n is the refractive index of the material [60]. In addition, the light absorption of single nanowire structure is found to be improved due to the leaky-mode resonance caused by the optical resonances around the nanowire diameter [61]. This identified resonance effect has shown a strong dependence on the nanowire diameter and the incident angles. However, by adjusting the structure dimensions, high light absorption enhancement can be achieved. Furthermore, for the ordered periodic nanostructure, the light absorption can be further improved due to the diffraction effect, the collective resonances and the changes in the optical density states [10]. Therefore, the best nanowire structure has demonstrated a 73 times increment, exceeding previously mentioned limit of $4n^2$ by effectively coupling light into the wave guiding modes of the structure [56]. In addition, the reported ordered nanostructure has shown a high light absorption enhancement at different incident angles. Therefore, those nanostructures have demonstrated a promising solution to enhance the power conversion efficiency for the solar cells devices.

2.4.1 Si Nanostructured Inorganic Solar Cells

Si nanostructure inorganic solar cells have opened up the door to lower quality material and lower cost process while maintaining high power conversion efficiency. The cell can either form radial junction or axial junction for carrier transportation [10, 62]. For the radial junction, not only the light absorption is increased, but the defect tolerance is also increased. Wong et al. has fabricated a nanowire based Si solar cell with a J_{sc} value of

Chapter 2 Literature Review

34.3 mA/cm² [62]. Fig. 2.13 gives the illustration of the cell fabrication process. It involved lithography and RIE etching to form the desired nanowire structure on Si bulk wafer substrate. Plasma-enhanced chemical vapor deposition deposited Si₃N₄ was used to passivate the junction surface to improve the cell performance. The Si nanowire was then electrically connected by depositing a thin layer of transparent conducting oxide (TCO).

Figure 2-13 : (a)-(e) Schematic of the fabrication process of Si nanowire solar cell. (f) Cross-sectional view of the cell [62].

Figure 2-14 : V_{oc} , J_{sc} and FF as a function of roughness for the fabricated SiNW solar cell [56].

In addition, the performance of the fabricated Si nanowire solar cell depends on the nanowire dimension. Fig. 2.14 shows the V_{oc} , J_{sc} and fill factor of SiNW cell observed by

Chapter 2 Literature Review

Yang et al. [56]. The roughness factor (FF') is defined as the actual surface area divided by the geometry area. As FF' increases, J_{sc} increases due to better light trapping ability of the nanowire structure. However, the V_{oc} and fill factor degrades mainly due to the increased surface recombination caused by the larger surface area. Therefore, the actual performance depends on the trade-off between the increased current and degraded voltage as the wire height increases.

Li et al. have reported the highest J_{sc} of 37.4 mA/cm² using a nanodome structure [15]. Fig. 2.15 shows the experimental process for the fabrication of the nanodome Si cell. After forming the nanowire structure, the nanodome structure was fabricated using the low pressure chemical vapor deposition (LPCVD). The p-n junction area was formed by using the ion implantation to form the emitter layer. The reported current density approached the theoretical limit of Si solar cells, indicating that most of the light is absorbed by this structure.

Figure 2-15 : Illustration of the fabrication steps of the nanodome based solar cells devices[15].

2.4.2 Si Nanostructured Hybrid Solar Cells

The application of Si nanostructures to hybrid solar cells has also been actively researched and played a critical part in improving cell efficiency [25].

Jeong et al. has reported a power conversion efficiency of 11.1% for the hybrid solar cell by incorporating the nanocone structure as shown below in Fig. 2.16 [25]. By introducing the nanocone structure, the light absorption has been substantially improved as confirmed by the high short circuit current density of 35.6 mA/cm^2 , which is close to that achieved for crystalline Si [25]. The fabricated nanocone structure can effectively trap the sunlight within the nanostructure and induce strong scattering. Hence, the effective path length of the sunlight is significantly elongated, leading to a higher absorption and current. The

Chapter 2 Literature Review

high efficiency achieved for the Si nanocone hybrid solar cell indicates its potential for practical application.

Figure 2-16 : Schematical illustration of the fabricated Si nanocone based hybrid solar cell [25].

He et al. have successfully fabricated the hybrid solar cell with an efficiency of 10.3% using the Si wafer and Spiro polymer [20]. Fig. 2.17 shows the experimental process involved. Starting with planar N-type wafer, the Si nanowire structure was fabricated using the electroless chemical etching with a HF-AgNO_3 solution. Spiro-OMeTAD was then spin coated on top of the nanowire structure to form the junction. The electrode was deposited on both sides of the film to complete the cell. Compared with the planar Si cell, the hybrid cell has demonstrated improvements in all the solar cell characteristics (V_{oc} , J_{sc} and fill factor).

Figure 2-17 : Schematic description of the fabrication process for Si/Spiro hybrid solar cell [20].

In addition, He et al. has successfully fabricated Si/PEDOT:PSS hybrid solar cell by combining the conventional pyramid structure with the nanowire structure as shown in Fig.2.18 [21]. A high power conversion efficiency of 9.9% was achieved. The pyramid structure was fabricated using the KOH solution which gave rise to anisotropic etching. After forming the pyramid structure, the Si nanowire structure was formed on the pyramid structure using the metal-catalyzed electroless etching method. The polymer PEDOT:PSS was then spin coated on the structure to form the hybrid solar cell. The nanostructure fabrication process was all solution based and at room temperature.

Figure 2-18 : Schematic illustration for the hybrid solar cell with pyramid and nanowire structures[21].

2.5 Simulation of Nanostructures

Simulation work on the optical properties of nanostructures is important in understanding the physics behind the interaction of electromagnetic waves of light with the nanostructures, and determining the optimum structure that will give rise to maximum absorption and the best cell efficiency.

The simulation of light absorption properties of nanostructures based solar cell device is carried out using numerical methods. Many numerical methods, such as the finite element method (FEM) [63], finite difference time domain (FDTD) [64], finite-difference frequency-domain (FDFD) [65] and transfer matrix method (TMM) [66] et al., have been applied to solve the Maxwell equation for the solar cell device to obtain the spatial distribution of the electric-field within the structure. In this section, we present the FEM method that is used in our simulation of the optical properties of Si nanostructures, since the FEM method can handle very complex geometry [63]. The FEM is implemented using the software High Frequency Structure Simulator (HFSS) [67].

The FEM method is a numerical process for boundary-value problems to find the approximate solutions by converting the partial differential equations into a set of linear algebraic equations [63]. Firstly, the structure to be simulated is divided into many smaller sections called finite elements. For those finite elements, normally triangular elements are used for two dimensional structures and tetrahedral elements for three dimensional structures as shown in Fig. 2.19 [63]. Since we are simulating a three dimensional structure for the solar cell device, the finite elements used by HFSS are tetrahedra, and the entire collection of tetrahedra is called a mesh. A solution is found for

Chapter 2 Literature Review

the EM fields within the finite elements, and these fields are interrelated so that Maxwell's equations are satisfied across inter-element boundaries. Therefore, the whole spatial distribution of the electric-field within the nanostructure can be obtained.

Figure 2-19 : Finite element mesh with (a) triangular elements for two dimensional structure and (b) tetrahedral elements for three dimensional structures [63].

The steps involved in the numerical calculation by the HFSS are shown Fig. 2.20. Firstly, an initial mesh structure is generated by HFSS by dividing the structure into a collection of tetrahedra. After that, the HFSS calculate the electromagnetic field within the structure. Based on the current solution, the HFSS will identify the region with a high degree of error. The mesh will be updated by dividing the structure into smaller tetrahedra structure. Based on the newly established mesh, HFSS will calculate the new solution. This process is repeated until the convergence criteria are satisfied.

Figure 2-20 : Flow chart of HFSS during the adaptive analysis [67].

In summary, compared with Si inorganic solar cell devices which normally requires lithography and involves high temperature processes, the simple and solution based process for the fabrication of hybrid Si/polymer solar cells can substantially reduce the manufacturing cost. In addition, the power conversion efficiency of the nanostructured based Si hybrid solar cells though not as high as that of crystalline Si cells, is expected to be further improved though selecting different polymers and addressing the interface quality between Si and the polymer. Furthermore, the theoretical study by simulation can help to identify the optimal structural parameter to guide the actual fabrication.

Chapter 3 SiNH/PEDOT:PSS Hybrid Solar Cell

In this chapter, high efficiency hybrid solar cells based on Si nanohole (SiNH) structure and poly (3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) are fabricated and characterized. The SiNH structures are fabricated on Si substrates using the metal-catalyzed electroless etching (MCEE) method, and the cells are obtained by spin coating of PEDOT:PSS on top. The hybrid cells are optimized by varying the hole depth, and a maximum power conversion efficiency (PCE) of 8.3% is achieved at the hole depth of 1 μm . To better understand the experimental results, we have also simulated the optical characteristics of periodic SiNH structures on Si thin film, and the results are discussed in the context of light trapping and scattering.

3.1 Silicon Nanohole PEDOT:PSS Hybrid Solar Cell

3.1.1 Introduction and Motivation

Recently, low cost Si nanowires (SiNWs)/polymer hybrid solar cells have been actively researched as they can potentially lower the cost of solar cells [20, 47]. The hybrid solar cells incorporating both Si and organic semiconductor enjoy the benefits of both materials, which include high power conversion efficiency, low material cost, and low temperature and simple solution based process capability [68]. Furthermore, due to the use of the nanowire structure, the cells have excellent antireflective and light trapping properties, and exhibit significantly enhanced light absorption. In addition, the metal induced electroless chemical etching method used to achieve the nanowire structure is simple, low cost and applicable to large area wafers. Such hybrid cells, however, suffer from the drawbacks that the stand-alone SiNWs tend to break easily, and agglomerate

Chapter 3 SiNH PEDOT:PSS Hybrid Solar Cell

when the wire length increases [22]. Recently SiNH structure has been developed to overcome these shortcomings of the SiNW structure [16]. The interconnecting SiNH structure is mechanically more robust, facilitates carrier transport and eases electrode formation compared to the SiNW structure. Moreover, it has also been reported that the SiNH structure has much higher light absorption than the SiNW structure due to its better light trapping ability [18]. SiNH solar cell device based on pure Si material has been recently demonstrated by Peng et al. with a short circuit current of 32.2 mA/cm^2 and an efficiency of 9.51% [16]. In the chapter, we present a low cost metal induced chemical etching approach to fabricate SiNH structures. The complete solar cell is then fabricated by spin coating PEDOT:PSS onto the SiNH structure to form a heterojunction device. The SiNH/PEDOT:PSS hybrid solar cells fabricated exhibit a power conversion efficiency of 8.3%. The process developed can be easily transferred to Si thin film and thus paves a way for the development of thin film Si/polymer hybrid solar cells with high efficiency.

3.1.2 Experiments Details of Hybrid SiNH/PEDOT:PSS Solar Cell

The starting $625 \text{ }\mu\text{m}$ thick N-type Si (100) wafers were cleaned sequentially in piranha solution at $90 \text{ }^\circ\text{C}$ and RCA solution at $75 \text{ }^\circ\text{C}$ for 10 minutes each. Electron-beam evaporation was used for the deposition of 25 nm thin layer of Ag film on the Si substrate. After that, KrF excimer laser with wavelength of 248 nm , pulse duration of 20 ns and pulse frequency of 10 Hz was used to anneal the Ag film to result in the formation of a monolayer of Ag nanospheres. The excimer laser has beam dimensions of $3 \text{ mm} \times 3 \text{ mm}$ square. The laser power density used was 300 mJ/cm^2 and the sample was placed on a moveable computer-controlled X-Y stage. During the laser annealing, the laser

Chapter 3 SiNH PEDOT:PSS Hybrid Solar Cell

beam position was fixed and the stage moved in the X direction. After the completion of the scanning over the sample in the X direction, the stage was moved in the Y direction by 2.8 mm, and the scan along the X direction was repeated. The laser beam only illuminated each spot of the sample once. After the formation of the Ag nanospheres, the sample was next immersed in a mixture solution of hydrogen dioxide (H_2O_2) and hydrofluoric acid (HF), where etching of Si occurred to form a SiNH structure, with the Ag nanospheres acting as catalyst. The solution concentrations used for H_2O_2 and HF are 4.6 M and 0.44 M respectively. The wet etching process was governed by the mechanism proposed by Li et al. based on the local coupling of redox reaction [69]. The remaining Ag nanospheres inside the SiNHs were then removed using a HNO_3 solution. After that, conductive PEDOT: PSS mixed with 5 wt.% dimethyl sulfoxide (DMSO) was spin coated on the SiNH structure to form a p-n junction. Finally, a layer of Ag grid and Ti/Pd/Ag were evaporated on the PEDOT:PSS layer and the back side of Si respectively to form the electrodes and complete the solar cell device. In the experiments, cells with four different nanohole depths (H) of 0.5 μm , 1 μm , 2 μm and 4 μm were fabricated by controlling the etching time. Scanning electron microscopy (SEM, LEO 1550 Gemini) was used to analyze the surface morphology of the SiNH structure. The light reflectance of the SiNH structure was investigated using a Lambda 950 UV/VIS/NIR spectrometer with an integrating sphere. The current density voltage characteristic (J-V) of the cells was analyzed using a solar simulator (San-EI Electric). The incident photon-electron conversion efficiency (IPCE) was measured using a spectral response/IPCE measurement system.

3.1.3 Surface Morphology of SiNH Structures

Figure 3.1.a shows the SEM image of the sample after the laser annealing of the Ag layer. It is clearly observed that a layer of Ag nanospheres is formed on the surface of the Si substrate. Most of the Ag nanospheres have diameters that range from ~ 200 nm to ~ 400 nm, and the separations between neighboring Ag nanospheres vary from ~ 300 nm to ~ 1000 nm. The planar Ag film initially deposited using the e-beam evaporation experienced internal stress. Upon the laser pulse irradiation, it gained enough energy to break up and reshape to form nanospheres, so as to reach a low energy state [70, 71]. Fig.3.1.b depicts the SEM picture of the top view of the SiNH structure with $H = 1$ μm . The diameters of the SiNH and their separations follow those patterns of the starting Ag nanospheres. Fig. 3.1.c-f depict the cross-sectional views of the SiNH structures with hole depth of ~ 0.5 μm , ~ 1 μm , ~ 2 μm and ~ 4 μm respectively, which were achieved with the corresponding etching times of ~ 15 s, 30 s, 60s, and 120 s. It can be seen that the SiNHs fabricated are vertically aligned. Fig. 3.1.g shows the tilted view of the 1 μm SiNH structure coated with PEDOT:PSS polymer of ~ 120 nm thick. Note that PEDOT:PSS is found mainly on the top surface of the SiNH structure and does not penetrate into the holes.

Figure 3-1 : (a) Ag nanosphere formed upon laser annealing, (b) top view SEM of the nanohole structure with H of 1 μm , (c-f) cross-sectional views SEM of the SiNH structure for the hole depth of 0.5 μm , 1 μm , 2 μm and 4 μm respectively and (g) tilted view of the SiNH structure with depth of 1 μm and with the PEDOT:PSS coated on top.

3.1.4 Etching Mechanism of Forming SiNH

Figure 3.2 shows the schematic description of the mechanism of the nanohole structure formation based on aqueous $\text{HF}/\text{H}_2\text{O}_2$ solution etching.

Figure 3-2 : Schematic description of the Si etching with Ag as catalyst to form SiNH [24].

The mechanism of the MCEE method applied to fabricate the SiNH structures is based on the galvanic displacement reaction [24, 72]. Two processes take place at the same time as shown below: reduction of Ag⁺ and oxidation of Si. The reaction is at the interface between the Ag nanoparticle and the silicon surface. At the cathode, it is the reduction reaction of the Ag⁺ as shown in Eq. 3.1. At the anode, it is the oxidation reaction of the silicon material.

During the wet etching process, the silver will form Ag⁺ ions. The Si in contact with the Ag⁺ ions will be oxidized to SiO₂. The SiO₂ formed will then be dissolved by HF. In addition, as shown by Peng et al., this process has preference to etch along the Si (100) crystallographic direction [72]. Hence, with the silver metal nanoparticles function as the etching catalyst, the nanohole structure is formed.

3.1.5 Optical and Electrical Characterizations of SiNH Structures

Figure 3.3 shows the reflectance spectra of the SiNH structures with different H . For comparison, the reflectance of a planar Si wafer was measured and shown in the inset of Fig. 3.3. The reflectance of planar Si is generally high and over 30%, due to the large differences between the refractive indices of the silicon substrate and air. In contrast, the reflectance is significantly reduced for the SiNH structures with different depths over the solar spectrum of interest from $\lambda = 300$ nm to 1100 nm. At H of 0.5 μm , the reflectance is relatively high with an average value of 12.6%. At such a small H , the light harvesting ability of the nanostructure is relatively weak. It is found that the reflectance reduces with increasing H from 0.5 to 2 μm , mainly due to the stronger light trapping ability of the SiNH structures at greater hole depth [59, 73]. As the dimension of the SiNH structure is comparable with the wavelength of main spectrum of sunlight, there is strong scattering within the SiNH structure which prolongs the effective optical path length and traps light[10]. When H increases further to 4 μm , the average reflectance does not decrease but increases slightly instead, attributed to the rougher surface formed. This can be seen from the SEM image of the surface with $H = 4$ μm as shown in Fig. 3.4, compared to the surface of the structure with a smaller $H = 1$ μm , as shown in Fig. 3.1.b. With longer etching time, the surface where there is no Ag nanoparticle reacted with the solution resulting in a rougher surface.

Figure 3-3 : Reflectance spectra of the SiNH structures with different hole depths.

Figure 3-4 : SEM of the surface of the nanohole structure with H of 4 μm.

Figure 3.5 plots the Incident Photon-Electron Conversion Efficiency (IPCE) of the SiNH hybrid solar cell with varying H . The value of the planar cell is also plotted as a reference. The IPCE values are improved as the hole depth increase to 2 μm. Among them the cell

Chapter 3 SiNH PEDOT:PSS Hybrid Solar Cell

with $H = 2 \mu\text{m}$ has the highest IPCE, and it peaks at 68.1% at $\lambda = 590 \text{ nm}$. The high IPCE results from the lowest reflectance observed for this structure. At $H = 0.5 \mu\text{m}$, the IPCE is low which is consistent with the high reflectance as seen in Fig. 3.3. It is observed that for $H = 4 \mu\text{m}$, the IPCE drops even below that for H of $0.5 \mu\text{m}$, which is not in accordance with their reflectance results shown in Fig. 3.3. This lower IPCE at shorter wavelength is attributed to a higher recombination rate for the photo-excited minority carriers [10], arising from the rougher and more defective surface. Such surface also contributes to a higher series resistance because of the poorer contacts formed between the Si and the PEDOT:PSS and results in lower IPCE. It is noted that the IPCE at $\lambda > 800 \text{ nm}$ is generally lower and comparable for all the cells with different H . This is because the wavelength is larger than the periodicities of the SiNHs and hence the scattering of light is weaker. The absorption thus occurs deeper in the Si substrate and is less dependent on the SiNH depth. Besides, there is increased absorption of light in the PEDOT:PSS film in this wavelength range [74].

Figure 3-5 : Incident Photon-Electron Conversion Efficiency (IPCE) of the SiNH hybrid solar cells.

Chapter 3 SiNH PEDOT:PSS Hybrid Solar Cell

Table 3.1 : Summary of the Photovoltaic Parameters.

SiNH depth (μm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
0.5	24.0	0.52	46.1	5.7
1	25.0	0.55	60.4	8.3
2	25.7	0.54	46.0	6.3
4	23.7	0.52	45.1	5.6

Figure 3.6 shows the current-density-voltage (J - V) curves of the SiNH hybrid solar cells with different H , under the illumination of the standard AM 1.5 G irradiation with a total energy density of $100 \text{ mW}/\text{cm}^2$. The value for the planar cell is also plotted for comparison. It is found that the cell performance is improved after the introduction of the silicon nanohole structure. Table 3.1 summarizes the power conversion efficiency (PCE), short circuit current (J_{SC}), open circuit voltage (V_{OC}) and fill factor (FF) of the cells. Four samples were studied and characterized for each cell, and the results presented represent the average values of the samples. The PCE increases with H and reaches a maximum of 8.3% for the cell with $H = 1 \mu\text{m}$. It then decreases as H is further increased and exhibits a value of 5.6% at $H = 4 \mu\text{m}$. As for V_{OC} , it is relatively stable and varies between 0.52 V to 0.55 V. The open circuit value has a strong dependence on the light generated current and saturation current of the solar cell, which is in turn mainly determined by the recombination in the solar cell device. Since the same high quality single crystalline Si material has been used, the material quality and the recombination inside the Si material is relatively the same as H changes. Hence, a stable V_{oc} is observed. The J_{SC} increases initially and at $H = 2 \mu\text{m}$ reaches a maximum of $25.7 \text{ mA}/\text{cm}^2$, before it decreases with increasing hole depth, which is consistent with the IPCE results. This is attributed to the rougher and more defective surface that results in a higher recombination rate of photo-

Chapter 3 SiNH PEDOT:PSS Hybrid Solar Cell

excited minority carriers, as well as the high series resistance. On the other hand, the FF increases from 46.1% to 60.4% as H increases from 0.5 μm to 1 μm . This is because as the hole depth increases, the light absorption ability is enhanced due to a strong scattering effect. Most of the light will be absorbed at the top of the sample where the SiNH structure exists. Hence, the effective minority carrier diffusion length is reduced which facilitates carriers collection [75] and gives rise to a high FF at H of 1 μm . However, at larger H of 2 and 4 μm , the FF drops to only 46.0% and 45.1% respectively because of the high series resistance values. With longer etching time, the surface becomes rougher and more defective, leading to increased surface recombination and higher series resistance. This is consistent with the series resistances calculated based on the slopes of the J - V curves ($dJ/dV|_{V=V_{OC}}$) in Fig. 3.6, which are 9.4, 4.1, 8.5 and 10.4 Ωcm^2 respectively for the cells with $H = 0.5, 1, 2$ and 4 μm . It is noted that the variation of the J_{sc} is smaller than that of the FF . This is because that although the series resistance also affects J_{sc} , its dependence on J_{sc} is generally not as strong as that of FF . Besides, there is enhanced absorption at larger H that compensates for the drop in J_{sc} . Hence J_{sc} does not change as much as the FF with increasing hole depth.

Figure 3-6 : Current-density-voltage (J-V) curves of the SiNH hybrid solar cells under the illumination of the standard AM 1.5 G irradiation.

It should be noted that as the dimension of those nanohole structure becomes sufficiently small, in the scale of the de Broglie wavelength of the generated electrons or the holes, which is normally less than 10 nm [76], the quantum confinement effect will be observed. The energy state of the generated carrier will be quantized, and they are confined to transport in two dimensions or even one dimension. It may then be more difficult for the carriers to be separated and collected. The effective bandgap of the Si material would also increase and affect the optical absorption characteristics[77]. On the other hand, since the dimension of the nanostructure is very small, there is a high chance that the confined carriers can tunnel through energy barrier to facilitate their transportation [76]. In addition, the mean free path of the generated carriers can be longer than the dimension of the nanostructure to result in ballistic transport, leading to negligible resistivity when the carriers travel [78]. All the above quantum effects arising from very small dimension nanostructures will likely impact negatively on light absorption, carrier transport,

Chapter 3 SiNH PEDOT:PSS Hybrid Solar Cell

separation and collection, and hence affect the cell efficiency. For the case of our hybrid cells based on the Si nanoholes, the dimensions are relatively large and hence the quantum effect will be weak. Should the dimension of the nanostructure be reduced, then all the above effects should be taken into account in the design and modelling of the solar cells.

The N-type silicon substrate for the fabrication of the hybrid Si/PEDOT:PSS has a resistivity of 1-3 $\Omega\cdot\text{cm}$, corresponding to an doping concentration of $\sim 2 \times 10^{15} \text{ cm}^{-3}$. As the doping concentration reduces, the resistivity will increase, together with the reduction of the generated electron-hole pairs. Therefore, FF , V_{oc} , J_{sc} and cell performance will drop as demonstrated by Matthias et al. [79]. It should also be noted that as the carrier concentration increase, for example $2.6 \times 10^{17} \text{ cm}^{-3}$, a decrease of J_{sc} while an increase of V_{oc} can be observed [79]. The reduction of J_{sc} is caused by the increased recombination and shorter lifetime of minority carrier at this high carrier concentration [80]. For the increase of V_{oc} , it is mainly due to the decrease in the saturation current density [79]. Therefore, by properly choosing the doping concentration, an optimal value can be identified to optimize the cell efficiency.

In conclusion, a simple and low cost approach for fabricating hybrid SiNH solar cells has been proposed. The SiNH structure, which is produced with laser thermal annealing and electroless chemical etching process, demonstrates strong light absorption ability. Hybrid cell devices with different hole depths have been fabricated. The optimized structure is identified with a hole depth of 1 μm , which reveals the highest power conversion

Chapter 3 SiNH PEDOT:PSS Hybrid Solar Cell

efficiency of 8.3%. Cells with longer hole depth lead to poorer performance because of the rougher surface and higher series resistance arising from the poor contact. It is believed that the cell performance can be further improved through optimizing the SiNH structural dimensions such as the hole diameter and spacing, and the spin coating speed which controls the thickness of the PEDOT:PSS layer. Note that the fabrication technique can also be easily adapted to Si thin film solar cell to improve its cell efficiency.

3.2 Simulation of Light Absorption in SiNH/PEDOT:PSS Structure

3.2.1 Introduction and Motivation

In the previous section, we have discussed the fabrication and characterization of hybrid SiNH/organic solar cells. To fully understand the effects of the structural parameters of the SiNH structure on the performance of the cells, theoretical foundation should be established to determine their effects on the optical characteristics of the structure, such as absorption. In this section, we carry out a simulation study to investigate the effects of the hole diameter (D) and periodicity (P) of a periodic SiNH structure on its optical absorption. It is found that optimal absorption condition is achieved for the hybrid SiNH structure when P is 600 nm and the diameter to periodicity (D/P) ratio is 0.8, giving rise to the highest ultimate efficiency (η_{UE}) of 30.5%. We have also compared the optical absorption of the SiNH structure with optimized Si nanowire (SiNW) structure and found that the former offers better light absorption efficiency than the latter.

3.2.2 Simulation Methodology

Chapter 3 SiNH PEDOT:PSS Hybrid Solar Cell

Figure 3.7 shows the schematic illustration of the simulated hybrid SiNH/PEDOT:PSS structure. The overall film thickness is fixed at $2\ \mu\text{m}$ (T_3), and the depth of SiNH is fixed at $1\ \mu\text{m}$ (T_1). The thickness of the PEDOT:PSS layer is set as $40\ \text{nm}$ (T_2). We allow the diameter (D) and the periodicity (P) of the structure to vary to determine the optimum structure that will give rise to maximum light absorption. For the bottom of the cell, it is the silicon/air interface. Below the air, a perfectly matched layer boundary condition is applied. The simulation was conducted using the software High Frequency Structural Simulator (HFSS) based on the finite element method [63]. The unit square cell is bounded by periodical boundary conditions. The refractive indices of Si and PEDOT:PSS are obtained from the literatures [81, 82]. For the simulation, plane wave is incident normally onto the nanostructure with a wavelength (λ) ranging from $300\ \text{nm}$ to $1100\ \text{nm}$, covering the main solar spectrum of interest. The optical characteristic is obtained by solving the electric field distribution after the interaction between the sunlight and the nanohole structures.

Figure 3-7 : Schematics illustration of the SiNH hybrid structure with (a) three-dimensional view and (b) cross-sectional view.

3.2.3 Light Absorption of Hybrid SiNH Structure

Figure 3.8 shows the optical characteristics of the hybrid SiNH structures with different P and at a fixed D/P ratio of 0.8. Fig. 3.8.a and b depict light absorption in the Si material and PEDOT:PSS respectively, whereas Fig. 3.8.c and d show the overall reflectance and transmittance spectra of the hybrid structure. The optical characteristics of a 2 μm thick planar Si film with 40 nm PEDOT:PSS on it are also plotted for comparison. For the hybrid planar structure, the absorption in Si is low, especially for long wavelength light over 600 nm. This is because due to the absence of light trapping, sunlight is easily reflected or penetrated through the film as confirmed by the high reflectance and transmittance as shown in Fig. 3.8.c and 3.8.d. On the other hand, for the hybrid SiNH structures, the absorption in Si is enhanced compared to the planar one. At the smallest P of 200 nm, the improvement in light absorption is marginal and occurs mainly at shorter wavelengths of $\lambda < 550$ nm. This is attributed to the comparable structural dimension and wavelength of light that induces strong scattering and absorption [73]. As P increases to 400 nm, the absorption of long wavelength light ($\lambda > 550$ nm) is significantly increased compared to the planar and $P = 200$ nm structures. This is due to the larger structural dimension resulting in stronger scattering of light at longer wavelengths. In addition, the introduction of the sub-wavelength SiNH lowers the reflectance and further enhances light absorption [83]. At $P = 600$ nm, the absorption for $\lambda < 600$ nm drops slightly and is significantly improved for $\lambda > 600$ nm, as compared to the other structures with smaller P . The scattering of incident light is dominant for $\lambda > 600$ nm, which substantially prolongs the optical path length of light, leading to the high absorption observed. The transmittance (Fig. 3.8.d) is noted to be low, indicating that most of the light is absorbed

Chapter 3 SiNH PEDOT:PSS Hybrid Solar Cell

before reaching the bottom of the structure. Overall, the structure with $P = 600$ nm gives rise to a high broadband absorption over the main solar spectrum from 300nm to 1100 nm. When P is further increased to 800 nm, the absorption for $\lambda > 800$ nm remains similar to that of $P = 600$ nm, however, it is significantly reduced for $\lambda < 800$ nm. Consequently, the overall performance is degraded. It is also worth noting that the absorption within the PEDOT:PSS film is also enhanced for the SiNH structure, especially for larger P where stronger scattering is induced at longer wavelength light, and where the absorption coefficient is higher in PEDOT:PSS.

Figure 3-8 : Optical characteristics of the SiNH hybrid structure with varying P at a fixed D/P ratio of 0.8. (a) Light absorption in Si, (b) absorption in PEDOT: PSS, (c) light reflectance and (d) light transmittance of the overall structure.

Chapter 3 SiNH PEDOT:PSS Hybrid Solar Cell

Figure 3.9 shows the optical characteristics of the hybrid SiNH structures with different D/P ratios and at the optimum P of 600 nm. It is noted that for all the structures with different D/P ratios, light absorption is clearly enhanced as compared to the planar structure for $\lambda > 600$ nm. This is attributed to scattering arising from the comparable wavelength of light and the periodicity of the SiNH structures. Among them, the structure with the smallest $D/P = 0.4$ offers the least absorption enhancement as the hole diameter is relatively small compared with P , and hence only weaker scattering is induced. As the D/P ratio increases from 0.4 to 0.8, the larger D induces stronger scattering around the nanostructure and hence results in higher absorption. Therefore, incident light is effectively absorbed in the SiNH structure without penetrating the film, leading to the low transmittance and high absorption observed. When $D/P = 0.9$, the large D leads to SiNH that are very close to each other, and with very little Si materials left in between. Hence there is stronger light transmittance [73, 83] and weaker light absorption. In addition, for the oscillation in the Figure 3.8 and 3.9, it is mainly related to the resonance of the nanostructure.

Figure 3-9 : Optical characteristics of the SiNH hybrid structure with varying D/P ratio at a fixed P of 600 nm. (a) Light absorption in Si, (b) absorption in PEDOT: PSS, (c) light reflectance and (d) light transmittance of the overall structure.

3.2.4 Ultimate Efficiency of Hybrid SiNH Structure

From the above discussion, it is noted that the light absorption is sensitive to the change of the structural parameters. In order to have a better measurement of the light absorption to find the optimal parameters, the ultimate efficiency (η_{UE}) is calculated [9, 84]:

$$\eta_{UE} = \frac{\int_{300}^{1100} \frac{E_g P(\lambda) A(\lambda)}{E} d\lambda}{\int_0^{\infty} P(\lambda) d\lambda} \quad (3.4)$$

where E_g is the band gap of Si, E and λ are the photon energy and wavelength of incident sunlight respectively, $A(\lambda)$ is the absorption efficiency and $P(\lambda)$ is the spectral irradiance

Chapter 3 SiNH PEDOT:PSS Hybrid Solar Cell

of standard AM1.5G solar spectrum. Fig. 3.10 shows the ultimate efficiency as a function of P for different D/P ratios. Note that the planar Si hybrid structure exhibits an η_{UE} of only 16.4%, whereas all the hybrid SiNH structures reveal much higher η_{UE} . For most of the structures with different D/P ratios, η_{UE} is observed to peak at $P = 600$ nm. This is mainly because the periodicity is close to the peak of the solar spectrum, which results in strong scattering in the SiNH structure, and consequently prolongs the optical path length of sunlight. This enhanced optical path length is very important especially for long wavelength light which has a low absorption in Si. With changing D/P ratio, the highest η_{UE} of 30.5% is observed at $D/P = 0.8$, which is consistent with the strongest absorption noted for this structure, as discussed earlier. We have also compared light absorption between the optimal SiNH/PEDOT:PSS and SiNW/PEDOT:PSS structures. For meaningful comparison, the SiNW/PEDOT:PSS structure simulated is designed to have dimensions similar to those of the nanohole structure. It comprises SiNWs are of 1 μm length and with a 1 μm Si thin film underneath. The thickness of the PEDOT:PSS layer is also fixed at 40 nm. The optimal absorption is found to occur at a structural periodicity of 500 nm and a wire diameter/periodicity ratio of 0.7. This gives rise to a maximum η_{UE} of 28.7%, which is lower than that achieved for the optimal SiNH hybrid structure. Therefore, besides offering a more robust and interconnected network, the SiNH structure reveals stronger light trapping capability as compared to the SiNW structure.

Figure 3-10 : Ultimate efficiency of the SiNH hybrid structures.

Figure 3.11.a shows the unit cell of the hybrid SiNH/PEDOT:PSS structure while Figs. 3.11.b-d plot the normalized E-fields across the cell structure with incident wavelength of $\lambda = 400$ nm, 750 nm and 960 nm respectively. For the SiNH structure, the light absorption is noted to improve significantly as confirmed by the E-field distributions observed at the different wavelengths. When the wavelength is 400 nm, E-field is enhanced mainly at the top of the hybrid SiNH/PEDOT:PSS structure, indicating that the sunlight is absorbed before it reaches the bottom of the structure, and no E-field is seen at the bottom of the film. From the E-field that is still very high above the hybrid SiNH/PEDOT:PSS structure, it is deduced that light reflectance is relatively strong at this wavelength. As the wavelength increases to 750 nm, the E-field above the hybrid SiNH/PEDOT:PSS structure is relatively weak, indicating lower light reflectance. A stronger E-field pattern is observed within the hybrid SiNH/PEDOT:PSS structure, signifying that the sunlight is effectively coupled into the structure. However, due to the

Chapter 3 SiNH PEDOT:PSS Hybrid Solar Cell

low absorption coefficient of Si at this wavelength, sunlight cannot be fully absorbed in a single pass. Instead, sunlight will pass through the film and therefore a weak E-field is observed at the bottom of the film. When the wavelength is increased to 960 nm, a stronger E-field is observed within the hybrid SiNH/PEDOT:PSS structure, which indicates a strong resonance. The absorption path length is significantly increased, leading to a significant improvement in light absorption for the SiNH structure [85]. It is shown that the field within the SiNH region is strong, indicating more sunlight is trapped within the SiNH structure. Consequently, more electron-hole pairs are generated within the SiNH region, especially at the top of the SiNH structure.

Figure 3-11(a) Unit cell of the hybrid SiNH/PEDOT:PSS structure. Normalized E-fields distribution for different wavelengths when (b) $\lambda = 400$ nm, (c) $\lambda = 750$ nm and (d) $\lambda = 960$ nm.

Chapter 3 SiNH PEDOT:PSS Hybrid Solar Cell

Figure 3.12 shows the angular dependence of the hybrid SiNH/PEDOT:PSS structure. It is clearly shown that for both TE and TM polarized sunlight; the structure shows a high ultimate efficiency. Especially for the TM polarized sunlight, it shows an ultimate efficiency above 28 % until the incident angle is increased beyond 70°. On the other hand, for the TE polarized sunlight, it starts to drop sharply when the incident angle is over 50°. In addition, the rotation of the E-field of the incident angle has also been investigated. It is found that, as the E-field is rotating in the plane perpendicular to the SiNH structure, the variation is small. The ultimate efficiency value only varies between 30.4% and 30.5%. Therefore, the hybrid SiNH/PEDOT:PSS structure has demonstrated a stable properties as the polarization of the incident light changes.

Figure 3-12 Angular dependence of optical absorption of hybrid SiNH/PEDOT:PSS structure.

In summary, we have studied light absorption in a robust and interconnected SiNH/PEDOT:PSS hybrid solar cell structure using the finite element method. The optimal absorption condition is achieved when the structural periodicity is 600 nm and

Chapter 3 SiNH PEDOT:PSS Hybrid Solar Cell

the diameter to periodicity ratio is 0.8, which offers the highest ultimate efficiency of 30.5%.

3.3 Conclusion

In conclusion, we have proposed a simple and low cost approach for fabricating hybrid SiNH solar cells using laser thermal annealing and electroless chemical etching process. The cell with a hole depth of 1 μm demonstrates the highest power conversion efficiency of 8.3%, whereas cells with deeper hole depth exhibit poorer performance due to their rougher surface and higher series resistance arising from the poor contact. In addition, we have simulated light absorption in the SiNH/PEDOT:PSS hybrid solar cell structure using the finite element method. The optimal absorption condition occurs when the structural periodicity is 600 nm and the diameter to periodicity ratio is 0.8, which offers the highest ultimate efficiency of 30.5%. Hence, by introducing the nanohole structure into the solar cell device, light absorption can be substantially enhanced to improve the cell efficiency.

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

4.1 Introduction and Motivation

In the previous chapter, we have discussed the fabrication of Si nanohole (SiNH) structures using Ag nanoparticles and the metal-catalyzed electroless etching technique. However, the SiNH structures formed tend to have a random position distribution and there is also a large distribution in terms of the SiNH diameters. In this chapter we study the fabrication of periodic SiNH structures having a hexagonal unit cell using polystyrene (PS) spheres. The PS spheres method has been actively employed for the fabrication of nanowire structures, but not commonly for SiNH structures [12, 86]. It can achieve highly periodic structure at lower cost as compared to the conventional lithographic technique, and allows the dimensions of the nanostructures formed to be readily controlled by using PS spheres with different diameters [12, 54, 86].

In our work PS spheres with different initial diameters are used to control the periodicity of the SiNH structures, and etching of the PS spheres is then performed to reduce their sizes to determine the diameters of the SiNH formed. SiNH structures with different structural dimensions have been fabricated and are investigated in terms of their microstructures and optical reflectance. Compared with planar Si wafer, such structures exhibit much lower reflectance due to the enhanced scattering introduced by the SiNHs. In addition, we simulate the optical absorption of such SiNH structures by varying their structural periodicity and hole diameter, to determine the optimum one that gives rise to

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

maximum solar absorption. The optimum structure is found to have a structural periodicity of 693nm and hole diameter of 560 nm, and it yields the highest ultimate efficiency of 28.8%.

4.2 Fabrication and Characterization of SiNHs

The starting N-type Si (100) wafers were cleaned sequentially in solution of Acetone, IPA and DI water for 10 mins each using ultrasound bath. The PS spheres solution (microparticles gmbh, German) with concentration of 10% (weight ratio) in aqueous solution was dropped into water to form a monolayer of floating PS spheres. The cleaned Si samples were then dipped into the water and lifted gently to gather a uniform layer of PS spheres on the Si surface. After that, the samples were dried naturally in air. PS spheres with 4 different diameters of 330, 476, 600 and 800 nm have been used. This process is governed by the Langmuir–Blodgett method. Currently, we have successfully achieved acceptable uniformity for four inches wafer. Larger substrates can also be used if the container allows, though uniformity may be an issue. The PS patterning technique is essentially simple without the involvement of any sophisticated equipment, and can be easily scaled up for high volume manufacturing at low cost. These PS spheres formed on top of the Si wafers were subjected to oxygen plasma etching with corresponding duration of 150, 200, 250 and 350 seconds to reduce their sizes to 210, 320, 400 and 460 nm respectively, as deduced from scanning electron microscopy (SEM) images. The samples were then loaded into an electron-beam evaporator to deposit a thin layer of 40 nm gold film. Following that, the samples were placed in a solution of toluene in ultrasound bath to remove the PS spheres. Consequently, a patterned Au film was formed

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

on the Si surface to serve as a mask for the subsequent formation of SiNH structure. After that, the samples were subjected to reactive ion etching for 5 mins to form SiNHs, using an RF power of 250W, and a gas mixture of BCl_2 and Cl_2 with flow rates of 100 and 60 sccm respectively. After the etching, the films were dipped into a gold etchant (KI solution) to remove the gold film on Si. The surface morphology of the SiNH structures formed was analyzed using SEM (LEO 1550 Gemini), while the optical reflectance of the samples was examined using a Lambda 950 UV/VIS/NIR spectrometer incorporated with an integrating sphere.

Figure 4-1 : The SEM images of the initial PS spheres formed on the Si surface. The diameters of the spheres are (a) 330 nm, (b) 476 nm, (c) 600 nm and (d) 800 nm.

Figures 4.1.a – d show the SEM pictures of the PS spheres with four different initial diameters of 330, 476, 600 and 800 nm respectively. It is clearly seen that all the PS spheres are periodically arranged on the Si surface having a hexagonal unit cell, with a periodicity (P) that is about the initial PS ball diameter. Fig. 4.2.a – d show the

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

corresponding SEM images after the O₂ plasma etching to reduce the PS ball diameters, deposition of a thin Au layer and removal of PS spheres. A patterned Au film with a hole array is seen for each sample, with the hole diameters (D) following closely those of the etched PS spheres of $\sim 210, 320, 400$ and 460 nm. Fig. 4.3 shows the cross-sectional views of the SiNH structures formed after the RIE etching, where SiNH with a height of $\sim 700 - 800$ nm are observed. For those with smaller D of 210 and 320 nm, the cross-sections of the SiNHs tend to be conical, while for those with larger D of 400 and 460 nm, the cross-sections tend to be trapezoidal.

Figure 4.4 shows the light reflectance (R) of a planar Si film and the SiNH structures over a range of wavelength (λ) from 300 to 1100 nm, covering the major part of the solar spectrum of interest. For the planar Si film, R is high and more than 35% over the entire spectrum. In contrast, R of most of the SiNH structures is significantly reduced to $\sim 5\%$ for major part of the spectrum in the range of $500 \text{ nm} < \lambda < 1050 \text{ nm}$. This is attributed to strong scattering by the SiNH structures as their dimensions are comparable with the wavelength of sunlight. Therefore, light is effectively trapped resulting in lower reflectance and stronger absorption. A strong dependence of R on the dimension of the SiNH structure is also observed. Among the four samples, the structure with the smallest D of 210 nm has the lowest R at shorter wavelength range of $\lambda < 450$ nm, attributed to the dimension of the structure being comparable with λ . At $D = 320$ nm and 400 nm, R is noted to be lowest at around $\lambda = 500$ nm and 600 nm respectively. At the largest D of 460

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

nm, R is observed to be higher at shorter wavelength as compared to the other samples, and it is comparable only when $\lambda > 700$ nm.

Figure 4-2 : The SEM images of gold film after PS ball formation. (a) PS ball diameter 330 nm and O₂ plasma of 150 s, (b) PS ball diameter 476 nm and O₂ plasma of 200 s, (c) PS ball diameter 600 nm and O₂ plasma of 250 s, (d) PS ball diameter 800 nm and O₂ plasma of 350 s.

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

Figure 4-3 : The cross-sectional SEM images of gold film after the nanohole formation. (a) PS ball diameter 330 nm and O₂ plasma of 150 s, (b) PS ball diameter 476 nm and O₂ plasma of 200 s, (c) PS ball diameter 600 nm and O₂ plasma of 250 s, (d) PS ball diameter 800 nm and O₂ plasma of 350s.

Figure 4-4 : Light reflectance of the periodic nanohole structure fabricated.

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

4.3 Simulation of Light Absorption of Hexagonally Arranged SiNH

4.3.1 Introduction and Motivation

Considerable research has been conducted on the simulation of the optical properties of nanostructure solar cells. However, most of the work is focused on periodic structure with square unit cells [11, 55, 87]. In contrast, another common configuration that is based on hexagonally arranged array, as those that we have fabricated in the previous section, has not been well studied in terms of the light absorption properties. In this section we have conducted a systematic study of the light absorption of hexagonally arranged SiNH structure using the finite element method. We vary the structural periodicity and hole diameter to determine the optimum structure that will give rise to maximum light absorption. The optimum structure is found to have a periodicity of 693 nm and hole diameter of 560 nm, and it yields the highest ultimate efficiency of 28.8%. A comparison between the hexagonally arranged SiNH structure and squarely arranged SiNH structure is also conducted and it is found that their light absorption is comparable.

4.3.2 Simulation Details

Figure 4.5 presents the 3-dimensional and top views of the periodic SiNH structure with a hexagonal unit cell used in the optical simulation, which corresponds to the structures that have been fabricated using the PS spheres. Note that though the actual cross-sections of the SiNH are not very uniform and rectangular as seen from Fig. 4.3, however for simplicity, we have assumed so in our simulation. Indeed we expect the actual structures fabricated with conical and trapezoidal cross-sections to be better in terms of absorption, due to the more gradual change in the refractive indices with depth. In our simulation, we

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

have assumed SiNH of depth $T_1 = 1 \mu\text{m}$ distributed periodically within a thin Si film of thickness $T_2 = 2 \mu\text{m}$. As it has been found that absorption increases monotonically with hole depth, therefore we have just assumed a hole depth of $1 \mu\text{m}$ and focused our study on the effects of P and D on the optical characteristics of the SiNH structures. The simulation was carried out using the commercial software High Frequency Structural Simulator based on the finite element method [63]. Periodic boundary conditions were used to model the periodic structure. The incident plane wave was incident normally on the SiNH structures with λ ranging from 300 nm to 1100 nm. The refractive index of Si is taken from the literature [81]. The electric field distribution of the incident light in the SiNH structure was determined, from which the optical characteristic could be deduced. In addition, for a useful comparison of the different SiNH structures for solar energy absorption, their ultimate efficiencies (η_{UE}) are calculated by assuming an internal quantum efficiency of 100% [9, 88].

Figure 4-5 : Schematics illustration of the hexagonally arranged SiNH structure with (a) 3-dimensional view and (b) top view.

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

4.3.3 Light Absorption of Hexagonally Arranged SiNH

Figure 4.6 depicts light absorption of a 2 μm thick planar Si and SiNH structures as a function of the periodicity P from 346 to 866 nm, with a fixed D/P ratio of 0.81. It is clearly seen that all the SiNH structures exhibit stronger light absorption as compared with the planar one. When P is small at 346 nm, there is minimal scattering for the longer wavelength sunlight, which instead mainly penetrates through the film and results in only marginal absorption enhancement. With decreasing λ , light scattering and absorption increases and the absorption is close to 100% for $\lambda < 500$ nm. As P increases to 520 nm, which is near the peak of the solar spectrum, light absorption is improved over the whole solar spectrum, especially for λ from 400 nm to 800 nm. At larger P of 693 nm, light absorption is further improved especially for long $\lambda > 800$ nm. However, as P reaches 866 nm, overall light absorption is reduced compared to the structure with $P = 693$ nm, as the structural dimension is now larger compared to the peak wavelength of the solar spectrum. In conclusion, maximum light absorption is achieved at $P = 693$ nm.

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

Figure 4-6: Light absorption spectra of the hexagonally arranged SiNH structures as a function of the periodicity and a fixed D/P ratio of 0.81.

Figure 4.7 shows the light absorption characteristics of the SiNH structures as a function of the D/P ratio, with P fixed at the optimum value of 693 nm. At small D/P ratio of 0.35, the diameter of the holes is only 240 nm and much smaller than the wavelength of solar spectrum of interest. Therefore, there is only minimum scattering and the incident light can easily penetrate through the film. Consequently, the light absorption enhancement is only marginal as compared to the planar sample. When the D/P ratio is increased to 0.58, D is ~ 400 nm and therefore there is strong scattering of the incident light resulting in higher absorption. When the D/P ratio is further increased to 0.81, D is ~ 560 nm which is near the peak wavelength of solar spectrum. This results in strong scattering and a high broadband light absorption is achieved. With a further increase of the D/P ratio to 0.98, the Si film comprises mainly SiNH and there is little Si material and hence light

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

absorption is reduced, especially at longer wavelength where the absorption coefficients of Si are lower. Hence, maximum light absorption is achieved at $D/P = 0.81$. The signal oscillations observed in the light absorption spectra are attributed to the resonant and guided mode of the nanostructure which occurs when the wavelength of light is comparable to the structural dimensions. The peaks in the spectra indicate the supported modes for the nanostructures.

Figure 4-7 : Light absorption spectra of the hexagonally arranged SiNH structures with a varying D/P ratio with a fixed P of 693 nm.

To better compare the solar energy absorption characteristics between the different SiHN structures, their η_{UE} are calculated and shown in Fig. 4.8. Note that the η_{UE} of the 2 μm planar Si film calculated for comparison is 14%. It is observed that for samples with different P , η_{UE} generally increases initially and reaches a peak, before it decreases with increasing D/P ratio. As the maximum absorption of the structures occurs at wavelengths that are near the peak wavelength of the solar spectrum, the trend of η_{UE} observed is quite

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

similar to those seen for the absorption results presented earlier on. The highest η_{UE} value of 28.8% is achieved at $P = 693$ nm and D/P ratio = 0.81.

Figure 4-8 : Ultimate efficiency of the SiNH structures with different structural periodicity and D/P ratios.

Though there are several differences between the SiNH structures fabricated and simulated, which include the thickness of the Si layer, the degree of periodicity and the cross-sections of the SiNH, it is noted that the trend of the results observed is generally consistent. Experimentally it has been observed that the wavelength at which the reflectance is the lowest (i.e. maximum absorption), increases with the structural dimensions. This is noted in the simulation and attributed to the enhanced scattering of light when the wavelength is comparable to the dimension of the SiNH. On the other hand, there is no strong oscillation in the optical characteristics of the fabricated SiNH

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

structures, in contrast to that observed in the simulated results. This is ascribed to the fact that the fabricated SiNH structures are not perfectly periodic and regular in dimensions. Nevertheless, both the experimental and simulated results show that the SiNH structures with hexagonal unit cell fabricated using the PS spheres method are promising to be applied in Si solar cells for light trapping. The simulation results obtained of a thin Si film of 2 μm reveal a high ultimate efficiency of 28.8%.

Figure 4.9 presents the angular dependence of the ultimate efficiency of the hexagonally arranged SiNH structure to account for a more realistic application of solar cell, since sunlight will not always be incident normal to the cell surface. The angular dependence of the planar 2 μm thin film is also plotted for comparison. For the planar film, the η_{UE} is 13.8% for the vertical incident light. As the incident angle increases, the η_{UE} for the TM polarized light increases while that for the TE polarized light decreases. For incident angle up to 70° , the performance of the SiNH structure is better compared to the planar Si structure for both polarizations of light. It is clearly seen that for both TE and TM polarized sunlight for the SiNH structure, η_{UE} increases initially and reaches a peak, and then decreases with the incident angle (θ). The highest light absorption is achieved when θ is 10° , which gives rise to η_{UE} of 31.3% and 32.2% for TE and TM light respectively. Under normal incidence, when the structure periodicity is comparable with the wavelength of sunlight, fewer guided resonance modes are excited due to the structure symmetry, which negatively affects light absorption [89, 90]. However, at a small deviation from normal incidence, the symmetry is broken leading to the excitation of

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

more guided resonance modes which contributes to slightly higher absorption for $\theta = 10^\circ$ [89, 90]. On the other hand, at larger θ , it is easier for sunlight to couple to the leakage channels which can substantially reduce the light absorption. Note that the light absorption for TM polarized light is still high at 29.3% at a large θ of 70° . This indicates that the hexagonally arranged SiNH structure can still absorb sunlight well at oblique incident angles, which is important for the practical application of the solar cells. In addition, the effect of varying the E-field by rotating it in the plane perpendicular to the SiNH structures has also been investigated. It is found that, the light absorption is very stable while the rotation of the E-field. The η_{UE} remains at 28.8%. The variation of the light absorption is slightly smaller compared with square lattice SiNH structure studied in Chapter three. Therefore, the simulated hexagonally arranged SiNH has demonstrated a very stable light absorption property as the E-field polarization changes.

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

Figure 4-9 : Angular dependence of optical absorption of hexagonally arranged SiNH structure and the planar 2 μ m thin film structure.

Figure 4.10 shows a comparison of light absorption of hexagonally arranged and squarely arranged SiNH structure. The result for a planar 2 μ m thick Si film is also included as a reference. The optimum hexagonal SiNH parameters are used for the simulation. For the squarely arranged SiNH structure, we have studied its absorption as a function of the periodicity and diameter, and found that the maximum absorption occurs at P of 600 nm and D/P ratio of 0.8. It is seen from the results that both the hexagonally and squarely arranged SiNH structures exhibit much better light absorption as compared with the planar Si, due to a better refractive index matching at the top surface and light trapping by the SiNH structure. The light absorption for both types of SiNH structures is comparable and slightly higher for the squarely arranged SiNH over the wavelength range from 700 to 900 nm. When compared in terms of their ultimate efficiencies, the

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

squarely arranged SiNH structure achieves a η_{UE} of $\sim 30\%$, which is also slightly higher than that of the hexagonal structure of 28.8%. This may be because the hexagonal arranged SiNH structure has more symmetric planes than the squarely arranged SiNH, which consequently leads to a decrease in the number of excited modes inside the film [89, 90] , and hence lower light absorption.

Figure 4-10 : Light absorption spectra of both the hexagonally arranged and squarely arranged SiNH structure. The planar 2 μm thin film serves as a reference.

4.4 Conclusion

Hexagonally arranged silicon nanohole structures have been fabricated with different structural dimensions using polystyrene spheres. Due to the comparable dimensions of the SiNHs and the sunlight wavelength, strong scattering is induced leading to a substantially reduced light reflectance. In addition, a systematic analysis of light

Chapter 4 Optical Absorption Enhancement in Si Nanohole Structure with Hexagonal Unit Cell for Solar Cell Application

absorption based on optical simulation has been conducted for the hexagonally arranged silicon nanohole structure. The effects of the structural periodicity and diameter of the nanoholes on light absorption have been investigated. It is found that maximum light absorption occurs at a periodicity of 693 nm and hole diameter of 560 nm, yielding an ultimate efficiency of 28.8%. A comparison of light absorption between hexagonally and squarely arranged SiNH structures has been carried out. It is found that their light absorption is comparable. From the study, it is deduced that the hexagonally arranged silicon nanohole structure can give rise to high ultimate efficiency and is promising to be applied in thin film Si solar cells.

Chapter 5 Simulation Studies of SiNH Structures

In the previous chapters we have studied experimentally and theoretically the optical characteristics of two types of Si nanohole (SiNH) structures, which are the random SiNH structure fabricated using the metal-catalyzed electroless etching (MCEE) method and the periodic SiNH structure patterned using polystyrene spheres balls. There are many other possible SiNH structures with varying degrees of light trapping ability that can be explored and potentially applied in solar cells for light absorption enhancement [91, 92].

Prior to the actual fabrication of the structures, it is always useful to study their optical properties using theoretical optical simulation as that is low cost and can be readily achieved. In this chapter we study three different SiNH structures in terms of their optical characteristics using simulation based on the finite element method. (1) In order to guide the actual fabrication process of the SiNH structure to save the cost and time, the theoretical study of the light absorption characteristics of the SiNH structure with different properties is simulated with the finite element method. Firstly, the reflectance and absorption characteristics of the slanting SiNH structure where the SiNHs are not aligned normal to the surface of the Si, but instead at an oblique angle, have also been simulated to provide a design guideline for its application in the solar cell. It is found that by the introduction of the slanting structure, the light absorption is improved for the slanting SiNH structure as compared to the conventional vertical SiNH structure. (2) We have also conducted a systematic study on light absorption in a SiNH structure that has randomness introduced into its structural parameters which include the hole diameter,

Chapter 5 Simulation Studies of SiNH Structures

position and depth. It is found that light absorption is enhanced for the random structures as compared to their periodic counterparts. (3) In addition, we also propose a hybrid nanostructure that comprises Si nanoholes incorporated with nanopyramids and nanoholes for thin film Si solar cells. The hybrid structure demonstrates a stronger light trapping ability that is beyond the Lambertian limit. This is achieved with the smaller dimension nanohole structure effectively reduces shorter wavelength light reflectance, and the larger dimension nanopyramid structure enhances significantly longer wavelength light trapping.

5.1 Light Absorption of Slanting Nanoholes

5.1.1 Introduction and Motivation

The simple and low cost maskless approach based on the metal nanoparticles catalyst electroless etching has been used for the fabrication of large scale SiNH arrays, which can be potentially applied to c-Si solar cells to improve their power conversion efficiency (PCE) and reduce their cost. It is also found that this technique shows a strong preference along the (100) crystallographic orientation of Si [93, 94]. Therefore, it is possible to fabricate slanting SiNH structure by using Si wafer with a different crystallographic orientation and controlling the etching solution concentration. For example, slanting Si nanowire structure with the slanting angle of 40 degree has been fabricated using the Si (111) wafer [93]. Separately, it has been demonstrated that the Si (111) wafer exhibits a better PCE than the Si (100) wafer, especially for Si based hybrid solar cells [52]. Therefore, slanting SiNH structure based on Si (111) wafer shows a potential solution to improve the cell performance while reducing the processing cost.

Chapter 5 Simulation Studies of SiNH Structures

To investigate the potential enhancement of light absorption of the slanting SiNH structure, we perform a systematical design and analysis of the structure. The slanting angle is set at 40 degree based on that reported for the Si (111) NH structure [93]. The influence of the SiNH diameter (D) and structure periodicity (P) on light absorption has been examined to deduce the optimal structural parameters measured using the ultimate efficiency (η_{UE}). The electric field (E-field) distribution arising from the interaction of the sunlight and slanting SiNH structure has also been investigated. It is found that the absorption is significantly enhanced due to the much-suppressed light reflectance and a strong light harvesting ability of the SiNHs, which prolong the optical path length of sunlight significantly within the structure. In addition, a comparison of the light absorption of the slanting and the vertically aligned SiNH structures is also conducted. It is found that the absorption of the slanting SiNH outperforms the vertical counterpart by about ~ 10%.

5.1.2 Simulation Methodology of Slanting SiNH

Figure 5.1 shows the schematic of the three dimensional, top-view and cross-sectional view of the slanting SiNH structure used in the simulation. The slanting angle of the SiNH is fixed at 40 degree as reported [93]. The height (H) of the SiNH is fixed at 1 μm and the thickness of the underlying Si thin film is also set at 1 μm . The D and P of SiNH are varied to obtain the optimal condition for light absorption. The incident light is normally shone on the SiNH structure with the wavelength (λ) ranging from 300 nm to 1100 nm. It covers the main part of solar spectrum of interest for Si solar cells. The commercial software High Frequency Structural Simulator has been used for the simulation.

Figure 5-1 : The simulated slanting SiNH structures. (a) 3D view (b) top view and (b) cross-sectional view of the slanting SiNH structure.

5.1.3 Light Characteristic of the Slanting SiNH

Figure 5.2.a shows the absorption spectra of the slanting SiNH structures with different P and a fixed D/P ratio of 0.8. It is clearly shown in the figure that the change of P has little impact on light absorption at wavelengths below 500 nm. In addition, when P increases, the absorption edge shifts towards the long wavelength region. When P is at 500 nm, the light absorption ranging from 500 nm to 600 nm is the highest. This is because when P is 500 nm, light of comparable wavelength is scattered more efficiently around the SiNH structure, inducing stronger light absorption. As P increases to 600 nm, the peak of the absorption spectrum shifts to the range between 600 and 700 nm. At P of 700 nm, a high and broadband light absorption is achieved. However, when P is further increased to 800 nm, the performance is degraded. The above observations made of the simulation results

Chapter 5 Simulation Studies of SiNH Structures

can be explained using the theory of wave optics [55, 95]. When P is small, the wavelength of the infrared light is much larger than the typical feature size of SiNH dimension. Therefore, the long wavelength light will easily pass through the SiNH structure without strong scattering effect, leading to a high transmittance [55]. Consequently, the light absorption for long wavelength light is low. When the SiNH dimension is comparable with the sunlight wavelength, strong scattering is induced, prolonging the effective optical pass length of the light significantly [96, 97]. However, as P further increases, the separation between the neighboring SiNH structures is getting larger, leading to a high light reflectance and transmittance [55]. Hence, the light absorption drops in our case when P is 800 nm.

Figure 5.2.b shows the light absorption spectra for the slanting SiNH structure with a varying D/P ratio when P is 700 nm. At D/P ratio of 0.6, the absorption of sunlight shorter than 700 nm is low with a value around 0.65. For light with wavelength around 700 nm, the absorption is enhanced because that the P of the structure is 700 nm and it induces strong scattering for light around 700 nm. As the D/P ratio increases to 0.8, the light absorption improves over the solar spectrum from 300 nm to 1100 nm. However, with a further increase of the D/P ratio to 0.9, the absorption of long wavelength light drops. When the structural periodicity is fixed at 700 nm and the D/P ratio is increased to 0.9, the hole diameter increases and there is hence less Si material in the structure. Consequently, the structure approaches that of a planar film resulting in high reflectance.

Figure 5-2 : Absorption spectra of the slanting SiNH structure (a) with different P at a fixed D/P ratio of 0.8 and (b) with different D/P ratios when P is 700 nm.

Figure 5.3 depicts the η_{UE} for the slanting SiNH structures with different P as a function of the D/P ratio. It can be seen that η_{UE} generally increases and then decreases as the D/P ratio changes from 0.5 to 0.95. The optimized D/P ratios for the SiNH structures with different P are located around 0.75 to 0.85. For small P of 300 nm, η_{UE} is low due to the feature size of the SiNH structure being much smaller than the long wavelength light. Hence, it may not generate strong scattering effect. The long wavelength will be easily reflected or penetrated through the SiNH structure, leading to a low η_{UE} . As P increases, the optimized η_{UE} increases because the dimension of the SiNH is approaching the center of the main sunlight spectrum. The maximum η_{UE} of 32.9% is achieved when P is 700 nm and D/P ratio is 0.85. It is also higher than that of its vertical counterpart SiNH structure, which has a highest η_{UE} of only 29.7%. Therefore, it indicates that the slanting SiNH structure has better light absorption ability than the vertical SiNH structure. However, when P is further increased to 900 nm, there is a decrease in η_{UE} . Therefore, the optimal P is achieved with a value of 700 nm. In addition, the D/P ratios between 0.7

Chapter 5 Simulation Studies of SiNH Structures

and 0.95 all yield high η_{UE} , indicating a large tolerance of D/P ratio, which is important and favorable for the fabrication process.

Figure 5-3 : The ultimate efficiency values of the slanting nanohole structure with different P and D/P ratios.

Figure 5.4 gives a comparison of the optical characteristics among the slanting and vertical SiNH structures, and planar Si thin film. It is clearly shown in Fig. 5.4.a that the light reflectance is significantly reduced for both the slanting and vertical SiNH structures as compared with the planar film. This is because the sharp variation of the refractive index between the air and the planar film induces large light reflectance [59, 73]. In contrast, for the SiNH structures the effective refractive index is lower, providing a buffer layer between the air and the underlying Si film. Therefore, the light reflectance can be significantly suppressed due to the better refractive index matching property. It is observed that the light reflectance is further reduced for the slanting SiNH compared with

Chapter 5 Simulation Studies of SiNH Structures

the vertical one for light with wavelength longer than 700 nm. For the light transmittance, the slanting SiNH demonstrates the lowest value over the whole solar spectrum from 300 nm to 1100 nm due to its strong light trapping ability. Consequently, it is shown in Fig.5.4.c that both the slanting and vertical SiNH structures exhibit much higher light absorption than the planar Si film, and the slanting SiNH structure achieves the highest light absorption. For wavelength between 300 nm to 700 nm, the light absorption between the slanting and vertical structures is comparable. While for wavelength longer than 700 nm, the slanting SiNH structure demonstrates a much higher and broadband absorption than the vertical one. Therefore, the slanting SiNH reveals a much enhanced light absorption ability, which is especially critical for longer wavelength light for Si solar cell. Therefore, because of the better refractive index matching with the Si and the air and strong light trapping ability of the slanting SiNH structure, light reflectance is substantially suppressed and light absorption is significantly enhanced over the whole solar spectrum. In addition, we have also done a comparison between an optimum slanting Si nanowire structure aligned also at 40° with $P = 800$ nm, $D/P = 0.7$ with the nanohole structures as shown in Fig. 5.4. The optimum ultimate efficiency of the former is 33.4% whereas for the latter is 32.9%. The results are comparable and indicate their good light harvesting ability. Despite their comparable light absorption, nanohole structures are mechanically more robust and hence favoured as compared to the free-standing nanowires that are fragile and easily broken. Besides, the proposed nanohole structure is interconnected and thus offers excellent carrier transport within the structure, which is in contrast to the isolated nanowire structure.

Figure 5-4 : (a) Reflectance, (b) transmittance and (c) absorption spectra of the planar 2 μm thin film and the optimal vertical (V-SiNH) and slanting (S-SiNH) SiNH structures.

Figure 5.5.a shows the unit cell of the slanting SiNH structure while Figs. 5.5.b to d show the normalized E-fields across the cell structure with incident wavelength of $\lambda = 400 \text{ nm}$, 750 nm and 990 nm respectively. For the planar thin film Si solar cell, the absorption is small because of the high reflectance and the lack of light trapping mechanism [10]. In contrast, the slanting SiNH structure can effectively trap sunlight in the structure. This is seen in the enhanced E-field distributions observed at different wavelengths. When the wavelength is 400 nm , E-field is enhanced mainly at the top of the slanting SiNH structure, indicating the sunlight is absorbed before it reaches the bottom of the structure, and no E-field is seen at the bottom of the film. From the E-field

Chapter 5 Simulation Studies of SiNH Structures

that is still very high above the slanting SiNH structure, it is deduced that light reflectance is relatively strong at this wavelength. Therefore, the absorption is low with a value below 80%. As the wavelength increases to 750 nm, the E-field above the slanting SiNH is relatively weak, indicating lower light reflectance. A stronger E-field pattern is observed within the slanting SiNH structure, signifying that the sunlight is effectively coupled into the structure. However, due to the low absorption coefficient of Si at this wavelength, sunlight cannot be fully absorbed in a single pass. Instead, sunlight will pass through the film and therefore a weak E-field is observed at the bottom of the film. When the wavelength is increased to 990 nm, a stronger E-field is observed within the slanting SiNH structure, which indicates a strong resonance. The absorption path length is significantly increased, leading to a significant improvement in light absorption for the SiNH structure [85].

Figure 5-5 : (a) Unit cell of the slanting SiNH. Normalized E-fields distribution for different wavelengths when (b) $\lambda = 400$ nm, (c) $\lambda = 750$ nm and (d) $\lambda = 990$ nm.

Chapter 5 Simulation Studies of SiNH Structures

To consider a more realistic device structure, we have also simulated the same nanohole structure with a layer of 200 nm thick silver at the back. It is found that the optimum ultimate efficiency occurs at about the same P and D/P ratio as for the structure without the back reflector. Interestingly the optimum ultimate efficiency obtained is 32.4% which is also almost identical to that of the structure without the back reflector. The result suggests that most of the incident radiation has already been absorbed in a single pass by the nanohole structure. This is consistent with the results that we have shown in Fig. 5.5 about the electric field distribution within the structure.

Figure 5.6 shows the effects of the incident angle of light on the optical characteristics of the slanting Si nanohole structure for both TE and TM polarized light. It is observed that for both polarization of light, the ultimate efficiency drops with increasing incident angle. For the case of TM polarization, the ultimate efficiency is not very sensitive with respect to the incident angle, whereas for the case of TE polarization, a sharp drop in ultimate efficiency with incident angle is observed. It is noted that a similar dependence of the ultimate efficiency on the TM and TE polarization as a function of incident angle has been previously reported by Lin et al. [98] for their vertical nanowire and nanohole structures.

Figure 5-6 : The ultimate efficiency of the slanting SiNH structure at different incident angles for both TE/TM polarized light.

5.1.4 Experimental Details of Fabrication of Slanting SiNH

In this work, we have also successfully fabricated slanting SiNH structures using the metal-catalyzed electroless etching technique, which is the common approach used to fabricate Si nanostructures [93, 94]. By controlling the etching solution concentration, we have managed to obtain not only the commonly reported slanting angle of 40 degree, but also 70 degree. Fig. 5.7 shows the fabricated slanting SiNH structure. P type Si (111) wafer with resistivity of 1-50 $\Omega\cdot\text{cm}$ was used in the experiment. Firstly, the sample was cleaned by acetone, IPA and water sequentially for 10 min. It was then put into a Piranha solution (H_2SO_4 and H_2O_2 with a volume ratio of 3:1) for 10 min to clean the organic residue off the surface. After that, it was etched with HF solution (5%) to remove the native oxide from the surface. Following that, the sample was immersed into an AgNO_3/HF solution (4.6 M HF and 5 mM AgNO_3) for 30s to deposit a thin layer of Ag nanoparticles on the surface. Fig. 5.7.a shows the deposited Ag nanoparticles after this

Chapter 5 Simulation Studies of SiNH Structures

process. It is clearly seen that a uniform monolayer of Ag nanoparticles is sitting on top of the Si surface with diameter ranging from ~ 100 nm to ~ 150 nm. After that, the sample was immersed into a HF/H₂O₂ solution to form the hole structure. The Ag nanoparticles function as the etching catalyst in this step, such that wherever there are Ag nanoparticles, the silicon beneath will be etched. After 30 min of etching, the sample was put into a HNO₃ solution to remove the Ag catalyst. Fig. 5.7.b shows the fabricated slanting nanohole structure with an angle of 73 degree when the HF and H₂O₂ concentrations are 4.6 M and 20 mM respectively. When the HF and H₂O₂ concentrations were changed to 4.6 M and 2 mM respectively, a different slanting angles ~ 40 degree is obtained. The result achieved here is consistent with that reported by Huang et al. [99]. Note that the structure obtained experimentally deviates from the one that was used in our simulation earlier on. For example, the diameter and periodicity of the structure fabricated using the metal-catalyzed electroless etching technique cannot be well-controlled and vary over a wide range with $D \sim 100$ nm to 150 nm and $P \sim 150$ nm to 200 nm. These values are also not close to the optimum dimensions that we have deduced from our simulation. Besides, the array fabricated is not periodic which is in contrast to the simulated structure that is orderly. Despite the above, it should be emphasized that there are other techniques, such as using anodic aluminum oxide mask, that can achieve ordered array of silver nanoparticles, and slanting hole structure with the optimum dimensions.

Figure 5-7 : The SEM images of the as-prepared slanting SiNH structure. (a) Top view of the deposited Ag nanoparticles, cross sectional view of the slanting SiNH with an etching concentration of (b) 4.6 M HF and 20 mM H₂O₂ and (c) 4.6 M HF and 2 mM H₂O₂.

In summary, optical simulation has been used to provide a design guideline for the slanting SiNH structure. The effect of the structural periodicity and hole diameter on the light absorption have been investigated. The light absorption is significantly enhanced compared with the planar film due to its better refractive index matching and light trapping property. In addition, it is found that the optimum condition is achieved when the periodicity is 700 nm and diameter/periodicity ratio is 0.85. The highest ultimate efficiency achieved is 32.9%, which is better than that of the optimum vertical SiNH structure of 29.7%. Therefore, the slanting SiNH structure provides an option that can potentially improve the cell efficiency of Si solar cells.

5.2 Light Absorption of Random SiNH Structure

5.2.1 Motivation

To render Si solar cells more cost competitive, Si nanostructures, such as nanowires [10, 11], nanodomes [54] and nanocones [12], have been introduced for light trapping so that the thickness of Si layer needed is reduced. So far, most of the experimental and theoretical work in this area focuses on periodic nanostructures, which are technologically challenging to achieve and costly to realize over a large area. There exist simple and low cost techniques to fabricate nanostructures [24], which nevertheless give rise to disorders such as variations in the positions and dimensions of the nanostructures. To date the effects of such disorders on the optical performance of the nanostructures have not been extensively studied. Recently, Bao et al. [100] and Du et al. [101] have investigated theoretically light absorption for a nanowire structure with random wire length, diameter and position. It was found that light absorption is improved due to the presence of additional resonance modes and broadening of the existing modes. We have studied SiNH structure in the previous chapters which has been found to be better than the SiNW structure in terms of improved light absorption, carriers transport and mechanical robustness [16]. In this section, we further investigate optical characteristics of SiNH structure with randomness introduced into its structural parameters, which include the nanohole radius, depth and position. The results are compared with periodic SiNH structures, and it is found that the random structures offer substantially improved light absorption. The highest absorption is achieved for the structure with random hole position. An ultimate efficiency of 33.8% is obtained, which is 12.7% higher than that of a periodic structure.

Chapter 5 Simulation Studies of SiNH Structures

5.2.2 Simulation of Random SiNH Structures

Figure 5.8 shows the schematic of the periodic nanohole structure (PNS), while Fig. 5.8.b, 5.8.c and 5.8.d show the random nanohole structures (RNS) with respectively randomness in the radius (R), depth (H) and position of the holes. For the PNS, H is fixed at $1\text{ }\mu\text{m}$ and there is an underlying Si film of $1\text{ }\mu\text{m}$ thick, such that the total thickness of Si is $T_I = 2\text{ }\mu\text{m}$. We have simulated the effects of the structural parameters on the optical absorption of the PNS, and identified the optimum structure with $R = 240\text{ nm}$ and periodicity $P = 600\text{ nm}$, that gives rise to the highest ultimate efficiency. The optimum periodic structure will serve as a starting point and reference for our simulation studies to introduce randomness into the structure. For the simulation of RNS, we define a square unit cell with the area of $2.4\text{ }\mu\text{m}$ by $2.4\text{ }\mu\text{m}$ on the x-y plane. Each unit cell is divided into 16 smaller 600 nm by 600 nm sub-cells, with each sub-cell having a SiNH centered within it. This corresponds to the optimum periodicity deduced of $P = 600\text{ nm}$. The 16 SiNHs in the sub-cells have either their depths, positions, or radii randomly generated within certain ranges, as shall be explained shortly. For the $2.4\text{ }\mu\text{m}$ by $2.4\text{ }\mu\text{m}$ unit cell, a perfectly matched layer boundary condition is applied in both the $\pm z$ directions, while periodic boundary condition is used in both the x and y directions to simulate a large area two dimensional structure.

For the RNS with random hole depth, H is allowed to vary randomly from its original value of $1\text{ }\mu\text{m}$ by $\pm 20\%$, that is, H varies from $0.8\text{ }\mu\text{m}$ to $1.2\text{ }\mu\text{m}$, while R is fixed at its optimum value. This variation is based on our experimental observation of SiNHs fabricated using the electroless chemical etching with Ag catalyst formed by laser

Chapter 5 Simulation Studies of SiNH Structures

annealing of a thin Ag film (see Chapter Three). For the fabricated non-periodic SiNH structure, the radius is correlated to the thickness of the starting Ag layer, and generally is not well-controlled and varies over a wide range. For our simulation of RNS with random radius, R is allowed to vary randomly from its optimum value of 240 nm by ± 60 nm, reaching the maximum possible radius without overlapping with neighboring holes in adjacent sub-cells, while H is fixed at its optimum value. Note that the case of $R = 300$ nm corresponds to the situation where each SiNH occupies the entire sub-cell. Similarly, for the RNS with a random hole position, each hole is allowed to change its original center position within one sub-cell by a maximum of ± 60 nm in both x and y directions, while R and H are fixed at their optimum values. The case of the hole position shifted by 60 nm would correspond to the SiNH located at the edge of the sub-cell.

The optical characteristics of these nanohole structures were simulated using the commercial software High Frequency Structural Simulator based on the finite element method. For the simulation, plane wave is incident normally onto the nanostructures with a wavelength λ ranging from 300 nm to 1100 nm. The optical characteristics are obtained by solving the electric field distribution upon the interaction between incident sunlight and the nanohole structures. The refractive index of Si is obtained from the literature [81]. To ensure that the optical characteristics simulated truly reflect randomness in the structural parameters, the simulation was carried out eight times with different random values generated for each RNS. The light absorption spectra obtained are then averaged to derive the light absorption of the RNS. The ultimate efficiency of the RNS are calculated and compared with that of the optimum PNS.

Figure 5-8 : Schematics illustration of (a) periodic SiNH structure, and random SiNH structures with variation in (b) hole radius, (c) hole depth and (d) hole position.

5.2.3 Light Characteristic of Random SiNH

Figure 5.9 shows the optical characteristics of the RNS with varying R and compared with those of the optimum PNS. It can be seen that the RNS has lower reflectance compared to the PNS over the entire wavelength range investigated. In terms of light transmittance, it is almost zero for $\lambda < 700$ nm, indicating that most of the light is absorbed before reaching the bottom of the nanohole structure. This is similar to the results observed for the PNS, and indicates that the presence of randomness in the

Chapter 5 Simulation Studies of SiNH Structures

structure does not compromise the light trapping ability of the nanohole structure. On the other hand, it is noted that light transmittance is higher for the RNS at longer wavelength of $\lambda > 1000$ nm. However this part of the solar spectrum is not important for Si as its absorption coefficient is relatively diminished. Nevertheless, due to the lower reflectance, overall the absorption in this long wavelength range is still better for the RNS as compared to the PNS, as can be seen in Fig. 5.9.c. As for the entire solar spectrum considered, it is noted that the RNS generally offers better absorption relative to the PNS. The same is also observed for the structures with random depth and position, as illustrated in Figs. 5.10.c and 5.11.c. Therefore it is indeed beneficial to have randomness in the SiNH structure as it will help improve light absorption.

Figure 5-9 : (a) Light reflectance, (b) transmittance, and (c) absorption of the SiNH structures with random hole radius.

Chapter 5 Simulation Studies of SiNH Structures

As seen in Fig. 5.9.c, the absorption spectrum of the PNS is noted to be oscillatory for $\lambda > 600$ nm, which indicates the presence of guided modes in the structure. In contrast the light absorption spectrum of the RNS is much flatter and stronger, as the structural symmetry is broken by variation in the hole radius [89, 90]. The structural disorders result in additional resonances and broadening of the existing resonance, and consequently more light coupled into the guiding modes of the RNS and hence enhanced light absorption [102]. Therefore, the absorption can be significantly increased and the spectrum is broadened. Table 5.1 shows the ultimate efficiency of the PNS and RNS. The ultimate efficiency of 33.6% for the structure with random R is higher than that of the PNS of 30%, representing an improvement of about 12%.

Table 5.1 : Ultimate Efficiencies of Different Random SiNH Structures.

Periodic nanohole	Random Hole Radius	Random Hole Depth	Random Hole Position
30.0%	33.6%	32.9%	33.8%

Figure 5.10 and 5.11 show the optical characteristics of the SiNH structures with random hole depth and position, respectively. It is found that their light absorption spectra reveal a similar trend as seen earlier for the case of the structure with random hole radius. The light absorption for the RNS is higher than the PNS, and it is also not as oscillatory in the long wavelength range. For the random hole depth structure, due to the hole depth randomness, the incident light experiences a more gradual change in the effective refractive index. Consequently, due to the better index matching between air and the

Chapter 5 Simulation Studies of SiNH Structures

SiNH structure, light reflectance is substantially reduced as seen in Fig. 5.10.a [59, 73]. The ultimate efficiency achieved is 32.9%, which is 9.7% higher compared with that of the PNS. For the case of the structure with a random hole position, the ultimate efficiency achieved of 33.8% is also improved compared to that of the PNS. In addition, we have simulated a structure incorporating randomness in all the three structural parameters, and the ultimate efficiency of 33.8% is achieved. In conclusion, it is noted that generally light absorption is improved for non-periodic SiNH structures with variation in hole radius, depth and position, as compared to the periodic SiNH structure. This suggests that it is indeed advantageous to use lower cost techniques such as electroless chemical etching with Ag catalyst for the fabrication of such SiNH structures to enhance light absorption. This is important in the attempt to develop low cost and high efficiency Si nanostructures based solar cells.

Figure 5-10 : (a) Light reflectance, (b) transmittance, and (c) absorption of the SiNH structure with random hole depth.

Figure 5-11: (a) Light reflectance, (b) transmittance, and (c) absorption of the SiNH structure with random hole position.

In summary, finite element method has been used to simulate the optical characteristics of SiNH structures with randomness introduced into the structural parameters which include the hole radius, depth and position. The light absorption of the random nanostructures is significantly improved compared to the periodic SiNH structure due to reduced reflectance, additional resonances induced and broadening of the existing resonance. Therefore, the structural randomness is beneficial for light absorption in silicon nanohole structures.

5.3 Light Trapping in Hybrid Nanopyramid and Nanohole Structures

5.3.1 Motivation

To address the issue of weak optical absorption in Si thin films, nanostructures such as nanowires [10, 103], nanocones [12] and nanodomes [54] have been incorporated for light trapping. Other techniques such as plasmonic scattering [104] and diffraction grating [105] have also been investigated. Although the above approaches have demonstrated a strong light trapping ability to boost light absorption, it still remains a challenge for the cell performance to reach the Lambertian limit, which sets the thermodynamic limit for light absorption [90, 106, 107]. This limit is derived based on ray optic with incident light randomly scatters by a thin film [60, 108]. At this limit, the maximum optical path length is enhanced by $4n^2$ times, where n is the refractive index of the material. Such enhancement is important for long wavelength light near the band gap that has a small absorption coefficient [60, 108].

Recent theoretical work has demonstrated the potential to reach the Lambertian limit based on wave optic [54, 109-112]. In this section, we propose a hybrid nanostructure for thin film Si solar cells that combines nanopyramid (NP) and nanohole (NH) structures, which exhibits efficiency that is higher than the Lambertian limit. The hybrid nanostructure is designed with the smaller NH structure to suppress light reflectance for short wavelength light and the larger NP structure to enhance light trapping for long wavelength light. It is noted that the standalone NP and NH structures are not able to reach the Lambertian limit. However, by integrating them, a maximum ultimate efficiency (η_{UE}) of 38.3% at normal incidence of light has been achieved for a 2 μm thick

Chapter 5 Simulation Studies of SiNH Structures

Si solar cell with an optimized hybrid structure. This is higher than the Lambertian limit of 37.0% for the corresponding equivalent 1.33 μm thick Si thin film. The hybrid structure has also revealed a high η_{UE} at oblique incident angles up to 50 degree for TM polarized sunlight. Note that both the NP and NH structures can be fabricated by inexpensive approaches [17, 107, 113]. Therefore, the proposed hybrid structure is promising in improving optical absorption and power conversion efficiency of thin film Si solar cells.

5.3.2 Simulation Methodology

Figure 5.12 shows the (a) 3-dimensional, (b) top and (c) cross-sectional views of a thin film Si solar cell with the hybrid nanostructure. The nanostructure has a square unit cell of dimension P , which is also its period, and each cell comprises an inverted NP and a NH intersected at the apex of the NP. The height of the NP, which is from the base of the pyramid to the peak, is taken to be the same as the period P . The overall height of the hybrid structure is fixed at $T_1 = 1.5 \mu\text{m}$, while the overall thickness of the Si thin film is fixed at $T_2 = 2 \mu\text{m}$. On top of the hybrid structure there is a thin layer of non-absorbing Si_3N_4 with a thickness t that serves as an antireflection and passivation layer. The hybrid structure is placed on a perfect electric conductor (PEC) at the bottom, which serves a similar function as the metal electrode in a real device to reflect sunlight back to the hybrid structure. The optical constants of the crystalline Si and Si_3N_4 are taken from the literature [81]. A full wave finite element method (FEM) was used to simulate the interaction between the incident light and the solar cell [63]. By solving the Maxwell's equation, the spatial electric field distribution in the solar cell can be obtained, from which its optical characteristics can be calculated. To optimize the cell performance, the

Chapter 5 Simulation Studies of SiNH Structures

structure periodicity P was varied from 400 nm to 1000 nm, the diameter to period (D/P) ratio of the NH from 0.3 to 0.9 and the thickness of Si_3N_4 t from 20 nm to 100 nm. The incident light has a wavelength (λ) range from 300 nm to 1130 nm, covering the main solar spectrum of interest for Si. For comparison of photovoltaic performance of cells with different structural parameters, the ultimate efficiency was calculated by assuming an ideal internal quantum efficiency of 100% [9, 88].

Figure 5-12 : The simulated hybrid structure of nanopyramid and nanohole thin film solar cell structure. (a) 3-dimensional schematic, (b) top view and (c) cross-sectional view of the hybrid structure. The blue color represents Si material while the yellow color refers the nonabsorbing Si_3N_4 that is on top of the hybrid structure. The red color represents the perfect electric conductor.

Chapter 5 Simulation Studies of SiNH Structures

5.3.3 Lambertian Limit

The concept of Lambertian surface is introduced by Goetzberger [114] and Yablonovitch [60] in the early 1980s based on randomizing light directions in solar cells. By definition, for a Lambertian surface, it will fully randomize the reflected and the transmitted light. There is no dependence on the direction and position for the photon flux density per solid angle [115]. Two assumptions are generally made for the Lambertian cell [60, 108, 116]. Firstly, the structure feature size is considered much larger than the sunlight wavelength. Consequently, it will not generate wave effects between the light and the film. Secondly, immediately the light enters into the material, there is no correlation between the internal light and the external incident angle. In other words, the light is totally random in terms of the angular distribution.

The approximated equations of the Lambertian limit for light absorption has been derived for a weak absorber such as Si thin film as shown below: [60, 108].

$$A_{\text{limit}} = 1 - \frac{1}{1 + 4n^2\alpha d} \quad (5.1)$$

where d is the film thickness, α the absorption coefficient of the material and n the real part of the refractive index.

5.3.4 Light Absorption of Hybrid SiNH and Pyramid Structure

The optimized hybrid structure that gives rise to the highest ultimate efficiency has the following structural parameters, $P = 800$ nm, $D = 560$ nm, and $t = 80$ nm. In Fig. 5.13, we compare light absorption of the optimized hybrid structure, the planar film without nanostructure and the Lambertian limit of the corresponding equivalent $1.33 \mu\text{m}$ thick Si

Chapter 5 Simulation Studies of SiNH Structures

thin film. The Si planar film has the same thickness of 2 μm as the hybrid structure, and also with an 80 nm thick Si_3N_4 layer on top and a PEC layer at the bottom. It is clearly seen that light absorption in the hybrid structure is high over a broadband and is significantly enhanced compared with the planar film. For shorter wavelength of $\lambda < 450$ nm, the absorption is around 90% and slightly lower than that of the Lambertian limit which are approaching 100%. For $450 \text{ nm} < \lambda < 700 \text{ nm}$, which covers the main solar spectrum, the absorption of the hybrid structure is 95%, which is much better than that of the planar film and is comparable with the Lambertian limit. For $700 \text{ nm} < \lambda < 800 \text{ nm}$, the absorption in the hybrid structure is slightly lower than the Lambertian limit. However, for $800 \text{ nm} < \lambda < 1100 \text{ nm}$, it is generally higher than the Lambertian limit, indicating the strong light trapping ability of the hybrid structure at long wavelength. Compared with the planar film without the nanostructure, the hybrid structure reveals much improved light absorption enhancement over the whole solar spectrum. For the short wavelength light region, the light absorption enhancement is mainly contributed by the smaller nanohole structure. For the longer wavelength light, the enhancement is due to the larger pyramid structure. The optimized hybrid structure has a high η_{UE} of 38.3%, as compared to the Lambertian limit of 37.0%. Hence, it offers a potential means to surpass the Lambertian limit and achieve high efficiency thin film Si solar cells.

Figure 5-13 : Absorption spectra of the optimized hybrid structure, planar Si thin film cell of 2 μm thick, and Lambertian limit absorption for 1.33 μm thick Si thin film cell.

In order to achieve a high broadband light absorption and hence high efficiency solar cell, it is critical to suppress light reflectance at shorter λ and improve light trapping at longer λ . For shorter $\lambda < 700$ nm, the design consideration is focused on suppressing light reflectance at the top surface. Firstly, due to the gradual change in the size of the NP, light scatters and couples effectively into the hybrid structure owing to much improved refractive index matching [59, 73]. In addition, the comparable feature size of the NH with the shorter λ and the antireflection coating has played a role in achieving this objective. For longer $\lambda > 700$ nm, the focus is on improving light absorption since the absorption coefficient is weak in Si in this wavelength range. When P is much smaller than λ , only a few guided resonance modes are excited in the Si thin film and hence light absorption enhancement is marginal. On the other hand, when P is much larger than λ , although more guided resonance modes are excited, they are easily coupled and leaked to

Chapter 5 Simulation Studies of SiNH Structures

the increased external channels [112, 117, 118]. When P is comparable but slight smaller than λ , the number of guided resonance modes increases quadratically with decreasing λ [112, 117], and the maximum absorption is achieved when $P = \lambda$, giving rise to an enhancement factor of $4\pi n^2$ [112, 117]. Therefore, at $P = 800$ nm, the NP and NH can effectively guide the incident light within the hybrid structure, resulting in enhanced absorption above the Lambertian limit for $800 \text{ nm} < \lambda < 1100 \text{ nm}$. The slight drop in absorption when $\lambda < P$ is attributed to an increase in the number of leakage channels. Hence light is not well confined in the hybrid structure, but is instead leaked through higher order channels [112, 117]. Overall, the optimized hybrid structure has achieved a much improved light absorption by suppressing light reflectance with the smaller feature size NH structure and enhancing light trapping due to the excited guided resonances from the larger size NP.

Figure 5.14 shows the angular dependence of the η_{UE} of the hybrid structure for both TE and TM polarized lights. The η_{UE} is nearly constant for both polarizations of light when the incident angle (θ) is less than 10 degree. Beyond that, it decreases with the rate being faster for the TE polarized light. Note that the η_{UE} is still larger than the Lambertian limit up to $\theta = 50$ degree for TM polarized light, and it is maintained above 34% even at $\theta = 70$ degree. The decrease in light absorption at larger θ is attributed to an increase in coupling to the leakage channels at increasing θ , resulting in a substantial reduction in light absorption [117]. It is worth noting that the high η_{UE} observed even at larger θ suggests that the hybrid structure is very promising for practical application as sunlight is rarely incident normally on a solar cell.

Figure 5-14 : The angular dependence of the ultimate efficiency of the hybrid cell for both TE and TM polarized light.

In summary, we have proposed a hybrid solar cell structure that comprises nanopyramids and nanoholes. The optimized structure has the periodicity of 800 nm, nanohole diameter of 560 nm and Si_3N_4 thickness of 80 nm. The hybrid solar cell has light absorption that is substantially increased above the Lambertian limit, achieving an ultimate efficiency of 38.3%. The ultimate efficiency value is maintained above the Lambertian limit even for incident angle up to 50 degree for TM polarized sunlight. The results suggest that the proposed hybrid nanostructure is very promising in achieving high efficiency thin film Si solar cells.

5.4 Conclusion

In summary, we have studied light absorption for the SiNH structure with different configurations and arrangements. For the slanting SiNH structure, the optimal condition is achieved when the periodicity is 700 nm and diameter/periodicity ratio is 0.85. The

Chapter 5 Simulation Studies of SiNH Structures

highest ultimate efficiency achieved is 32.9%, which is higher than that of the vertical counterpart of 29.7%. For the SiNH structure with randomness introduced into its structural parameters, namely, the hole radius, depth and position, light absorption is significantly improved compared to the periodic nanohole array due to reduced reflectance, additional resonances induced and broadening of the existing resonance. Therefore, structural randomness is beneficial for light absorption in silicon nanohole structure. This means that lower cost fabrication techniques that introduce randomness into the SiNH structure are better as compared to the costly lithographic techniques that produce periodic structures. Lastly, the hybrid solar cell structure that comprises nanopyramids and nanoholes has been investigated. The optimized structure has a periodicity of 800 nm, nanohole diameter of 560 nm and Si_3N_4 thickness of 80 nm. The hybrid solar cell has light absorption that is substantially increased above the Lambertian limit, achieving an ultimate efficiency of 38.3%.

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

6.1 Introduction and Background

To further reduce the cost of Si/organic hybrid solar cell, it is important that the device is fabricated on Si thin films, rather than bulk Si wafers. Therefore we have also studied the formation of poly-crystalline Si (poly-Si) based on laser annealing of amorphous silicon (a-Si) thin films. Besides achieving crystallization, our approach of using the laser annealing process has also resulted in the formation of nanostructures on the surface of the poly-Si films, which is important for light trapping and enhancement of optical absorption. Such thermally annealed poly-Si films can be used to form thin film poly-Si solar cells and poly-Si/organic hybrid cells. Our study in this work is mainly focused on the laser annealing of a-Si thin films, and their resultant microstructures and crystallization, as well as the formation of nanostructures on the surface.

Two studies on the crystallization of a-Si thin films with concurrent nanostructures formation using laser annealing are presented. Firstly, diode-pumped solid-state neodymium doped yttrium orthvanadate (DPSS Nd:YVO₄) UV laser will be used to crystallize 400 nm thick amorphous silicon (a-Si) thin film, which also results in the formation of nano-dome structure on the surface. Secondly, a femtosecond pulsed laser is used to crystallize 1.6 μm thick a-Si thin film and concurrently form nanocone structure on the surface. In addition, we have studied the use of the same femtosecond laser to

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

directly anneal crystalline Si wafer to form nano-ripple structure for light trapping and optical absorption enhancement.

6.2 Review of Crystallization of Si Thin Films

There are three different crystallization methods that are commonly used to form poly-Si from a-Si. They are solid phase crystallization, metal induced crystallization and laser annealing crystallization. A review of these methods is presented in the following sections.

6.2.1 Solid Phase Crystallization (SPC)

Solid Phase Crystallization (SPC) is the most direct method of realizing poly-Si film by annealing a-Si in a furnace with a protective gas. It normally requires an annealing time of over 10 hours with temperature of at least 600 °C. The thermodynamically metastable a-Si will transform to poly-Si given sufficient thermal energy to overcome the energy barrier [119]. The most critical factor that affects the crystallization process is the nucleation rate of a-Si film, which is mainly determined by the disorder in the deposited a-Si. With a higher degree of disorder, it is more difficult for the film to nucleate and higher annealing temperature and longer time are required to crystallize the film [119]. The disorder in turn is determined by the deposition conditions of the a-Si. In order to increase the SPC nucleation rate, the a-Si should be deposited at higher temperature and slower rate. Although poly-Si can be achieved using the SPC method, however, the poly-Si formed was observed to have a high density of structural defects which significantly impede the mobility of charge carriers [119]. In addition, the high temperature and long

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

annealing time required make it difficult to adopt the use of low cost and large area substrates, such as plastic and glass.

6.2.2 Metal Induced Crystallization (MIC)

Metal Induced Crystallization (MIC) is an advanced SPC technique because it substantially reduces the crystallization temperature required. The typical annealing temperature for MIC process is around 500 °C [120]. A thin layer of Al [121], Ni [122] or Au [123] is first coated on the substrate, which is then followed by the deposition of an a-Si thin film. Due to the presence of the metal atoms, the Si-Si covalent bond is weakened and the crystallization energy barrier is lowered because of the opposite diffusion direction of metal and Si atoms [124]. Since the MIC process mainly depends on the type of metal used, it imposes fewer requirements on the deposition condition of the a-Si film. In addition, due to lower annealing temperature, cheaper substrates can be used. However, the residual metal inside the poly-Si film can seriously degrade the performance and the long term stability of solar cells fabricated using poly-Si films formed by the MIC technique.

6.2.3 Laser Annealing Crystallization

Laser annealing crystallization uses laser beams with high energy density and short pulse duration to induce lateral solidification of a-Si film. The compatibility of the method with low cost substrate has rendered it attractive. The most commonly used lasers

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

are the XeCl, KrF, and ArF excimer lasers, with corresponding laser wavelengths of 308 nm, 248 nm, and 193 nm [125, 126].

When laser is shot on the a-Si film surface, three typical regimes of transformation can be identified, which are low energy regime, high energy regime and sequential lateral growth regime [127]. In the low energy regime, the laser beam energy is only sufficient to melt the top layer of the a-Si, while its bottom still remains as a continuous solid layer. Hence this is also referred to as the partial melting regime. When the laser beam energy is high enough to induce the complete melting of the whole a-Si layer, it is identified as the high energy regime, which is also called the complete regime. The exact energy required to induce this complete melting of the a-Si depends on many factors such as the a-Si thin film thickness, pulse duration and substrate temperature. As the underlying substrate is in amorphous state, the epitaxial growth to form crystallized Si is not possible. Between the low and high energy regimes, a narrow experimental window has been identified which is capable of leading to the formation of crystallized Si. It has been modeled by Im and coworkers that in this regime, the unmelted bottom layer is no longer continuous but is characterized to have many small islands separated by liquid Si [128]. As shown in Fig.6.1, the black dots represent unmelted islands which function as the nucleation seeds, from which the lateral growth can take place [119]. Therefore, this regime is also named as near-complete melting regime. The crystallization mechanism can be characterized as sequential lateral solidification (SLS) due to the coexistence of solid and liquid Si.

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

Figure 6-1 : Schematic of near-complete region and following crystallization process [119].

Laser induced crystallized a-Si thin film has been researched actively to form thin film poly-Si solar cells using the seed layer or layered laser crystallization (LLC) method. For the seed layer method, a 100 nm thick a-Si is deposited which is then followed by the laser crystallization to transform the a-Si into poly-Si. The layer is then epitaxially thickened using rapid thermal chemical vapor deposition to form a 2 μm thick absorbing layer. A 5.4% efficiency of the complete cell has been achieved by Gestel et al [129]. As for the LLC method used to crystallize a-Si, it is illustrated in Fig. 6.2 [130] where a thin layer of 600 nm highly boron doped a-Si film is first deposited. A continuous wave laser is then used to crystallize the film with a grain size of around 100 μm. After that, a 2 to 5 μm thick absorber layer is deposited and laser annealed simultaneously. Essentially, whenever a 10 nm of the absorbing layer is deposited, excimer laser beam is used to anneal the film, and this is repeated until the final absorbing thickness is reached. Finally, a highly phosphorus doped layer is deposited to form the emitter layer. The efficiency of

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

the reported solar cell is 4.8% [130]. With the process optimization, the efficiency has been improved to 5.2% recently [131].

Figure 6-2 : Schematic of the layered laser crystallization cell [130].

The poly-Si film has to be fabricated directly on low cost substrates, such as glass. The method of laser annealing as discussed above can bypass high temperature process to improve the film quality, yet without damaging the underlying glass [132]. Therefore, in our study of formation of poly-Si from a-Si thin films, we have chosen the laser annealing approach to obtain high quality poly-Si, operating in the near complete melting regime following the SLS process [133, 134].

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

6.3 UV Laser Crystallization of a-Si

6.3.1 Introduction

Poly-Si thin film has been actively studied for solar cell application due to the cost reduction as compared to crystalline bulk Si. As explained in the previous section, laser annealing is an important approach to obtain high quality poly-Si without damaging the substrate. Conventionally, excimer lasers with typical wavelengths of 248 and 308 nm have been used due to their short wavelength which can be easily absorbed by Si [135, 136]. However, the operation and maintenance cost of excimer laser is high. It also requires a long processing time to accomplish a uniform crystallization on a large substrate, given that the repetition rate for excimer laser is normally limited to 300 Hz [134]. Therefore, an alternative efficient approach of using diode pumped solid state (DPSS) Nd:YVO₄ UV laser has been pursued [134]. The crystallization mechanism is as follows: (i) there is a laser processing window where the power intensity of the optical beam is sufficient to melt the Si films and a stage of coexistence of solid and liquid regions can be sustained [137], as explained in the previous section, (ii) the crystallization then follows the SLS process in which generated Si crystal seeds can be dragged epitaxially in the desired lateral direction [127, 138], and (iii) further lateral growth of the previously formed grains via epitaxial growth could possibly be attained by properly adjusting the relative position between the sample and incident beam [133]. With repeated exposure to the laser beam, poly-Si film can be obtained.

In this section, we report on the laser induced crystallization and surface texturing of a-Si in a one-step process using 355 nm DPSS Nd:YVO₄ laser. The optimal laser annealing

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

condition for the crystallization of 400 nm thick a-Si and the concurrent formation of nano-dome structure on the surface has been identified. The material quality and light trapping ability of the laser treated a-Si are found to be improved. The developed process has potential application in the fabrication of high efficiency thin film Si solar cell.

6.3.2 Experimental Details

Figure 6-3 : Schematic illustration of laser crystallization process on a-Si thin film: (a) as deposited 400 nm a-Si on 100 nm SiO₂ coated glass surface; (b) laser annealing of a-Si thin film; (c) nanodome structure formation after laser annealing; (d) Secco etch to reveal the grain boundaries.

Figure 6.3 shows the schematic illustration of the laser annealing process. The a-Si film with a thickness of 400 nm was deposited on a glass substrate (corning 1737, 25 × 25 mm²) with a SiO₂ buffer layer of thickness 100 nm (Fig. 6.3.a) by the plasma enhanced chemical vapor deposition technique (PECVD, Cello Aegis-20). SiH₄ and SiH₄/N₂O were

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

used for the deposition of Si and SiO₂ respectively, operated at radio frequency (RF, 13.56 MHz) with a deposition pressure of 400 mTorr. The RF powers used for the growth of SiO₂ and a-Si were 20 W and 60 W respectively. In order to control hydrogen desorption, the deposition was conducted at a high temperature of 400 °C to obtain a hydrogen content of ~2 at.% in a-Si, as measured by Fourier transform infrared spectroscopy (FTIR).

The Q-switched DPSS Nd:YVO₄ laser (Coherent Avia-X) was used for the annealing of the a-Si deposited. The laser wavelength is 355 nm and the laser pulse frequency ranges from 1 kHz to 100 kHz. The pulse duration of the laser beam is 20 ns to 35 ns depending on the laser pulse frequency used. The output beam profile is Gaussian shape and the spatial mode is TEM₀₀ (M₂<1.3). The beam divergence is less than 0.3 mrad. During the crystallization, the laser beam with the diameter of 3.5 mm (@ 1/e²) was focused by a cylindrical lens with the focal length of 100 mm so as to obtain a line shape beam with the width of 50 μm. The crystallization was performed in air at room temperature. The position of the laser beam was fixed and a computer-controlled X-Y translation stage (with the accuracy of 5 μm) was used to move the sample in the x direction with the constant scanning speed of 20 mm/s. The laser pulse repetition rate was set at 20 kHz. Accordingly, the sample was translated by a distance of 1 μm between each laser pulse to facilitate the lateral crystalline growth [134]. After each scan, the sample was moved in the y direction by the distance of 100 μm to achieve the beam overlap of ~ 97 %. In order to find the optimum conditions, the laser scanning was conducted at various laser energy densities from 196 mJ/cm² to 507 mJ/cm². The morphologies of the laser treated samples were analyzed using field-emission scanning electron microscopy (FESEM, LEO, 1550

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

Gemini, resolution 1nm), and atom force microscope (AFM, NS3A). Raman spectra were recorded at room temperature with an excitation wavelength of 532 nm (WITec, alpha300 R, resolution 2 cm^{-1}). The reflectance and transmittance spectra were measured with Lambda 950 UV-VIS-NIR scanning spectrophotometer (PerkinElmer, resolution for UV/Visible light is 0.05 nm, for infrared light is 0.2 nm).

6.3.3 Crystallization of a-Si and Formation of Nanodome Structure

Figure 6-4: SEM images of (a) as-deposited a-Si and 400 nm thick a-Si thin films irradiated under different laser energy densities: (b) 266 mJ/cm², (d) 294 mJ/cm², (e) 380 mJ/cm², (f) 439 mJ/cm².

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

Figure 6.4.a-6.4.e depicts the SEM images of the laser treated Si surfaces with different energy densities from 266 mJ/cm^2 to 439 mJ/cm^2 . Fig. 6.4.a shows the untreated a-Si film with no surface modification. Fig. 6.4.b shows the surface profile with the energy density of 266 mJ/cm^2 , below which the laser is not able to melt the a-Si film. In this case, minor surface modification and small grain of poly-crystalline are observed due to partial melting of the a-Si film [128]. At the energy density of 294 mJ/cm^2 , major surface morphology change is observed (Fig. 6.4.c) compared with the as-deposited a-Si film. When the energy density is increased to 380 mJ/cm^2 , the film is crystallized and yields the nanodome structure as shown in Fig. 6.4.d. At this energy density, the crystallization falls into solid liquid growth regime as modeled by Im [127, 128, 138]. During the laser annealing, the a-Si film is almost completely melted with small solid islands at the interface of silicon and glass, acting as solidification seeds during cooling. Due to the temperature gradient between the solid and liquid silicon, it tends to lead to the hydrodynamic motion, which will instigate surface tension and capillary waves. Thus, the surface morphology is changed with the dome structure formed. Fig. 6.4.e illustrates that the continuous a-Si film breaks and shrinks into spherical beads, implying serious damage when the energy density is increased to 439 mJ/cm^2 . This agglomeration is speculated to be caused by outburst of the heterogeneously nucleated vapor bubble inside the silicon layer [139]. At this high pulse energy, the film is completely melted with vapor bubbles formed in the liquid film. Those bubbles then diffuse and burst at the outer surface, breaking the continuity of the film. Therefore, it indicates that the maximum energy density for crystallization is below 439 mJ/cm^2 .

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

Figure 6-5 : Raman spectra of 400 nm thick a-Si thin films irradiated with laser energy densities: 294 mJ/cm², 380 mJ/cm², 439 mJ/cm² and 507 mJ/cm² with intensity peak 520 cm⁻¹. The inset shows the Raman spectrum of the original as deposited a-Si film, with the peak at ~ 480cm⁻¹.

Figure 6.5 shows the Raman spectra of the a-Si thin films annealed at different energy densities to understand their crystalline property. For the as-deposited sample, it exhibits a broad and weak peak at ~ 480 cm⁻¹, which corresponds to the typical spectrum observed for a-Si [140]. With increasing laser energy density from 294 to 507 mJ/cm², the peaks of the Raman spectra shift towards 520 cm⁻¹, suggesting the formation of crystalline Si[141]. The estimated crystalline volume fractions of the crystallized Si are calculated from the Raman spectra [142]. When the energy density is 294 mJ/cm², 64 % of the film is crystallized, whereas at the energy density of 380 mJ/cm², ~ 98 % crystalline volume fraction is achieved. Although a further increase in the energy density can realize complete crystallization, however, it also leads to a loss of surface continuity. At the energy density of 507 mJ/cm², the spectral width is seen to be broadened and the peak is shifted backward to 515 cm⁻¹, due to the crystallization and the ablation of the a-Si film as explained previously.

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

Figure 6-6 : Surface morphologies of (a) original as deposited planar 400 nm thick a-Si thin film with a roughness of 3.4 nm and (b) UV laser irradiated film with laser energy density 380 mJ/cm^2 . The AFM scan area is $5 \mu\text{m} \times 5 \mu\text{m}$.

Figure 6.6 demonstrates the surface profiles of the as-deposited and laser processed 400 nm a-Si thin films by the AFM measurement. It is observed that a regular nano-dome pattern is achieved after UV laser treatment with the pulse energy of 380 mJ/cm^2 . The diameter of the nano-dome structure is around 300 to 500 nm with the height of ~ 200 nm. The primary reason for surface texturing is due to the difference in densities between the solid and liquid Si. Since the liquid Si is much denser than the solid silicon, as the solid region grows after melting, it tends to expand and produces ridges and hillocks around the grain boundary [143, 144]. More importantly, the previously produced nanostructure can act as a diffraction grating for the following laser beam illumination. Hence the generated diffracted waves along the surface interfere with the incident waves [143, 145], modifying the surface morphology when the interference is sufficiently strong.

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

6.3.4 Optical Characteristics of the Nanodome Structure

Figure 6-7 : (a) Reflectance, (b) transmittance and (c) absorption spectra of laser treated 400 nm thick a-Si thin films with laser energy densities of 294 mJ/cm², 380 mJ/cm², 439 mJ/cm² and 507 mJ/cm². The original as-deposited planar 400 nm a-Si is used as a reference. (d) Absorption spectra of a-Si thin film with thickness of 100 nm.

Figure 6.7 depicts the reflectance (R), transmittance (T) and absorption (A) spectra for the as-grown and laser treated 400 nm thick a-Si thin films treated with the energy densities of 294 mJ/cm², 380 mJ/cm², 439 mJ/cm² and 507 mJ/cm². The R and T spectra were measured by UV-VIS-NIR spectrophotometer, whereas the absorption spectra were obtained by $100 - R - T$. For the as-deposited a-Si, its reflectance (with peak value around $\sim 50\%$) and transmittance (with peak value around $\sim 85\%$) are high with strong oscillation for longer wavelength beyond 500 nm. Upon the scanning of the UV laser, the

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

absorption is increased and the reflectance and transmittance are lowered for all different pulse energies used. When the energy density is 294 mJ/cm^2 , the absorption increment is obvious for the short wavelength light ($< 600 \text{ nm}$). The reflectance drops from $\sim 35\%$ to $\sim 20\%$ for the wavelength of 400 nm . With no change in the transmittance, the absorption increases by 15% . Nevertheless, the improvement in long wavelength light region ($> 600 \text{ nm}$) is not evident. This is because at low laser energy, it is insufficient to induce crystallization and major surface modification for a-Si. The film remains amorphous and the feature size formed is much smaller than that of long wavelength light. The incident light fails to distinguish the structure and thus is relatively easy to penetrate through the film [95]. When the energy density is increased to 380 mJ/cm^2 , the nano-dome structure has a feature size comparable with 400 nm which is located near the peak of the solar spectrum. Hence, the interaction of the incident light with the structure is dominated by the scattering effect, which dramatically prolongs the optical path length of sunlight [97, 146]. Besides, the dome structure has a gradual change of the effective refractive index, which functions as a good antireflective coating. Furthermore, the point with occurrence of oscillation for reflectance and transmittance spectra shifts towards $\sim 800 \text{ nm}$ compared with $\sim 500 \text{ nm}$ of as deposited a-Si thin film and the absorption for the long wavelength (beyond 730 nm , corresponding to the band gap of a-Si: 1.7 eV) is effectively increased. This can be correlated with the band-gap variation after crystallization (band-gap changes to 1.1 eV for poly-crystallized Si). As a result, the absorption enhancement (or ultimate efficiency [9, 88],) improves by $\sim 200\%$ compared with as-deposited a-Si film and the ultimate efficiency increases from 8.1% to 23.9% . However, a further increase of the energy density to 439 mJ/cm^2 aggravates both the reflectance for wavelength beyond 700

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

nm and transmittance for short wavelength light below 600 nm. Together with the disappearing of oscillation phenomenon, it might be correlated with the fact that there is no complete film on the substrate due to agglomeration. Furthermore, the sensitivity of the layer thickness is investigated by reducing the a-Si film to 100 nm as shown in Fig.6.7.d. The results demonstrate that the absorption efficiency variance due to the change of thickness is not significant, with the peak value of absorption drops from ~90% to ~ 83%.

6.3.5 Comparison with Simulation

The experimental results obtained are compared with the simulation results as shown in Fig. 6.8. The details of the simulation can be found in the section of simulation methodology in chapter 5. For the numerical simulation, finite element method is used to solve the Maxwell's equation to model the laser induced structure. A unit dome cell bounded by periodical and perfect match layer with periodicity of 300/400 nm is irradiated by sunlight of wavelength ranging from 300 nm to 1100 nm. The height of the nanodome is 300 nm and the underlying silicon film is 100 nm. The absorption spectra are obtained after subtracting the reflectance on the top surface and transmittance on the bottom surface. It is seen that the experimental result is consistent with the simulation result for wavelength ranging from 300 nm to 800 nm, especially for the structure with a periodicity of 400 nm, which indicates good quality of laser processed nanodome texturing. It is also observed that the simulated absorption spectrum exhibits oscillation, in contrast to the experimental result, which is due to the interference among the perfect periodic structures.

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

Figure 6-8 : Absorption spectra of: (i) experimental 400 nm thick a-Si thin film irradiated with laser pulse energy 380 mJ/cm^2 and (ii) simulated Si nanodome structure with a periodicity of 300 nm and 400 nm. The dome height is 300 nm and the underlying film is 100 nm. The inset shows the simulated periodical nanodome structure.

In summary, 355 nm DPSS Nd:YVO₄ laser has been used to successfully crystallize and texture a-Si thin film in a one-step annealing process. The laser treated film with pulse energy 380 mJ/cm^2 yields a $\sim 200\%$ improvement in the optical absorption due to the nano-dome structure and band gap change after crystallization. Hence, laser annealing is a very promising solution for the realization of textured poly-Si films for applications in high efficiency Si thin film solar cells.

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

6.4 Femtosecond Laser Crystallization of a-Si

6.4.1 Motivation

In the previous section, UV laser has been used to successfully crystallize a 400 nm thick a-Si film. However, the thickness is not sufficient to deliver a good performance for thin film solar cells where a $\sim 2 \mu\text{m}$ thick film is required. Conventionally, crystallization of thicker Si layer is achieved either by layer laser crystallization which requires repetitive sequential deposition and laser annealing of thin a-Si layers [147] or by laser annealing of an a-Si seed layer, followed by epitaxial growth [138]. These processes usually require special equipment configuration and are costly. Therefore, there is a need to develop a simpler process that can crystallize thick a-Si layer. Near infrared femtosecond (FS) laser has been shown to provide a potential solution to achieve the crystallization of $\sim 2 \mu\text{m}$ thick a-Si film [148, 149]. The interaction between the femtosecond laser pulse and the a-Si layer is dominated by nonlinear photon absorption and nonequilibrium thermodynamics [150-152]. Meanwhile, due to the ultra-short pulse duration of the FS laser, there is reduced thermal diffusion and hence it is possible to have a precise control over the texturing process [153]. Extensive work has been reported by Mazur and Nayak on the texturing of c-Si wafer and a-Si to achieve conical structure with dimension around 5 - 10 μm [154-156]. On the other hand, the realization of smaller ordered cone structure at the nanoscale size has been rarely reported. In this section, we study the crystallization of 1.6 μm thick a-Si film and the formation of conical structure simultaneously using an ultrafast 775 nm FS laser in air. The average diameter of the conical structures formed can vary from 160 nm to 1.4 μm , which are much smaller than those previously reported [148, 154-156]. In addition, the developed cone structure has a

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

dimension comparable with the wavelength of solar spectrum of interest for Si. Hence, the structure demonstrates strong light trapping as the cone structure can induce strong scattering and enhance optical path length [55].

6.4.2 Experimental Details

The glass substrate is cleaned and the PECVD system was used to deposit the a-Si films with a thickness of 1.6 μm . For the laser annealing process, femtosecond pulsed laser (Clark-MXR, CPA 2001) based on the regenerative Ti-Sapphire amplifier using chirped pulse amplification technique was used. The pulse duration of the laser beam is 150 fs and the frequency is 1 kHz. The nominal wavelength of laser beam is 775 nm with the beam diameter of 3.5 mm ($@ 1/e^2$). The laser beam was focused by a cylindrical lens so as to obtain a line shape beam with the width of 50 μm . The laser annealing process was performed at room temperature in air. The sample was mounted on a computer-controlled X-Y translation stage with the accuracy of 5 μm . During the annealing, the position of the laser beam was fixed while the sample was moved in the x direction at a scanning speed of 10 mm/s. After a complete scan along the x direction, the sample was shifted in the y direction by 100 μm and then scanned again along the x direction. In order to find the optimum irradiation condition, the laser fluence (F) was varied from 255 mJ/cm^2 to 784 mJ/cm^2 . The morphologies of the laser treated samples were analyzed using field-emission scanning electron microscopy (FESEM, LEO, 1550 Gemini, resolution = 1 nm), and atom force microscope (AFM, NS3A). The samples were also characterized using Raman spectroscopy at room temperature with an excitation wavelength of 532 nm (WITec, alpha300 R, resolution = 2 cm^{-1}). The reflectance and transmittance spectra were measured with the PerkinElmer Lambda 950 UV-VIS-NIR scanning spectrophotometer

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

with an integrating sphere. The resolution for UV/Visible light is 0.05 nm and for infrared light is 0.2 nm.

6.4.3 Formation of Nanocone Structures

Figure 6.9 shows the AFM images of the as deposited and the laser-annealed films. Fig.6.9.a gives the surface morphology of the as-deposited a-Si film with an average surface roughness of ~ 4.3 nm. Fig. 6.9.b shows the surface profile of the a-Si film annealed with $F = 255$ mJ/cm². A dense ordered nanocone structure is formed on the surface, with an average cone diameter (D) of ~ 160 nm and height (H) of 60 nm. At $F = 333$ mJ/cm² (Fig. 6.9.c), the conical structure is getting larger and the average D and H increase to ~ 250 nm and ~ 150 nm, respectively. Fig. 6.9.d and Fig. 6.9.e reveal the surface profiles at $F = 372$ mJ/cm² and 490 mJ/cm² respectively, and a further increase in the dimension of the conical structure is observed. Fig. 6.9.f shows at $F = 588$ mJ/cm², the dimension of the cone has evolved into micro scale size with an average cone diameter of ~ 1.4 μ m, which results from a merging of neighboring smaller cones. At the largest $F = 784$ mJ/cm² (Fig. 6.9.g), the film is seriously ablated and the continuity is broken. The cones are either substantially merged to form rows of ridge structure or separated with a larger dimension. Figure 6.10 depicts the morphology of the FS laser treated Si surfaces with $F = 588$ mJ/cm² and 784 mJ/cm², respectively. It is clearly seen that at $F = 784$ mJ/cm², many larger cones are separated and on the right of the figure, some cones are noted to have merged.

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

Figure 6-9 : AFM images of 1.6 μm Si thin film treated with different laser fluences : (a) as-deposited, (b) 255 mJ/cm^2 , (c) 333 mJ/cm^2 , (d) 372 mJ/cm^2 , (e) 490 mJ/cm^2 , (f) 588 mJ/cm^2 and (g) 784 mJ/cm^2 . The AFM scan area is 5 $\mu\text{m} \times 5 \mu\text{m}$.

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

Figure 6-10 : SEM images of 1.6 μm Si thin film treated with laser fluences : (a) 588 mJ/cm^2 and (b) 784 mJ/cm^2 .

Figure 6.11 summarize the change of the conical structure dimension with laser fluence. It is shown that the average diameter and height increase with the laser fluence. Therefore, by controlling the laser fluence, it is possible to vary the cone diameter from 160 nm to 1.4 μm . Since the solar spectrum of interest for poly-Si thin film solar cells is between 300 nm and 1100 nm, nanostructures with feature size comparable with wavelength of sunlight can induce strong light trapping within the thin film [55]. Furthermore, many works on nanostructured solar cells have demonstrated that the enhanced light absorption of those nanostructures will contribute to a stronger optical absorption and consequently a larger photocurrent [15]. Therefore, the conical structure fabricated if incorporated into thin film Si solar cell, is very promising in improving its efficiency.

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

Figure 6-11 : Diameter and height of the as formed conical structures after laser irradiation under different laser fluences.

6.4.4 Crystallization of 1.6 μm a-Si Film

Figure 6.12 shows the Raman spectra of the films irradiated under different laser fluences. The inset shows the Raman spectrum of the as-deposited a-Si, which has a characteristic broad and weak peak located at $\sim 480 \text{ cm}^{-1}$ [140]. Upon irradiation, the Raman spectra exhibit a sharp peak centered near $\sim 520 \text{ cm}^{-1}$, suggesting that amorphous Si has been crystallized [141]. Additionally, we have also measured the Raman spectrum of the film from the backside and a similar 520 cm^{-1} peak is observed, confirming the whole thickness of the film has been crystallized. For the film under laser irradiation, the high level of excited electrons in the conduction band induced by irradiation substantially weakens the atomic bonds, which leads to atomic motion and structural transformation, resulting in crystallization [150]. The crystalline peak intensity increases with F until it reaches $\sim 490 \text{ mJ/cm}^2$. After that, it decreases with increasing F , attributed to the ablation of Si at higher energy. We have evaluated the crystalline volume fraction of the films

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

from their Raman spectra. The Raman spectra of the samples consist of two peaks, one located at $\sim 480 \text{ cm}^{-1}$ and the other located at $\sim 520 \text{ cm}^{-1}$, which correspond to the amorphous and crystalline phases, respectively. The crystalline volume fraction is given by $\frac{I_c}{I_c + \gamma I_a}$, where I_c and I_a are the integrated intensities of the crystalline and amorphous phases, respectively [142], and γ is the ratio of the backscattering cross-section of crystalline to amorphous phases. The value of γ has been calculated to be between 0.8 and 0.9 [142], and the most widely used value is 0.8 for mixed phase silicon, which is the value that we have adopted in our calculation. The highest crystalline volume fraction is 79% for the sample annealed with $F = 490 \text{ mJ/cm}^2$. It should be noted that the crystalline volume fraction is not homogeneous throughout the film. It decreases with increasing depth into the film. For example, for the sample annealed at $F = 588 \text{ mJ/cm}^2$, the top and bottom crystalline volume fractions are $\sim 72\%$ and $\sim 13\%$, respectively. This is because of the fact that optical absorption decays exponentially with thickness. This is an important consideration in the laser annealing, particularly for thicker films.

Figure 6-12 : (a) Raman spectra of 1.6 μm a-Si thin films treated with different laser fluences. (b) Crystallization volume fraction of c-Si film under different laser fluences.

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

6.4.5 Optical Characteristic of the Formed Conical Structures

Figure 6.13 depicts the reflectance (R in %), transmittance (T in %) and absorbance (A in %) spectra of the as deposited and laser treated $1.6\ \mu\text{m}$ a-Si thin films over a range of F from $294\ \text{mJ}/\text{cm}^2$ to $784\ \text{mJ}/\text{cm}^2$. R and T were measured by UV-VIS-NIR spectrophotometer and A was obtained by $100 - R - T$. It should be pointed out that around $850\ \text{nm}$, there are discontinuities in all spectra which are caused by the change of the grating in the spectrometer. For the as deposited a-Si, absorption is low with a value of $\sim 65\%$ for $\lambda < 600\ \text{nm}$ and almost zero for $\lambda > 700\ \text{nm}$ as the photon energy is below the bandgap of a-Si ($1.7\ \text{eV}$). At $F = 294\ \text{mJ}/\text{cm}^2$, R is reduced over the whole solar spectrum of interest due to the formation of the conical structure which can effectively couple light into the structure and suppress light reflectance (Fig. 6.13.a). In contrast, T does not change much compared to the unannealed sample but increases for longer wavelength light attributed to the fact that dimension of the conical structure being much smaller than the longer wavelength light and majority of the film remains in amorphous state. Hence, sunlight will not be absorbed effectively, but penetrate through the film easily instead. Correspondingly, A is increased to $\sim 90\%$ for $\lambda < 600\ \text{nm}$ and the improvement at longer λ is marginal. When F is increased to $372\ \text{mJ}/\text{cm}^2$, it is observed that there is slight decrease in R but T is substantially reduced, leading to a further improvement in light absorption. At this F value, larger conical structures are formed, inducing stronger interaction with light and resulting in longer optical path length and consequently the enhanced absorption. When F is further increased to $490\ \text{mJ}/\text{cm}^2$ and $588\ \text{mJ}/\text{cm}^2$, R remains almost the same as that of $372\ \text{mJ}/\text{cm}^2$, but T is further reduced. As more material is crystallized at a higher F , the absorption of longer wavelength light is

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

improved since the crystallized Si has a lower bandgap of 1.1 eV. Also, it is observed that the sample annealed with $F = 588 \text{ mJ/cm}^2$ has higher absorption in the long wavelength region. This is attributed to the larger dimension of the induced conical structure annealed at 588 mJ/cm^2 , resulting in stronger scattering of longer wavelength light and hence enhanced absorption. However, with a further increase in F to 784 mJ/cm^2 , T shows a reversal in trend and increases substantially, especially for shorter wavelength light. This is due to the ablation of the Si film at this high laser fluence. From the above experimental results and analysis, it is concluded that the increase in absorption of the laser treated samples is mainly caused by the bandgap change after the laser induced crystallization and the formation of the conical surface texture, resulting in antireflection and trapping of sunlight due to the multiple reflection [157, 158].

Figure 6-13 : (a) Reflectance, (b) transmittance, and (c) absorbance spectra of laser treated $1.6\mu\text{m}$ a-Si thin films with laser fluence of 294 mJ/cm^2 , 372 mJ/cm^2 , 490 mJ/cm^2 , 588 mJ/cm^2 and 784 mJ/cm^2 .

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

It is believed that for the FS laser annealing process, ultrafast or non-thermal melting of Si is the dominant mechanism [150, 151, 159], in contrast to the continuous-wave laser annealing and nanosecond excimer laser annealing. When the a-Si film is irradiated by the ultra-fast laser beam, a large number of quasifree electrons are generated in the conduction band [150, 160]. As the duration of the FS laser excitation is much smaller than the electron-phonon relaxation time, the energy of the excited electrons will not be transferred to phonons to achieve thermal equilibrium [150, 160, 161]. Such an ultrafast transition induced by the high-density electron hole pairs inherently carries no conventional molten phase as proved by the studies with femtosecond time-resolved optical microscopy and reflectivity measurements [162-164]. It causes the structure to be in a thermal inequilibrium state [150]. In addition, the high level of excited electrons could severely weaken interatomic bonds and the structure undergoes lattice instability, resulting in “cold” atomic motion that can lead to reorganization of the lattice in the time scale of hundreds of femtoseconds [152, 165]. Thus, the structural transformation and the film crystallization are realized. Meanwhile, in the one-step process, not only the film is crystallized, but also the nanoconical like structure is developed. This can be explained as a two-stage process. As described above, under the irradiation of the FS laser pulse, a large number of valence electrons are excited in the semiconductor through nonlinear absorption. The excited electrons accumulate in the conduction band, which leads to the excitation of plasmon polaritons at the surface [166]. The incident laser beam interferes with the generated surface wave to induce periodic modulation of the laser light intensity [167]. Hence, a transitional ripple structure is first formed. It is unstable and will melt and

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

turn into smaller cone structure to reach a lower energy state [168], and gives rise to what we have observed for our samples.

In summary, we have achieved the crystallization and formation of a large area quasi periodic nanocone structure on a 1.6 μm thick a-Si film by one-step ultrafast femtosecond laser annealing process. The amorphous Si film has been converted to crystalline Si and at the same time, micro/nano conical texturing is fabricated successfully on the surface of amorphous Si film. The micro/nano cones formed have diameters varying from ~ 160 nm to ~ 1.4 μm , which is useful in enhancing sunlight absorption in thin film Si. The developed process has potential applications for fabrication of high efficiency and low cost Si thin film solar cells.

6.5 FS Laser Fabrication of Ripple Structure

6.5.1 Motivation

During the past decades, there have been an intensive research and progress for laser induced periodic surface structure (LIPSS) by irradiating low energy density laser beam on dielectric material and semiconductor surfaces [132, 150-152, 169-174]. The most prominent advantage of the LIPSS structure is that the heat is confined only to the top surface of the material, without causing thermal constraint on the underlying substrate [132]. The induced LIPSS structure can be attributed to the interference between the incident and scattered laser light [170], nonlinear energy absorption and nonequilibrium thermodynamics process [150-152], local field enhancement [171, 172] or surface plasmons modes [172-174]. While early research on the LIPSS structure is focused on

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

using nanosecond laser [175], currently, picosecond or femtosecond (FS) laser has gained more attention due to better heat confinement and structural dimension control [176-179]. Since the FS laser pulse duration is shorter than the phonon relaxation time, upon the irradiation of the FS laser beam, more than 15% of the valence electrons are excited, which weakens the covalent bond and generates surface plasmon wave that further induces interference of the incident laser light [160, 161, 172, 176]. The low temperature process involved in the formation of the LIPSS structures has resulted in their applications in many areas, including switching transistor [180], MEMS [181], photovoltaic [156] etc. However, in most of previous work, the nano-ripple structures were only formed in small area of approximately the laser spot size such as in the annular region of the laser irradiated area of the substrate [182, 183]. Also, the modulation depth of the produced nano-ripples is still shallow and only in the order of 100 nm [177, 179, 184]. In this section, we report the FS laser induced fabrication of a well-controlled large area periodic nano-ripple structure on a Si substrate. The fabricated ripple structure has a periodicity (P) of ~ 600 nm and a modulation depth (H) of 300 nm, which is much deeper than those previously reported [177, 179, 184]. It is also found that light reflectance on the periodic nano-ripple structure is significantly suppressed compared with planar Si, due to the effective optical coupling between the incident light with the nano-ripple structure. This process can be potentially applied to fabricate Si-based photovoltaic cells, microelectronics devices, and optoelectronics devices.

6.5.2 Experiments

The substrate used is 625 μm thick Si (100) wafer. For the laser annealing process, femtosecond pulsed laser (Clark-MXR, CPA 2001) based on the regenerative Ti-

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

Sapphire amplifier using chirped pulse amplification technique was used. The beam profile emitted from the regenerative amplifier is approximately Gaussian shape with a diameter of 3.5 mm (@ $1/e^2$). The laser beam was focused by a cylindrical lens with the focal length of 100 mm so as to obtain a line-shape beam with the width of 50 μm . The laser fluence at the sample surface is adjusted by using a combination of a half-wave plate and a linear polarizer. In order to find the optimum irradiation condition, the laser fluence (F) was varied from 350 mJ/cm^2 to 787 mJ/cm^2 . The Si wafer was mounted on a computer-controlled X-Y translation stage. The laser surface treatment process was conducted in air ambient at room temperature. A large area surface treatment is achieved by scanning the line-shaped beam on the sample through controlled movement of X-Y stage. After laser treatment, the surface morphology was analyzed using field-emission scanning electron microscopy (FESEM, LEO, 1550 Gemini), and atom force microscope (AFM, NS3A). The reflectance spectra were measured with Lambda 950 UV-VIS-NIR scanning spectrophotometer (PerkinElmer).

6.6 Ripple Structure Formation

Figure 6.14 shows the optical and SEM images of FS laser scanning treated surface of Si substrate with an area of $30 \times 30 \text{ mm}^2$ where the laser fluence was set at 490 mJ/cm^2 . As shown in Fig. 6.14.a, it can be clearly seen that after laser irradiation, the Si surface was turned into dark black from the original shiny gray colour, which indicates the surface properties such as surface morphology, and phase state have been change after the laser treatment. Fig. 6.14.b shows the magnified optical image of the area labeled by “x” in Fig. 6.14.a, where it can be seen that the laser treated area is quite uniform and consistent

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

in terms of surface morphology. With further magnification with SEM as shown in Fig.6.14.c, it is observed that a periodic ripple surface structure has been formed.

Figure 6-14 : (a) Camera photo (b) optical microscope image of area labeled by “x” in (a) and (c) SEM image for the FS laser treated Si substrate.

In order to find the optimum laser parameters for the formation of the uniform LIPSS on Si surface, FS laser treatment on Si substrate was conducted with a number of laser fluences from 350 mJ/cm^2 to 787 mJ/cm^2 . It was found that below certain laser fluence of 411 mJ/cm^2 , no surface feature has been formed. Figure 6.15.a shows the SEM image of the laser treated Si surface at $F = 411 \text{ mJ/cm}^2$, the threshold fluence for the formation of the periodic ripples. It can be seen in Fig. 6.15.a that the formed ripple structure is not uniform, not covering the whole area, isolated, and most part of the Si surface remains unchanged. When the laser fluence increases to 450 mJ/cm^2 , the ripple structures formed cover more area and are more connected and uniform. The periodicity is found to be

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

around 750 nm, slightly lower than the wavelength of the incident laser light. Nevertheless, the periodic structure does not cover the whole scanning irradiated area shown in Fig 6.15.b. With a further increase in the laser fluence to 490 mJ/cm^2 , a well-defined, uniformly distributed periodic nano-ripples has been formed as shown in Fig. 6.15.c where the periodicity of the ripple is around 600 nm, which is lower than that of the ripple obtained at 450 mJ/cm^2 . When the laser fluence is increased to 676 mJ/cm^2 or above, as shown in Fig 6.15.d, it is found that well defined periodic ripples still exist but some of the adjacent ripples are joined up, indicating the degradation of the ripple structure. Some sub-micrometer sized holes are also formed on the surface.

Figure 6-15 : SEM images of laser processed Si wafer irradiated under different laser fluence (a) 411 mJ/cm^2 , (b) 450 mJ/cm^2 , (c) 490 mJ/cm^2 , and (d) 676 mJ/cm^2 .

Figure 6.16 shows the 3-dimensional AFM images and sectional view of the FS laser fabricated Si surface structure treated at the fluence of 490 mJ/cm^2 . It can be seen that the uniform periodic ripples has been formed. From the sectional view of the structure as

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

shown in Fig 6.16.b, the average periodicity is around 600 nm and the average depth of the ripple is about 300 nm, which is much deeper than those previously reported [177, 179, 184]. It is noted that some conical like structure is observed under the AFM images. This is because the formed nanoripple structure is unstable and it tends to melt and turn into cone structure to reach a lower energy state [168].

Figure 6-16 : (a) 3-dimensional (b) cross-sectional view of surface morphologies of sample irradiated with laser fluence of 490 mJ/cm². The AFM scan area is 5 μm × 5 μm.

The formation of periodic ripple structure can be explained by the excited surface plasmon polaritons at the surface of Si when irradiated with the FS laser pulses. Due to the ultra-fast pulse duration of the femtosecond laser, the time scale of the absorption of the femtosecond laser pulse and generation of quasi-free electrons in the conduction band of Si is much smaller than that of the electron-phonon relaxation time. Hence, the transient Si permittivity can be characterized by the Drude model as a function of the density of excited carrier (N_{e-h}) [160, 161]. Therefore, as N_{e-h} increases towards the Drude-plasma resonance, the real part of Si permittivity is zero. The critical carrier density can be calculated in our case using the formula below as [161]:

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

$$N_{cr} = \varepsilon_r \varepsilon_o m_e m_{opt}^* [1 + \omega^2 \tau_D^2] / (e \tau_D)^2 = 5.8322 \times 10^{21} \text{ cm}^{-3} \quad (6.1)$$

where $\varepsilon_r = 13.79$ is the relative permittivity of crystalline Si at 775 nm wavelength [81], ε_o is vacuum dielectric permittivity, m_e is the free electron mass, $m_{opt}^* = 0.18$ is the optical effective mass of the carriers [166], ω is the optical angular frequency, τ_D is the damping time given by 1 fs [166], and e is the electronic charge. As shown by Sipe and Bonse [160, 161], strong surface plasma resonance is observed near the critical N_{e-h} , leading to interference between the incident laser light and surface plasma electromagnetic wave. Under the irradiation of the FS laser pulse, a large number of valence electrons are excited in the semiconductor through nonlinear absorption. The excited electrons accumulate in the conduction band, which leads to the excitation of plasmon polaritons at the surface [166]. The excited plasmon polaritons generate a surface electromagnetic wave which scatters along the silicon-air interface. The incident laser beam interferes with the generated surface wave to induce periodic modulation of the laser light intensity [167]. For our experiment, the excited quasifree carrier density increases with the laser fluence level, which can be modeled as [161]:

$$N_{e-h} = F(1-R)[\alpha + \beta F(1-R) / 2\sqrt{2\pi\tau}] / (hc / \lambda) \quad (6.2)$$

where $R = 0.331$ is the surface reflectivity [185] and $\alpha = 9.5 \times 10^2 \text{ cm}^{-1}$ is the linear absorption coefficient at 775 nm, $\beta = 6.8 \text{ cm/GW}$ is the two-photon absorption coefficient, h is the Planck constant and c is the speed of light. Fig. 6.17 shows the excited carrier density as a function of the laser fluence. It is clearly seen that when the laser fluence is between 450 mJ/cm^2 and 588 mJ/cm^2 , the excited N_{e-h} is close to the critical carrier density, which is consistent with the observation in Fig. 6.15. Hence, the

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

incident laser light interferes strongly with the excited surface plasma electromagnetic wave to prompt the periodic modulation of the laser beam intensity. Therefore, a standing wave is generated with a periodic enhancement of the local field at the Si surface. The surface is ablated where the local field is strong, which consequently leads to the formation of the nano-ripple structure. On the other hand, when the fluence is too low or too high and there is no surface resonance, no ripple structure can be observed.

Figure 6-17 : The excited quasifree carrier densities in the conduction band of Si as a function the FS laser fluence and the critical carrier density with Drude plasma resonance.

Figure 6.18 shows the reflectance spectra (R) of the planar Si wafer and the laser processed Si wafer at $F = 490 \text{ mJ/cm}^2$. The wavelength range for the measurement is from 300 nm to 1100 nm. As shown in Fig. 6.18, it can be clearly seen that the reflectance of the planar Si wafer is quite high, especially at shorter wavelength range,

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

whereas the reflectance for the sample with periodic ripples is found to significantly decrease across the entire spectrum. The average reflectance has decreased from $\sim 39.7\%$ for the planar Si to $\sim 12.5\%$ for the laser treated sample over the spectrum ranging from 400 nm to 700 nm. The ultimate efficiency evaluated using the absorbance spectrum given by $100-R$ [55] reveals that the nano-ripple sample achieves an absorption enhancement of $\sim 41\%$ compared with planar Si wafer. The enhanced light trapping ability is attributed to the strong scattering effect induced by the nano-ripple structure. As the period of the ripple structure is 600 nm, the sunlight with the wavelength around 600nm can interact with the ripple structure effectively so as to increase the optical path length. Therefore, the FS laser fabricated ripple structure has demonstrated a strong light confinement ability, which may be potentially applied to solar cells and LEDs for effective photon management.

Figure 6-18 : Reflectance spectra of original Si wafer and nano-ripple structure with P of 600 nm and D of 300 nm irradiated with laser fluence of 490 mJ/cm^2 .

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

It should be pointed out that after the laser annealing, the electrical properties of the crystallized Si film is expected to be poor. This is because that the a-Si particle would tend to redeposit on top of the film during the laser annealing. In addition, the induced nanostructure surface is rough due to the laser induced melting and resolidification [186]. Furthermore, laser annealing may also introduce other material contamination, defects or dislocations. Those factors tend to degrade the electrical properties of the crystallized film. Therefore, post chemical etching processes are required to remove those defects. It has been demonstrated after the steps of removing the defects, high cell efficiency of 14.2% is achieved with a fill factor of 71.4, and short circuit current of 39.2 mA/cm^2 [186]. Hence, it indicates that a promising potential of using laser annealed Si nanostructure is promising for to realize the high performance silicon solar cell.

In summary, we have fabricated a large area uniformly distributed periodic ripple structure on Si surface by the femtosecond laser annealing. The induced ripple structure has a periodicity of 600 nm and modulation depth of 300 nm, which is much deeper than the previously reported values. The reflectance of the Si substrate with ripple structures is found to be significantly suppressed compared with the planar Si substrate. An absorption enhancement of $\sim 41\%$ was demonstrated.

6.7 Conclusion

In conclusion, two different methods are introduced in this chapter to achieve the crystallization and formation of nanostructure to enhance light trapping for thin film solar

Chapter 6 Laser Annealing of Thin Amorphous Film to Achieve Crystallized Si with Nanostructure Formation

cell. Firstly, a 355 nm DPSS Nd:YVO₄ laser is used to successfully crystallize and texture a-Si thin film in a one-step annealing process. With the pulse energy of 380 mJ/cm², a 400 nm thick a-Si is converted to poly-Si with nanodome texturing of periodicity around 300 to 500 nm. The absorption efficiency of the UV laser treated Si thin film is enhanced by ~ 200% compared with original a-Si. Secondly, a thick 1.6 μm a-Si film is also successfully crystallized with the nanocone structure formed using the ultrafast femtosecond laser annealing. The formed micro/nano cones formed have diameters varying from ~ 160 nm to ~ 1.4 μm. It is also found that due to the formation of the laser induced nanocone structure, the light absorption of the films have been substantially improved compared with the as-deposited film. In addition, the same femtosecond laser has been used to fabricate periodic ripple structure on Si surface with a structural periodicity of 600 nm and ripple modulation height of 300 nm. Compared with the planar Si substrate, the ripple structures have substantially suppressed the light reflectance, resulting in a ~ 41% improvement in light absorption. Therefore, the improved material quality and enhanced light trapping capability after the laser annealing renders it very promising for applications in Si thin film solar cells.

Chapter 7 Conclusion and Future Work

7.1 Conclusion

In this thesis, we have carried out a systematical study on the design, fabrication, characterization and simulation of hybrid Si nanohole (SiNH)/PEDOT:PSS based solar cells. Two methods based on the maskless metal-catalyzed electroless etching (MCEE) and reactive ion etching (RIE) etching with the aid of polystyrene spheres have been used for the fabrication of SiNH structures. In addition, silicon nanohole structures with different configurations have been investigated in terms of their optical absorption using simulation based on the finite element method, with an aim to study their potential applications in solar cell. For practical application, the Si nanohole (SiNH)/PEDOT:PSS hybrid cells would have to be implemented using thin film Si instead of bulk Si wafers. Therefore in this work we have also studied the formation of polycrystalline Si thin film from amorphous Si using laser annealing, and characterized them in terms of their crystallinity, morphology and optical reflectance.

In chapter three, high efficiency hybrid SiNH/PEDOT:PSS solar cells fabricated with SiNH structure and poly (3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) are presented. The SiNH structure has been fabricated using the MCEE method. The hybrid cells are optimized by varying the hole depth, and a maximum power conversion efficiency of 8.3% is achieved with a hole depth of 1 μm . A systematic simulation work on the light absorption of the hybrid SiNH/PEDOT:PSS solar cell is also conducted. The optimal light absorption is achieved with a structural periodicity of 600

nm and diameter to periodicity ratio of 0.8, which yields the highest ultimate efficiency of 30.5%.

In chapter four, periodic SiNH structures with hexagonal unit cells and different structural dimensions have been fabricated using patterned polystyrene spheres (PS) as mask. The fabricated SiNHs have periodicities of 330, 476, 600 and 800 nm and hole diameters of 210, 320, 400 and 460 nm. The surface morphology and the optical reflectance of the hexagonal SiNH structure have been investigated. Compared with planar Si wafer, such structures exhibit much lower reflectance due to the enhanced scattering introduced by the SiNHs. In addition, in order to identify the optimal condition for maximum light absorption, an optical simulation using the finite element method has also been carried. The optimum structure is found to have a periodicity of 693 nm and hole diameter of 560nm, and it yields the highest ultimate efficiency of 28.8%.

In chapter five, different configurations of SiNH structures, which include (i) slanting SiNH, (ii) random SiNH and (iii) hybrid nanohole and nanopyramid structures, have been theoretically investigated using optical simulation. In the first study, by having slanting holes instead of vertical holes in the structure, light absorption is found to be improved. The optimal condition is achieved when the periodicity is 700 nm and diameter/periodicity ratio is 0.85, which gives rise to the highest ultimate efficiency of 32.9%. This is higher compared to the 29.7% achieved for the structure with vertical SiNHs. In the second study, the effects of randomness in the hole diameter, depth and position of SiNH have been examined and they have been found to improve light absorption. Therefore the low cost approaches for realizing SiNH structures that are non-

periodic, such as the MCEE technique, are favorable in terms of boosting light absorption. (iii) In the third study, nanohole structures have been combined with pyramid structure to further improve light absorption. It is found that using the hybrid nanohole and nanopyrmiad structure, light absorption can be substantially improved beyond the Lambertian limit with an ultimate efficiency of 38.3%.

In chapter six, amorphous silicon thin films have been crystallized using the laser annealing method to achieve poly-crystalline silicon. Firstly, by using a 355 nm DPSS Nd:YVO₄ laser, a 400 nm thick amorphous Si has been successfully crystallized with the nanodome structure formed by the one-step laser annealing process. The light absorption has been improved ~ 200% compared with the original a-Si. Secondly, a 775 nm femtosecond laser has been used to crystallize a-Si films with a thickness of 1.6 μm while simultaneously form nanocone structure with diameters ranging between 160 nm and 1.4 μm . The light absorption is also substantially increased compared with the original a-Si film. In addition, this femtosecond laser has also been used to directly anneal crystalline Si wafers to form nano-ripple structure on the surface. By controlling the laser annealing density, a periodic ripple structure with a periodicity around ~ 600 nm has been developed, which is useful for trapping of light around the main solar spectrum.

7.2 Future Work

7.2.1 Removal of Silver Particle from the MCEE process

For SiNH structures fabricated using the MCEE method with silver catalyst, there is a small amount of silver remaining on the structure even after the HNO₃ etching. The presence of silver on the surface of the SiNH structure will promote carrier

recombination and seriously affect the cell performance. Therefore, it is important that the silver nanoparticles be removed to ensure that optimum cell performance is achieved. One potential solution that can be explored is to oxidize the SiNH using, for example ozone treatment, to form a thin layer of sacrificial SiO_2 . As the silver nanoparticles are found on the surface, it is expected that they will be captured within the oxide formed and can be subsequently removed when the SiO_2 is etched.

7.2.2 Structural Parameters Optimization

In the fabrication of SiNH/PEDOT:PSS hybrid solar cells, only the depth of the SiNHs have been varied to optimize the cell performance. The effects of other parameters such as the hole diameter and hole periodicity on the cell performance have been simulated but not verified experimentally. The MCEE technique that has been applied would not be suitable as it does not allow a good control of the structural parameters. It is proposed that SiNH structures fabricated using PS spheres with different structural parameters can be used for the fabrication of hybrid cells to verify experimentally the optimum structure that will give rise to maximum cell efficiency.

7.2.3 Surface Passivation for the SiNH Structure

The SiNH structures fabricated using either the MCEE or PS spheres have large surface area and many dangling bonds that promote the recombination of photogenerated electron-hole pairs. To reduce the recombination loss and improve the collection efficiency, the surface of the SiNHs has to be properly passivated. It is proposed that the passivation of the SiNH surface using Si_3N_4 or SiO_2 should be explored to study the effectiveness of the passivation in reducing the surface recombination loss. Note that the

passivation layer has to be sufficiently thin in order that it does not impede the transport of carriers. One potential method for the surface passivation is suggested as follows. After the formation of SiNH structure, a layer of $\text{SiO}_2/\text{Si}_3\text{N}_4$ can be deposited using the PECVD method. Following that, the top $\text{SiO}_2/\text{Si}_3\text{N}_4$ can be etched back to expose the top surface of the SiNH structure. In this way, the sidewall of the SiNH can be effectively passivated to improve the cell efficiency, while there is minimum series resistance introduced at the contact between the Si and the PEDOT:PSS layer .

7.2.4 Transfer to the Thin Film Technology

We have demonstrated SiNH/PEDOT:PSS hybrid solar cells using Si bulk wafer. For low cost practical applications, it is important that the cells be fabricated on thin film Si instead. As we have also studied the formation of polycrystalline Si thin films using laser annealing, it would be interesting to study the formation of SiNHs, and subsequently the fabrication of hybrid solar cells, using the poly-Si.

Lists of Publications

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