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**NANOSTRUCTURED SILICON THIN FILM SOLAR
CELL**

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SCHOOL OF ELECTRICAL & ELECTRONIC
ENGINEERING**

2014

NANOSTRUCTURED SILICON THIN FILM SOLAR CELL

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2014

Dedication

To my Mother. If not for your understanding, sacrifice, support, and belief in me, I would not be here. You gave me the courage to overcome the obstacles, and you always strived to be in support of your child.

To my companion and wife, Qu Ting. She lifted me up when I was down, and stood by me through all tough months and years. You are an amazing, patient, and simply loving being who lighted up my life. Thank you.

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Abstract

In this dissertation, a series of experimental and simulation studies were carried out in an effort to fabricate and characterize nanostructured silicon thin film solar cells. The nanostructures were designed for the purposes of enhancing light trapping within the active layer and improving the electrical performances of functional devices.

Silicon nanostructured thin film solar cell is believed to be important because its utilization of light trapping technology which enhances light absorption within the thin film material. In this dissertation, processes in fabricating silicon nanostructures were developed. We firstly summarized an electroless chemical etching technique using polystyrene nanospheres as self-assembled mask to fabricate size-controlled, periodic silicon nanopillars (SiNPs) and subsequent silicon nanocones (SiNCs) arrays. The nanocones were obtained based on the nanopillar structure using ammonia-related etching chemistry. With solution-based processes, the cost of the procedures is limited. The diameter, height, and period of the nanopillars and cones are systematically controlled.

Furthermore, we transferred this technology onto silicon thin film and demonstrated the accomplishment of silicon thin film nanostructures. SiNPs and SiNCs on glass were obtained by conventional reactive ion etching technique. The etching was masked by PS nanospheres again, and different morphologies (diameter and periods ranging from 200nm to 800nm) of patterned arrays were obtained with different masking condition and etching parameters. Optical properties such as reflectance and absorption of these

patterned silicon-on-glass nanostructures were characterized. With the integration of SiNPs and SiNCs, a significant reduction in reflectance and increase in absorption were observed.

Meanwhile, simulation efforts were also made in analyzing the optical effects of our nanostructures. Satisfactory results were achieved as simulations agreed in-principle with experimental results, thus serving as a theoretical support of our work. The simulation was performed using FDTD commercial software *Lumerical*.

Furthermore, solar cells were fabricated subsequently. Due to the enhanced properties in optical absorption, the external quantum efficiency and short circuit current of cells based on these nanostructures demonstrated a remarkable increase. The EQE for nanostructured sample can reach over 90% at wavelength of 600nm against only 60% of control sample. The cell efficiency is also increased from 1.6% for flat thin film cell to 3.8% for nanostructured sample. The impact of various nanostructures and dimensions were investigated ranging from 200 nm to 800 nm.

In summary, this dissertation firstly addresses the development and characterization of nanostructured silicon on both wafer and glass substrates, followed by further influences on subsequent nanostructured thin film photovoltaic (PV) devices. The work done will offer opportunities and approaches to further improve performances of PV device for potential implementation in commercial PV practices. This investigation effort is also potentially beneficial to other device applications where nano-patterning is in favor.

Table of Contents

DEDICATION	I
ACKNOWLEDGMENTS	II
ABSTRACT.....	III
LIST OF FIGURES	VI
LIST OF TABLES	X
ABBREVIATIONS.....	XI
CHAPTER 1 INTRODUCTION	1
1.1 ENERGY SOURCE AND MOTIVATIONS	1
1.2 SCOPE, OBJECTIVES AND CONTRIBUTIONS.....	5
1.3 LAYOUT OF THE DISSERTATION	6
CHAPTER 2 LITERATURE REVIEW ON SILICON THIN FILM SOLAR	
 CELL.....	9
2.1 SUNLIGHT RADIATIONS	9
2.2 SUNLIGHT ABSORPTION IN SOLAR CELL.....	11
2.3 THE AMORPHOUS SILICON THIN FILM	13
2.3.1 The Light-Induced Degradation of a-Si Thin Film – The	
Stäbler-Wronski Effect.....	15
2.3.2 Amorphous Silicon Thin Film Solar Cell.....	18
2.4 THE POLYCRYSTALLINE SILICON THIN FILM	19
2.4.1 Poly-Crystalline Silicon Thin Film Solar Cell.....	22
2.5 NANOSTRUCTURED SILICON SOLAR CELL	23
2.5.1 Different Morphologies	24
2.5.2 Simulation Efforts	28
2.5.4 Performance Enhancement	38
2.5.5 Making into a Device.....	41
2.6 CONCLUSION.....	45
CHAPTER 3 FABRICATION OF WAFER-BASED ORDERED SI	
 NANOSTRUCTURES.....	48
3.1 INTRODUCTION	48
3.2 EXPERIMENTAL PROCEDURES	49
3.3 RESULTS AND DISCUSSIONS.....	53
3.3.1 Morphologies	54
3.3.2 The Reflectance Measurement.....	67
3.4 SUMMARY.....	69

3.4.1	Limited Application of Solution-based Etching Methodology.....	69
3.4.2	Morphology Control in Thin Film Application	69
CHAPTER 4 SILICON THIN FILM NANOSTRUCTURES FOR EFFICIENT		
LIGHT-TRAPPING		71
4.1	INTRODUCTION	71
4.2	EXPERIMENTAL PROCEDURES	73
4.3	RESULTS AND DISCUSSIONS	76
4.3.1	SiNPs Morphologies	76
4.3.2	SiNCs Morphologies.....	85
4.3.3	Optical Characteristics	92
4.3.4	Simulation Efforts.....	100
4.4	SUMMARY.....	106
CHAPTER 5 NANOSTRUCTURED SILICON THIN FILM SOLAR CELL..		108
5.1	INTRODUCTION	108
5.2	IMPACT OF THE NANOSTRUCTURES.....	110
5.3	EFFECTS OF VARYING DIMENSIONS	113
5.4	SUMMARY.....	122
CHAPTER 6 CONCLUSIONS AND FUTURE WORKS.....		125
6.1	SUMMARY OF DISSERTATION.....	125
6.2	INNOVATIONS	127
6.3	FUTURE WORKS	129
JOURNAL PUBLICATIONS.....		133
REFERENCES.....		134

LIST OF FIGURES

FIGURE 1-1 ANNUAL PV INSTALLATION BY DIFFERENT TYPES OF SILICON TECHNOLOGIES [5].....	4
FIGURE 2-1 EFFECTIVE IRRADIANCE OF THE SOLAR SPECTRUM UNDER AM 1.5G FOR SINGLE BAND GAP Si SOLAR CELLS. THE EFFECTIVE IRRADIANCE IS DEFINED AS THE PRODUCT OF THE IRRADIATED POWER DENSITY AND (Eg/HN) [6]	10
FIGURE 2-2 THE OPTICAL ABSORPTION COEFFICIENT AS A FUNCTION OF WAVELENGTH [7]	14
FIGURE 2-3 CONDUCTIVITY AS A FUNCTION OF TIME BEFORE, DURING, AND AFTER EXPOSURE TO $\sim 200 \text{ MW} / \text{cm}^2$ OF LIGHT IN THE WAVELENGTH RANGE 600-900 NM[3].	16
FIGURE 2-4 CONDUCTIVITY AS A FUNCTION OF TIME BEFORE, DURING, AND AFTER EXPOSURE TO LIGHT ILLUMINATION FOR HYDROGENATED Si [4].	17
FIGURE 2-5 ABSORPTION COEFFICIENTS OF A-Si, C-Si, AND $\mu\text{C-Si}$	21
FIGURE 2-6 CROSS-SECTIONAL SEM IMAGE OF PDMS (POLY (DIMETHYLSILOXANE)) PATTERNED SiNWs GROWTH, AND SCALE BAR IS $1\mu\text{M}$ [37]	25
FIGURE 2-7 SEM IMAGES OF SILICON NANOWIRE ARRAYS: A) A LOW-MAGNIFICATION IMAGE; HIGH-MAGNIFICATION B) PLANE-VIEW AND C) TILTED-VIEW (CA. 15°) IMAGES. D) SEM IMAGE OF THE PS TEMPLATE USED TO GROW THE NANOWIRES. E) SIZE DISTRIBUTION OF SILICON NANOWIRES AND DIAMETER-REDUCED PS SPHERES [70]	26
FIGURE 2-8 SEM IMAGES IN A LARGE AREA OF A MONOLAYER OF SILICA NANOPARTICLES (A AND B), A-Si:H NC ARRAYS(C AND D), AND A-Si:H NW ARRAYS (E AND F), RESPECTIVELY [57].	27
FIGURE 2-9 SCHEMATICS OF SILICON NW ARRAYS WITH A (A) REGULARLY ARRANGED SQUARE LATTICE, (B) RANDOM NW CONTAINED IN REGULAR UNIT CELL USED IN [20], (C) 48% POSITION RANDOM, AND (D) 30% POSITION RANDOM STRUCTURE. [74].....	29
FIGURE 2-10 SCHEMATICS OF (A) THE CROSS-SECTIONAL VIEW AND (B) TOP VIEW OF THE 800 NM THICK Si FILM WITH SiNP ARRAY DECORATED SURFACE. THE SiNP LENGTH IS 1000 NM. THE RATIO OF DIAMETER TO PERIODICITY IS 0.5. [80]	30
FIGURE 2-11 SCHEMATIC OF THE CROSS-SECTIONAL VIEWS OF (A) THE SiNC AND (B) THE TOP VIEW [80]	30
FIGURE 2-12 RADIATIVE PROPERTIES OF NANOWIRE STRUCTURES WITH VARIOUS FILLING RATIOS, (A) ABSORPTANCE OBTAINED BY TMM AND MAXWELLGARNET APPROXIMATION, (B) REFLECTANCE OF NANOWIRES WITH DIAMETER OF 50, 65, AND 80 NM [43]	31
FIGURE 2-13 PROPOSED LIGHT TRAPPING SILICON NANO-HOLED STRUCTURES FOR THIN FILM PV APPLICATION, THE CORRESPONDING REFRACTIVE INDEX IS REFERRED TO CRYSTALLINE SILICON [82]	32
FIGURE 2-14 SCHEMATICS AND ELECTRON MICROSCOPY IMAGES OF THE P-I-N COAXIAL SILICON NANOWIRE [42].	34
FIGURE 2-15 FABRICATION PROCESS FLOW OF SiNPs ARRAYS[77]	36
FIGURE 2-16 DEMONSTRATION OF SiNCs ARRAYS[77]	37
FIGURE 2-17 SCHEMATIC ILLUSTRATION OF HEMISPHERICAL MEASUREMENT USING AN INTEGRATING SPHERE (A) MEASURED RESULTS OF ABSORPTION ON SAMPLES WITH A-Si:H THIN FILM, NW ARRAYS, AND NC ARRAYS OVER DIFFERENT ANGLES OF INCIDENCE (AT WAVELENGTH λ) 488 NM). (B) SIMULATED VALUE OF ABSORPTION ON SAMPLES WITH A-Si:H THIN FILM, NW ARRAYS, AND NC ARRAYS AS A TOP LAYER OVER DIFFERENT ANGLES OF INCIDENCE (AT WAVELENGTH λ) 488 NM) [57].....	39
FIGURE 2-18 PERFORMANCE ENHANCEMENT OF SILICON NANOSTRUCTURED THIN FILM, (A) ABSORPTION, (B) REFLECTION, AND (C) TRANSMISSION RESULTS. ULTIMATE EFFICIENCY IS SUMMARIZED IN (D) [72]	40
FIGURE 2-19 PERFORMANCE ENHANCEMENT OF SILICON DEVICE WITH NANO-PATTERN [86]	42
FIGURE 2-20 EXPERIMENTALLY MEASURED SHORT-CIRCUIT DENSITY J_{SC} AS A FUNCTION OF (A) PILLAR DIAMETER D , (B) PILLAR HEIGHT H [87].	42
FIGURE 2-21 COMPARISONS BETWEEN CELL WITH NANOSTRUCTURES AND CELL AFTER KOH-ETCH [88].....	44
FIGURE 2-22 THE RELATIONSHIP BETWEEN THE J_{SC} ENHANCEMENT AND THE SILVER NANOPARTICLE SIZE OF THE CELLS UNDER DIFFERENT COVERAGE DENSITIES FROM 5 TO 20%[94].	44
FIGURE 3-1 MONOLAYER FORMATION AFTER SPIN-COATING.....	50
FIGURE 3-2 NANOSPHERES AFTER SILVER COATING	51
FIGURE 3-3 THE REMAINING SILVER ON TOP OF SILICON NANOPILLARS AFTER ETCHING	52
FIGURE 3-4 PROCESS FLOW OF FABRICATION OF SiNPs AND SiNCs ON WAFER BASED SUBSTRATE.....	53

FIGURE 3-5 SEM IMAGE OF SiNPs SUCCESSFULLY OBTAINED.....	54
FIGURE 3-6 PS NANOSPHERES SIZE SHRINKAGE BEFORE AND AFTER O ₂ PLASMA RIE TREATMENT FOR: (A) BEFORE TREATMENT (B) 50s, (C) 100s, (D) 150s AND (E) 200s	56
FIGURE 3-7 SiNPs WITH HF-H ₂ O ₂ ETCHING TIME 4 MINUTES BUT DIFFERENT O ₂ TREATMENT DURATION. (A) BEFORE TREATMENT (B) O ₂ TREATMENT 50s, (C) 100s, (D) 150s AND (E) 200s	58
FIGURE 3-8 SEM IMAGE OF THE SiNPs AT LOWER MAGNIFICATION	58
FIGURE 3-9 CROSS-SECTION SEM OF SiNPs WITH ETCHING TIME (A) 1.5 MINS, (B) 3 MINS, (C) 6 MINS, (D) 8 MINS AND (E) PLOT OF PILLAR HEIGHT AGAINST ETCHING TIME.....	61
FIGURE 3-10 SiNPs UNDER ATTACK BY ETCHANTS WHEN HF CONCENTRATION INCREASES (E.G. HF:H ₂ O ₂ = 4:1 AND ABOVE, HF STANDS FOR 48% SOLUTION AS DISCUSSED IN SECTION 3.2).	62
FIGURE 3-11 SiNCs AFTER AMMONIA-BASED ETCH.....	63
FIGURE 3-12 SEM IMAGE OF SiNCs AT LOWER MAGNIFICATION	63
FIGURE 3-13 COMPARISON OF CONE MORPHOLOGY UNDER: (A) HIGHER ETCHANT CONCENTRATION 3.2M NH ₃ AND (B) LOWER ETCHANT CONCENTRATION 2.5M NH ₃	67
FIGURE 3-14 REFLECTANCE SPECTRA OF NANOPILLAR AND NANOCONES TEXTURED (SiNP DIAMETER ~ 250 NM, PILLAR HEIGHT ~1.2 MM, AND SiNC DIAMETER ~ 600 NM, HEIGHT ~1MM) SILICON WAFER AND BLANK WAFER.....	68
FIGURE 3-15 SEM IMAGE OF CROSS SECTION OF SiNPs	69
FIGURE 3-16 SEM IMAGE OF SiNPs UNDER HIGH-CONCENTRATION ETCHING	70
FIGURE 4-1 ROUGHNESS MEASUREMENT OF THE DEPOSITED SILICON THIN FILM OBTAINED BY ATOMIC FORCE MICROSCOPY	73
FIGURE 4-2 RAMAN SPECTRA OF THE SILICON THIN FILM (A) BEFORE AND (B) AFTER ANNEALING	74
FIGURE 4-3 (A) SEM AND (B) XRD IMAGES OF THE POLY-Si (SECCO ETCHED) FILM.	75
FIGURE 4-4 PROCESS DEMONSTRATION OF PS NANOSPHERES LITHOGRAPHY.....	77
FIGURE 4-5 SEM IMAGE SHOWING THE “MASKING” OF PS NANOSPHERES ON SILICON THIN FILM	77
FIGURE 4-6 SEM TOP AND TILT VIEW IMAGES OF SiNPs WITH DIAMETER 800NM (WITHOUT OXYGEN TREATMENT)	78
FIGURE 4-7 SEM TOP AND TILT VIEW IMAGE OF SiNPs WITH DIAMETER 600NM (OXYGEN TREATMENT 50s)....	78
FIGURE 4-8 SEM TOP AND TILT VIEW IMAGE OF SiNPs WITH DIAMETER 400NM (OXYGEN TREATMENT 100s) ..	79
FIGURE 4-9 SEM TOP AND TILT VIEW IMAGE OF SiNPs WITH DIAMETER 200NM (OXYGEN TREATMENT 150s) ..	79
FIGURE 4-10 SEM IMAGE OF SiNPs WITH DIAMETER SMALLER THAN 200NM WITH DISTORTED TOP DIMENSION (A) TOP VIEW (B) TILT VIEW (OXYGEN TREATMENT MORE THAN 200s)	80
FIGURE 4-11 SEM TOP AND TILT VIEW IMAGE OF SiNPs WITH PERIOD 800NM (DIAMETER ~200NM, WITH OXYGEN TREATMENT 250s)	81
FIGURE 4-12 SEM TOP AND TILT VIEW IMAGE OF SiNPs PERIOD 600NM (DIAMETER 200NM, WITH OXYGEN TREATMENT 150s).....	82
FIGURE 4-13 SEM TOP AND TILT VIEW IMAGE OF SiNPs WITH PERIOD 400NM (DIAMETER 200, WITH OXYGEN TREATMENT 80s).....	82
FIGURE 4-14 SEM TOP AND TILT VIEW IMAGE OF SiNPs WITH PERIOD 200NM (DIAMETER 200, WITHOUT OXYGEN TREATMENT).....	83
FIGURE 4-15 CROSS SECTION SEM IMAGE FOR ANALYSIS OF THE HEIGHT OF SiNPs: (A) 4 MINS ETCH CREATES HEIGHT OF ~900NM, (B) ~ 8 MINS ETCHING ETCHES THROUGH THE 2.5 MM Si THIN FILM.....	84
FIGURE 4-16 PROCESS DEMONSTRATION OF FURTHER FABRICATION OF SiNCs.....	86
FIGURE 4-17 PROCESS TO OBTAIN SiNCs (A) SiNPs WITH DIAMETER 800 NM AND PERIOD 800 NM, (B) AFTER 100s O ₂ PLASMA TREATMENT AND FURTHER RIE, (C) AFTER 200s O ₂ PLASMA TREATMENT AND FURTHER RIE AND (D) AFTER 300s O ₂ PLASMA TREATMENT AND FURTHER RIE	87
FIGURE 4-18 SEM TOP VIEW OF SiNCs.....	88
FIGURE 4-19 SEM TILT VIEW OF SiNCs (A) SiNPs WITH DIAMETER 600NM, PERIOD 600NM, O ₂ 200s AND FURTHER RIE, (B) SiNPs WITH DIAMETER 800NM, PERIOD 800NM, O ₂ 300s AND FURTHER RIE, (C) LOW MAGNIFICATION VIEW OF THE SAMPLE FROM (B)	89
FIGURE 4-20 SEM CROSS-SECTION VIEW OF SiNCs	90
FIGURE 4-21 MEASUREMENT CONFIGURATION OF INTEGRATING SPHERE (PERKIN ELMER)	92
FIGURE 4-22 MEASUREMENT RESULTS (A) REFLECTANCE SPECTRA AND (B) ABSORPTION SPECTRA (1-R-T) FOR SAMPLES WITH AND WITHOUT NANOSTRUCTURES.....	93

FIGURE 4-23 REFLECTANCE AND ABSORPTION SPECTRA OF SiNPs SAMPLES: (A) REFLECTANCE OF SiNPs WITH VARYING DIAMETERS AND (B) VARIOUS PERIODS AND $D \sim 200\text{nm}$, (C) ABSORPTION OF SiNPs WITH VARYING DIAMETERS AND (D) WITH VARYING PERIODS AND $D \sim 200\text{nm}$	96
FIGURE 4-24 REFLECTANCE AND ABSORPTION SPECTRA OF SiNCs SAMPLES: (A) REFLECTANCE OF SiNCs WITH VARYING DIAMETERS AND (B) VARIOUS PERIODS AND $D \sim 200\text{nm}$, (C) ABSORPTION OF SiNCs WITH VARYING DIAMETERS AND (D) WITH VARYING PERIODS AND $D \sim 200\text{nm}$	97
FIGURE 4-25 SCHEMATICS OF SiNPs AND SiNCs ARRAYS ON Si THIN FILM	100
FIGURE 4-26 SPECTRA OF FLAT Si THIN FILM.....	101
FIGURE 4-27 REFLECTANCE SPECTRA OF SAMPLES WITH SiNPs AND SiNCs	102
FIGURE 4-28 ABSORPTION SPECTRA OF SAMPLES WITH SiNPs AND SiNCs	103
FIGURE 4-29 GRADUAL CHANGE OF EFFECTIVE REFRACTIVE INDEX IN STRUCTURE OF SiNCs	105
FIGURE 4-30 PILLARS WITH $P = D$ DIMENSION	105
FIGURE 5-1 LAYOUT OF THE FABRICATED CELL.....	109
FIGURE 5-2 CROSS SECTION SEM IMAGE OF THE CONTROL CELL.....	110
FIGURE 5-3 EXTERNAL QUANTUM EFFICIENCY OF SAMPLES WITH AND WITHOUT SILICON NANOSTRUCTURES ($P = 600\text{ nm}$, $D = 600\text{ nm}$)	111
FIGURE 5-4 CURRENT-VOLTAGE CHARACTERISTICS OF SAMPLES WITH AND WITHOUT SILICON NANOSTRUCTURES ($P = 600\text{ nm}$, $D = 600\text{ nm}$)	112
FIGURE 5-5 EQE OF SAMPLES WITH DIFFERENT DIAMETERS AND SIMILAR PERIODS FOR: (A) SiNPs AND (B) SiNCs ($P=\text{PERIODS}$, $D=\text{DIAMETERS}$, IN nm)	114
FIGURE 5-6 EQE OF SAMPLES WITH DIFFERENT PERIODS AND SAME DIAMETER FOR (A) SiNPs AND (B) SiNCs ($P=\text{PERIODS}$, $D=\text{DIAMETERS}$)	118
FIGURE 5-7 SEM IMAGE OF PILLARS WITH SLANTED SIDEWALLS.....	123
FIGURE 6-1 ONE POSSIBLE MORE COMPLICATED NANOSTRUCTURE (A) DESIGN CROSS-SECTION, (B) SiNPs COATED BY SIZE-REDUCED PS SPHERES.....	130
FIGURE 6-2 HEXAGONAL-LATTICE AND SQUARE LATTICE	130
FIGURE 6-3 RANDOMIZED LOCATIONS OF SILICON NANOSTRUCTURES ACHIEVED	131

List of Tables

TABLE 3-1 BRIEF SUMMARY OF SiNPs HEIGHT UNDER DIFFERENT ETCHING TIME.....	61
TABLE 3-2 SUMMARY OF DIMENSION CONTROL OF SiNPs AND SiNCs	65
TABLE 4-1 SUMMARY OF VARIOUS STRUCTURES OF SiNPs AND SiNCs	90
TABLE 5-1 SUMMARY OF ELECTRICAL INFORMATION OF SiNPs SAMPLE WITH DIFFERENT DIAMETERS AND SIMILAR PERIODS	116
TABLE 5-2 SUMMARY OF ELECTRICAL INFORMATION OF SiNCs SAMPLE WITH DIFFERENT DIAMETERS AND SIMILAR PERIODS	117
TABLE 5-3 SUMMARY OF ELECTRICAL INFORMATION OF SiNPs SAMPLE WITH VARIOUS PERIODS AND SAME DIAMETERS	120
TABLE 5-4 SUMMARY OF ELECTRICAL INFORMATION OF SiNCs SAMPLE WITH VARIOUS PERIODS AND SAME DIAMETERS	121
TABLE 5-5 SUMMARY OF ELECTRICAL INFORMATION OF VARIOUS GROUPS OF THE DEVICES	122

Abbreviations

PV	Photovoltaic
mono-Si	Mono-Crystalline-Silicon
poly-Si	Poly-Crystalline Silicon
PCE	Power Conversion Efficiency
SiNPs/NP	Silicon Nanopillars/Nanopillars
SiNCs/NC	Silicon Nanocones/Nanocones
PS	Poly-styrene
FDTD	Finite Difference Time Domain
RIE	Reactive Ion Etching
SEM	Scanning Electron Microscope
AM	Air Mass
a-Si	Amorphous Silicon
c-Si	Crystalline Silicon
a-Si:H	Hydrogenated Amorphous Silicon
V_{OC}	Open Circuit Voltage
TCO	Transparent Conduction Oxide
SiNWs	Silicon Nanowires
VLS	Vapor Liquid Solid
J_{sc}	Short-circuit Current Density
DIRE	Dry Reactive Ion Etching
ICPE	Inductively Coupled Plasma Etching
DI	De-ionized
XRD	X-Ray Diffraction
GZO	Ga Doped Zinc Oxide
EQE	External Quantum Efficiency
AM 1.5G	Air Mass 1.5 Global
I-V	Current-Voltage
ff	Fill Factor

CHAPTER 1 INTRODUCTION

1.1 *Energy Source and Motivations*

Nowadays, global concern has been raised with the climate change and environmental pollution issues caused by consumption of traditional energy resources. With realization of increasing importance of exploring renewable energy alternatives, the demand for clean and renewable energy increases. Silicon solar cell has been one of the most promising routes for human beings to utilize our sun's radiation energy effectively. Researches in this area have been intensively conducted continuously. Once people realized that semiconductors could generate photo-current under illumination back in 19th century, it was the decade of 1950s when the first silicon-based solar cell was demonstrated [1]. With the development of photovoltaic (PV) technologies, all phases of Si materials, namely mono-crystalline-silicon (abbreviated as mono-Si for the rest of the dissertation), amorphous silicon, polycrystalline-Si (poly-Si) and etc., were examined carefully in laboratories all around the world. The world record, a 25% mono-Si based single junction solar cell, was fabricated by the University of New South Wales [2].

Until now, PV industry has been dominated by devices based silicon substrates, while large amount of the PV devices are working on crystalline silicon modules. Mono-Si was the first ever material used for silicon solar cell, and it is still playing a crucial role nowadays. Mono-Si can be manufactured with high purity, and its band gap is 1.12eV, one of the most ideal energy band

gap materials for single junction cell solar cells (optimum band gap is close to 1.3eV).

However, single crystalline silicon has an indirect band gap and its absorption coefficient is low. As a result, bulk silicon materials have to be used for effective light absorption. With the cost of purification and manufacturing, the total cost of commercial mono-Si modules is still un-favored against its competitor, regular energy source, e.g. oil and gas. Without subsidies from government, bulk mono-Si modules are hardly able to challenge the other energy generation sources.

Amorphous silicon is made by deposition (thin film). The deposition process is simple, low-cost, and large area compatible. It's easier to design different structures based on amorphous silicon materials, and subsequently integrated into electronic devices. Therefore, small power consumption devices, like watches, calculators, and etc have mainly used a-Si solar cells. Nevertheless, the well-known Staebler-Wronski effect [3], a degradation mechanism for hydrogenated a-Si solar cell under long-time illuminations, has been the main obstacle for its applications and this problem has yet to be thoroughly resolved. The reason to include hydrogenation process was to reduce the dangling bonds and the process had been proved to function effectively [4].

Due to the energy crisis we are facing, we have been forced to accept the fact that the cost of materials used for renewable energy generation has to be cut down, in order for the new energy source to really walk into our daily life. Therefore, the second generation of solar cell, mainly based on this thin

film with thickness less than tens of micrometers, has been investigated with extensive efforts.

After being discovered in 1970s, poly-Si solar cell has been researched continuously in the PV industry. It is also made through deposition technology, and the related manufacturing cost is low compared with mono-Si. A significant advantage of poly-Si against the other two types Si mentioned above is its stability in a well-functional device. Thin poly-Si film can be directly deposited on glass, stainless steel, and other cheap foreign substrates. It not only has the grained structure which facilitates carrier transportation, but also can be fabricated with low cost deposition with good control.

However, poly-Si has yet been able to be the answer, because it's also not "perfect". Due to poor absorption performance of the material in the visible range of solar spectrum, where the strongest intensity is located, thin film poly-Si solar cell has to maintain certain critical thickness for effective light absorption. In this case, the target of saving material cost has been hindered.

Fig. 1-1 presents a grand comparative picture of power generation by different types of contemporary PV technologies.

A point worth noted is that the largest share is factually hugely contributed by multi-crystalline Si module. In another word, wafer cells with crystal grains of several millimeters made by casting from Si ingots have the largest share in market.

Figure 1-1 Annual PV Installation by Different Types of Technologies [5]

Although the thin film portion is approximately 10% in 2012, it is largely from CdTe by First Solar. The actual contribution from poly-Si thin film is believed to be less than 1%. However, our intention is to emphasize the apparent trend that “thin film” devices are receiving increasing attention, as shown in the increase of the absolute amount of annual installation capability. From starting of 21st century (e.g. year 2000) where almost the whole PV market is occupied by wafer devices to current status where we can safely conclude that thin film technologies have taken around 10% of the pie. The driver of this increment has to be attributed to people’s ambitious goal of achieving reasonable conversion efficiency while controlling the cost. Therefore, as an active player within the thin film family, poly-Si thin film technology is worth our efforts in enhancing its performances.

The challenge in boosting efficiency of poly-Si thin film device is their light absorption capabilities. Intensive academic and industrial researches are conducted to realize high absorption while retaining the relatively low deposition cost. Within the various attempts, light trapping technology is one of

the favorites. Light trapping is a key research interest in so-called third generation solar cells researched to introduce advanced physical structures or concepts for more efficient absorption of light radiation, especially in the range of ultraviolet/infrared photons. The idea is straightforward that it is our aim to enhance the overall power conversion efficiency (PCE) by ensuring more light absorption while maintaining the low cost attributed to thin film fabrication procedures.

1.2 Scope, Objectives and Contributions

Poly-Si thin film solar cell requires more efficient light trapping technologies to enhance photon utilization in the fabrication of a final cell. It is therefore our objective to enhance the light absorption property of crystalline Si thin film, thus the thinness of the final cell can be well maintained, and the photocurrent in the fabricated cell can be enhanced. We desire to achieve this goal by introducing nanostructures on top of a solar cell to couple incident light wave efficiently into the thin film and trap them for a longer path before transmitting through the solar cell structure to increase the probability of capturing the photons and generating electron-hole pairs. Thus, a higher conversion efficiency solar cell will be realized.

In this dissertation, silicon nanopillars (SiNPs) and silicon nanocones (SiNCs) are developed utilizing low-cost, maskless, self assembled polystyrene (PS) lithography process. Well-ordered nanostructure array was successfully fabricated on silicon thin film. The fabrication processes were thoroughly analyzed and well-controlled dimension of the nanostructures were achieved.

Optical characteristics of these structures were measured in series. Simulation works based on finite-difference-time-domain (FDTD) method were conducted to compare with our experimental efforts. The effects of varying dimensions of nanostructures were evidenced both by experiments and simulations. In the last, thin film solar cells were fabricated from these structures. Enhanced performances after nanostructure integration were observed and presented.

1.3 *Layout of the Dissertation*

This dissertation presents the investigation on design, fabrication and characterization of silicon nanostructures based on poly-Si thin film. Effective optical measurements are shown and analyzed. Subsequent solar cells were made based on these nanostructures and the enhancement in their electrical properties is presented and explained. It is a significant attempt to utilize maskless PS nanospheres lithography to realize Si nanostructure-based thin film solar cells. Moreover, this dissertation also presents our effort in successfully simulating the nanostructures to validate our experimental results.

This dissertation includes 4 parts.

The *first part* (Chapter 1 and Chapter 2) starts with the general description of current solar cell market, the importance of crystalline silicon thin film solar cell, the remarkable significance of light trapping technology (which is also our research motivations), and the objectives of the dissertation. Chapter 2 reviews fundamental information about silicon thin film solar cell, including the definitions of amorphous-Si and poly-Si, as well as both why and how nanostructures for light trapping purpose are integrated. Different types of

nanostructures in literature are discussed, either from simulation efforts or experimental demonstrations. The ultimate goal of all researches is to enhance the electrical performance of the final cell. The increased light absorption property can boost the short circuit current J_{SC} of the sample. The theoretical backgrounds and research status are reviewed.

The *second part* (Chapter 3 and Chapter 4) is devoted to fabrication of silicon nanostructures. Chapter 3 introduces the fabrication of ordered silicon nanostructures, e.g. SiNPs and SiNCs on silicon wafer. The structure is achieved using an electroless chemical etching technique using polystyrene nanospheres as a self-assembled mask. The process is developed to fabricate size-controllable, periodic silicon nanopillars and subsequent nanocones arrays. The SiNCs are obtained based on the SiNPs structure using cost-effective ammonia-related etching chemistry. The diameter, height, and periodicity of the NCs can be systematically controlled. Optical measurement shows a good improvement in the reduction of reflectance properties with nanostructures. Chapter 4 discusses the fabrication of silicon nanostructures from silicon thin film on glass substrates. SiNPs and SiNCs on glass are obtained by conventional reactive ion etching (RIE) technique. The etching was also masked by PS sphere monolayer, and different morphologies of these patterns are obtained with different masking condition and etching parameters. The reflectance and absorption of these nano-patterned silicon-on-glass structures are characterized. In addition, simulation calculation in validating our optical measurement is also presented.

The *third part* (Chapter5) demonstrates the final integration of SiNPs and SiNCs into functional silicon thin film solar cells. Enhanced performances are observed with the reduction in reflectance and increase in light absorption. As a result, the external quantum efficiency and short circuit current of the cells based on these nanostructures are increased. Therefore, the target of realizing silicon nanostructures on silicon thin film solar cell in the pursuit of better performance is achieved.

The *last part* (Chapter 6) concludes the contributions of this dissertation. Experimental and simulation attempts are summarized and results are highlighted again. Furthermore, the proposals related to further improvement on experimental efforts are presented based on the limitations of our approaches. These are concluded as the future proposed works.

CHAPTER 2 LITERATURE REVIEW ON SILICON THIN FILM SOLAR CELL

2.1 *Sunlight Radiations*

Sunlight radiation is enormous, and potentially unlimited. The solar radiation energy arriving at earth atmospheric sphere per year is tens of thousands times more than the average energy consumption of our whole world in the same period. There are several phenomenons we are able to observe with naked eyes in daily life, e.g. reflection, refraction, deflection, etc. We may interpret these phenomenons as the energetic interaction between light, which is intrinsically an electromagnetic wave, and the substances inside the material. Fig. 2-1 shows the incident light irradiance density as a function of photon energy. It illustrates that potential maximum power conversion could be achieved by careful band gap engineering and design of light absorption capabilities. Bandgap engineering stands for the observation that, clearly, photons in different energy regime possess different irradiance. For instance, irradiance of photons with high energy (>2.5 eV) is less than photons in the lower energy regime. Therefore, effective capture of photons in low energy regime is important for PV devices.

However, silicon is poor in absorbing low energy photons with long wavelength. Silicon solar cell typically operates in the range of 400nm to 1100nm, e.g. 3eV to ~ 1.13 eV, with decreasing absorption capability from 400nm to 1100nm. To capture the long wavelength photons, it is reasonable that the application of light trapping structures will be useful for silicon thin

film based PV devices, because the purpose of light trapping serves to increase the light path of long wavelength photons inside the materials where they gain higher possibility to be absorbed.

Figure 2-1 Effective irradiance of the solar spectrum under AM 1.5G for single band gap Si solar cells. The effective irradiance is defined as the product of the irradiated power density and $(E_g/h\nu)$ [6]

When sunlight arrives at outer atmosphere, it possesses an average power density in the free space, around 1350 W/m^2 . The atmosphere surrounding the earth has a huge influence on the light absorption of an object placed on ground, and this influence is defined as *Air Mass* (AM). When AM is 0, it represents the condition of absorption outside our atmosphere, which is suitable for application of satellite or space shuttles. When AM equals 1, it represents vertical direct illumination on planet surface after passing through the air, and the power of AM1 is around 1040 W/m^2 . The main difference between AM0 and AM1 is the reduction of light intensity in several categories: ultraviolet reduction due to absorption from ozone, infrared reduction due to

absorption from steam, and reduction due to diffraction from suspending particles in air. When AM is 1.5, it demonstrates a typical direct radiation from an angle of 48.2° , with a power normalized to 1000W/m^2 . AM1.5 is typically used for testing of solar cell device [6].

2.2 Sunlight Absorption in Solar Cell

When light arrives at the cell, the absorbable portion of it will be kept in the semiconductor material to generate free-moving electrons, thus making current flow. Here, “absorbable” means that the energy of photons needs to be sufficient for the electrons to overcome the band gap barrier of the semiconductor. As a result, tremendous emphasis has been focused on efficient light absorption of the PV devices. There are several issues we need to consider when we apply photovoltaic technology to absorb sunlight. First of all, sunshine consists of radiations with different wavelengths, corresponding to different photon energies. So, it is difficult for a single device to cover most of the energy range. To combat this issue, band gap-engineering of solar cell material is considered to create the trade-off between light absorption and terminal output voltage. Secondly, sunlight radiation differs significantly with change of weather condition, geographical location, atmospheric composition etc.

Next, when light reaches the surface of semiconductor, part of the light is reflected back, part transmits through the material, and the rest is absorbed by the semiconductor. Photon absorption in semiconductor is a process dependent on the wavelength of light (photon energy), therefore photons which are absorbable to a semiconductor need to be sufficiently energetic – possessing

photon energy equal or larger than the band gap of the semiconductor. Light experiences a characteristic exponential decay in strength inside a semiconductor material, leading to a term called *skin depth*. The skin depth of a semiconductor is $1/\alpha$, where $\alpha(\lambda)$ is the material's absorption coefficient with respect to different wavelength. Because of this decay, the photon flux at one skin depth will fall to only 37% of the intensity at the surface. Take silicon as an example, it strongly absorbs in ultraviolet region while almost transparent in infrared. For visible spectrum range, the skin depth of silicon is $0.1\mu\text{m}$ for 400nm wavelength and $5.3\mu\text{m}$ for 700nm wavelength. Due to this great difference between different wavelengths, characterization of solar cell performance must be conducted with a universally-agreed standard, i.e. AM1.5.

Bulk silicon solar cell generally has hundreds of microns in thickness of silicon materials. However for PV application, crystalline Si (c-Si) only needs $\sim 25\mu\text{m}$ for effective light absorption, while the rest of the materials is only “supporting” the cell. By reducing the thickness, we could not only save cost, but also enhance the carrier extraction because the photo-generated minority carriers will see a shorter path into the external circuit.

It may sound intriguing that the cost of solar cell can be simply reduced by cutting down the thickness of the silicon active layer. However, we have limits for the thickness shrinking process due to poor absorption of the silicon films. Different properties of various silicon thin films will be discussed in following sections.

2.3 *The Amorphous Silicon Thin Film*

While silicon is a fourfold coordinated atoms that is normally tetrahedrally bonded to four neighboring silicon atoms, long range order of this tetrahedral-bonding is absent in amorphous silicon materials. Atoms in amorphous silicon form continuous disordered networks. Deposition methodologies (e.g. PECVD) is generally utilised in obtaining amorphous thin films at low temperature onto various foreign substrates. It is this unique advantage of low-cost deposition technology that facilitates the application of amorphous silicon thin film for a variety of electronic devices.

In amorphous silicon (a-Si) material, the irregular atomic arrangements allows the interactive action between photons with various wavelength and silicon atoms to occur more frequently than that in crystalline silicon, therefore allowing much more light to be absorbed. The better absorption of photons is shown in Fig. 2-2 [7]. In the visible range, its absorption coefficient is nearly one order higher than that of c-Si. Its intrinsic absorption coefficient reaches the value of 10^5 cm^{-1} . That means, for a-Si material, a thickness of around $1 \text{ }\mu\text{m}$ would be sufficient for PV application! Compared to the current bulk solar cells sold in the market, this is a huge reduction of material consumption.

Figure 2-2 The optical absorption coefficient as a function of wavelength [7]

Amorphous silicon has unique physical properties and it is able to be deposited in large area, which facilitates its PV devices being integrated into industrial applications. There is no bulky state of a-Si, and it has the following advantages compared to c-Si:

- 1) Low cost manufacturing process. It can be deposited on glass, stainless steel, plastic, etc. and the materials consumed for a-Si thin film solar cell is only 5-10% of mono-Si cell. Considerations need to be taken on the materials wasted during deposition in order to achieve further cost saving. Furthermore, a-Si deposition is done in comparably low temperature condition which brings down the cost and equipment demand significantly.

- 2) Large area deposition capability. This feature can facilitate a-Si being integrated into auto-process mass production in industry.

3) Multi-purpose device. Changing deposition conditions (e.g. chemical vapor concentration) will easily generate films with different characteristics, thus ready for different types of needs in terms of power output, voltage output, or current output. It can be designed with layered structure for these different requests.

4) Flexible cells are easily made. Amorphous silicon can be easily deposited on flexible substrate, and its atomic network structure allows the strain and stress induced during affordable mechanical deformation.

Nevertheless, a-Si has its drawbacks. The power conversion efficiency of a-Si PV cell obtained in laboratory condition right now is still well below those achieved by c-Si [8], and its stability, which is the hugest obstacle on its pathway to occupy market shares, has yet to be completely resolved till now.

2.3.1 The Light-Induced Degradation of a-Si Thin Film – The Stäbler-Wronski Effect

During deposition of a-Si material, hydrogen will be incorporated into the layer and combined steadily with the dangling bonds outside silicon atoms. These saturated combinations can effectively passivate silicon layer and eliminate most of surface states.

However, hydrogen atoms have their negative role. After staying under illumination for a long period of time, the conductivity of the material will decrease, sometimes in several orders, before reaching a stable state. The

following graph is a demonstration of this decrease. Fig. 2-3 shows the degradation of electric conductivity before/after illumination [3].

Figure 2-3 Conductivity as a function of time before, during, and after exposure to $\sim 200 \text{ mW} / \text{cm}^2$ of light in the wavelength range 600-900 nm[3].

After heat annealing at 150°C - 200°C , the light conductivity can be resumed to starting value. This mechanism has been well-known as the *Stäbler-Wronski Effect*. The mechanism can be simply summarized as the creation of defect states in the middle of energy band where electron-hole recombination has its largest possibility. Thus carrier lifetime will be reduced, and diffusion length is also decreased. Thermal annealing can remove these defect states and reverse them back to stable states, which makes the device function properly again.

Hydrogen dilution with silane during film deposition is still utilized worldwide because heat annealing is shown to reverse the degradation. Fig. 2-4 shows the changes of hydrogenated a-Si (a-Si:H) before/after light illumination

from Guha's work [4]. The curve states that dark conductivity decreases only by a small amount after illumination, and the conductivity resumes after short annealing process. The reason why hydrogenated a-Si will have less light-degradation effect is still under debate, and it will not be addressed in this report. However, the fact that using diluted silane to deposit a-Si film does improve the film quality is not debatable.

Figure 2-4 Conductivity as a function of time before, during, and after exposure to light illumination for hydrogenated Si [4].

The *Stäbber-Wronski Effect* is the main disadvantage of a-Si thin film in PV application, which weakens its attractions. Amorphous Si deposition is cost effective, but its comparative instability hinders the potential application in more areas. Attempts to solve this problem are the key issues in a-Si related PV technology.

2.3.2 Amorphous Silicon Thin Film Solar Cell

Carrier diffusion length is very short in a-Si:H film, even after doping. This characteristic will directly lead to high carrier recombination in the device. For compensation, thinner thickness of the film may be used. However, less thickness will deteriorate light absorption and lead to smaller photo current eventually at the external load. Finally, a solution has emerged to solve this problem – using a p-i-n structure for a-Si:H thin film solar cell. The p and n layers are doped with boron and phosphorus respectively, while the i layer is intrinsic a-Si:H. Under illumination, the carriers are mainly generated inside the i layer, and then diffuse into respective p and n layers. Open circuit voltage (V_{OC}) is directly related to the band gap of the intrinsic layer, and the Fermi level difference between n layer and p layer. Therefore optimization of the doping of n and p layers is crucial, especially the p layer. In order to increase V_{OC} , people use a-Si:H alloyed with other elements, e.g. carbon to replace the common a-Si:H p layer to increase its band gap. As a result, it not only allows more photons to pass through, but also boosts the open circuit voltage. So-called p-i-n single junction structure is a sequential deposition of these three layers on top of glass-superstrate. Transparent conducting oxide (TCO) like indium-tin-oxide is normally coated on glass before deposition of active layers. The invention of TCO increases utilization of incoming light and also serves as top contact. Bottom contact after n layer deposition can be directly derived onto the n-layer, and the common materials are Al and Ag. Silver is used mainly in laboratory as it possesses higher reflection which increases light absorption and

short circuit current as well. Aluminum is preferred in industrial level because of its lower cost.

Another typical structure of a-Si:H solar cell is an n-i-p layout. Since holes possess a much lower (up to the order of 2 in ratio with the value of electron) mobility than electrons in silicon thin film, the p type film needs to be placed at the side of incoming light. Therefore, an n-i-p structure uses a substrate which is not transparent. Typical structure can be Ag/n/i/p, deposited in sequential order. On top of p layer, conductive oxide is used. However, this layer must permit more light to go through, therefore its thickness is well controlled and “comb shape” metal wires maybe added on top for better conductivity.

2.4 The Polycrystalline Silicon Thin Film

Although a-Si thin film has been extensively researched for more than 20 years and its PV cell efficiency has been constantly rising, it is still a challenge for doping the a-Si layer and finding an appropriate method to resolve its stability issue. Thus, a-Si thin films are largely used in primarily small-power generation devices like watch, calculator, toy, etc.

For power generation up to high level, e.g. residential power supply, people are always trying to explore new Si phases which can possess the pros of c-Si and a-Si while eliminating the cons of them. Polycrystalline silicon (poly-Si) thin film has been proved to be the answer, potentially. It has the

advantageous electric properties of c-Si and also can be deposited with low-cost procedures.

Poly-Si is a material consisting of a number of small silicon crystals which marks itself different from single-crystal silicon and amorphous silicon. It is usually deposited using low-pressure chemical vapor deposition reactor at high temperature with different doping arrangements. Therefore, poly-Si can be deposited in large area with high purity as well as controlled doping profiles. It has been applied in most of integrated circuits and information display industries, and its PV application has been researched with tremendous efforts.

The categorization of poly-Si is divided based on the grain size. It's normally composed of large amount of grains with size ranging from several hundreds of nanometers up to hundreds of micrometers. For instance, microcrystalline silicon ($\mu\text{c-Si}$) stands for material with grain sizes around 10~30 μm , while nanocrystalline silicon (nc-Si) represents grain sizes about 10 nm. In a more general sense, poly-Si consists of two types: one being large-grain material consist of 100% crystalline Si with various grain sizes, while the other being material which is partially crystallized, small-grain material in mixture with a-Si material.

These new types of silicon phases can be easily and cost effectively deposited on cheap substrates, which makes their future application promising. Poly-Si has higher absorption at long wavelength range, as shown in Fig. 2-5, while it also keeps the high absorption in the visible range. For PV application, this means the necessary thickness can be smaller than what's needed for a-Si. With surface texturing to trap the light with multi-reflection inside the thin film,

poly-Si is confidently considered as the material for new generation of thin film solar cells.

Figure 2-5 Absorption coefficients of a-Si, c-Si, and μ c-Si

There are many defects existing in poly-Si film, and they are mainly at the grain boundaries, dislocations, and impurity sites. Until now, a complete physical theory to explain the influence by these defects has not been fully established, and it is these defects that the industry players are trying to overcome, in order to apply poly-Si PV cell in more areas.

The defects in poly-Si will introduce potential barriers between grains, which influence carrier mobility and diffusion behaviors. The defects at grain boundaries also act as recombination centers for the minority carriers, decreasing the diffusion length and jeopardizing the open circuit voltage of the cell. Since the diffusion length will be shortened due to defects at grain boundaries, thus the size of grains matters significantly. Generally speaking, a good PV cell must have material with reasonably large grains.

Although physical models have yet been completely created to analyze the defects inside the layer, it is in-principle an agreed fact that defects influence negatively the performance of the PV cell. During preparation of poly-Si film, it is a common target to pursue large grain which means fewer boundaries. Furthermore, it is also desirable to make grains “perpendicular” to the substrates, where the effects of boundary defects can be minimized.

The last aspect regarding poly-Si is – how to manufacture it. The most common technique is using chemical vapor deposition (CVD). Plasma enhanced CVD (PECVD) technique is useful to obtain poly-Si when the hydrogen content is carefully adjusted [9-16]. Furthermore, low pressure CVD (LPCVD) can also be used for the purpose, but it requires high temperature [17-22]. Hot wire CVD (HWCVD) is a technique developed based on PECVD but with much faster deposition rate, and it is still under research for its promising properties [23-33].

2.4.1 Poly-Crystalline Silicon Thin Film Solar Cell

While the total solar power generation of the world is more than Giga watts per year, the consumption of Si raw material increases to hundreds of tons. Although it is still arguable whether we have sufficient supply/recycle of this semiconductor raw substance, it is essential to establish a supply chain of low cost. Therefore, it is necessary to establish a cell production process at low cost, leading to increased need for thin film based devices.

Poly-Si is one of the major players in thin film based application. Its application has been rapidly expanding because of its low cost fabrication and

large-scale productivity, while high power conversion efficiency (e.g. 13%) is maintained. On the other hand, growth of bulk poly-Si material is mostly done by casting in industries nowadays. It has to be maintained at high quality, and this can be assured from several testing techniques which feedback the characteristics of the material. For instances, photo-conductivity decay measurement produces the minority carrier lifetime in the material, and laser beam induced current measures the grain boundary carrier recombination velocity.

2.5 *Nanostructured Silicon Solar Cell*

The purpose of reviewing the status of a-Si and poly-Si thin film solar cells in our dissertation is not to reach a conclusion about which is prevailing or more dominating. Our intention is to bring the interest to the thin film PV industry where benefits and obstacles have been identified.

Commercial silicon solar cells have been available for 50 years, and it can now convert sunlight into electricity at efficiencies about 20% (e.g. power conversion efficiency, shorten as PCE, stands for the ratio of the electrical output of a solar cell to the incident energy in the form of sunlight). However, as we reduce the thickness of the material to be “thin” enough for a reasonable PCE (i.e. >10% with 10-30 μm thickness), light absorption becomes an issue. Limited absorption, due to its indirect band gap, reduces the PCE of Si thin film solar cell.

The improved light absorption was proposed to be achieved by light trapping mechanism which elongates optical path within the thin film. Utilizing

nanostructured silicon material is one of the key techniques which are expected to realize this improvement. The structure is designed to scatter the incident photons and couple the light into the underneath thin film in order to increase the light path. Better absorption is resulted and photons are utilized more efficiently as compared to flat thin film. Accordingly, better short circuit current can be expected as well as higher efficiency. This section is our major interest in our literature review where different aspects regarding nanostructured silicon thin film solar cell are addressed.

2.5.1 Different Morphologies

In traditional thick Si solar modules, light trapping is typically achieved by introducing micron-sized pyramidal textured surface that causes scattering of light into the solar cell, thereby enhancing the effective optical path in the cell [34, 35]. However, this methodology is not feasible for thin-film cells, as the cell thickness is ever smaller than the texture size and the texturing is not conveniently achievable from non-single-crystal materials.

Light trapping technologies for thin film applications aim to establish an interaction between the nanostructures and incident light. Light is scattered by the nanostructured surface into the material (e.g. absorber) underneath, leading to increased light path and thus to enhanced absorption. Different morphologies of the nanostructures are believed to decide different pattern of scattering, thereby influencing the light path in the active materials. For instance, cone-shaped texture is believed to create a gradual refractive index change along the normal-incident light path into the material. Morphologies are described to be optimized by mathematical simulations, as discussed in the remaining of this

section. However, these morphologies are largely constrained by experimental feasibilities, which is the physical process constitutes the nanostructures. Thus, large amount of explorations have been conducted in order to discover the suitable structures, with the common goal of maximizing light absorption. The improved light absorption is beneficial to reduce the use of raw materials in thin film applications without sacrificing the PCE.

The development of nanofabrication technologies enables researchers to explore various nanostructures at reasonably low cost. Silicon nanowires (SiNWs) were successfully developed for device integration [36-47].

Figure 2-6 Cross-sectional SEM image of PDMS (poly (dimethylsiloxane)) patterned SiNWs growth, and scale bar is 1 μm [37]

The method to prepare such SiNWs was primarily bottom up growth through catalyzed vapor-liquid-solid (VLS) mechanism [48-53]. An example is shown here in Fig. 2-6, where gold colloids were used for nanowires synthesis by VLS mechanism using SiCl_4 as the precursor gas in the chemical vapor deposition system. Using a thin polyelectrolyte layer, gold colloids are electrostatically attracted to and immobilized on the substrate to act as seeds for Si nanowires grown using VLS-CVD method.

The growth of SiNWs was realized even on glass substrates [54]. However, catalysts metal elements unavoidably penetrate into the silicon

material and remain as scattering centers. Further influence on the electrical properties was reported by researchers[55].

In the past decades, two-dimensional silicon nanostructures have attracted significant attention. They have found potential applications in areas including photonic crystals [56, 57], photovoltaic devices [44-46, 57-68], and lithium-ion batteries [69-71]. Among all these research efforts, integration of Si nanostructures on glass to realize high efficiency thin film Si solar cells cheaply and efficiently is of particular interest. One potential third generation solar cell material system is based on silicon nanostructures such as SiNPs which have gained much attention attributed to their outstanding optical and electrical properties [72-76].

Figure 2-7 SEM images of silicon nanowire arrays: a) a low-magnification image; high-magnification b) plane-view and c) tilted-view (ca. 15°) images. d) SEM image of the PS template used to grow the nanowires. e) Size distribution of silicon nanowires and diameter-reduced PS spheres [59]

As shown by Huang [59] in Fig. 2-7, The SEM image clearly shows homogeneously distributed nanowire arrays covering large areas. Fig. 2-7b and c

show plane-view and tilted-view (ca. 15°) SEM images of the silicon nanowire arrays, respectively. SEM images have been used to analyze the size distributions of the silicon nanowires and diameter-reduced PS spheres, and the result is shown in Fig. 2-7e. The mean diameter of the nanowires is 252 nm, which matches well with the corresponding value for the diameter-reduced spheres, 253 nm.

Another interesting nanostructure which was intensively researched was silicon nanocones [77]. by tuning the diameter, height, center-to-center spacing (period), Li et al. reported that the SiNCs arrays exhibit superior light absorption as compared to SiNPs arrays [73]. In demonstration of fabrication, SiNCs can be directly etched through RIE [57, 78] or through a subsequent modification stage from SiNPs [79].

Figure 2-8 SEM images in a large area of a monolayer of silica nanoparticles (a and b), a-Si:H NC arrays (c and d), and a-Si:H NW arrays (e and f), respectively [57].

Fig. 2-8 shows the SEM images from Zhu's experimental results [57].

Fig. 2-8a and b show SEM images of silica nanoparticles forming hexagonally-

packed monolayer on a-Si:H thin film. Fig. 2-8c and d show SEM images of a-Si:H NC arrays after reactive ion etching (will be discussed in section 4.3). Each NC was also ~ 600 nm long. The tip diameter of these NCs was ~ 20 nm, while the base diameter was ~ 300 nm. It is believed that the conical shape is due to the gradual shrinkage of the size of the silica nanoparticle. Fig. 2-8e and f show SEM images of a-Si:H NW arrays. The diameter of each NW was ~ 300 nm. Each nanowire was ~ 600 nm long.

2.5.2 Simulation Efforts

Device simulation provides a platform to cost-effectively analyze the impacts of different nanostructures. Large amount of researches aim to explore the “optimized” Si nanostructures for thin film PV applications. In another world, the goal is to maximize power conversion efficiency by boosting light absorption capabilities.

Randomized SiNPs structure were studied and reported by Du et al [72]. All considered structures are arranged in an x-y plane and surrounded by air. Sunlight is directly incident on the top of the structure along z direction. The regularly arranged NW array in a square lattice is shown in Fig. 2-9a. The lattice constant (period) is chosen as 500nm, and the filling ratio is 0.5 (defined as the ratio of the NW top surface area to the unit cell top surface area in one unit cell), which means the radius of the NW is about 199nm.

Figure 2-9 Schematics of silicon NW arrays with a (a) regularly arranged square lattice, (b) random NW contained in regular unit cell, (c) 48% position random, and (d) 30% position random structure. [72]

Fig. 2-9c and d stands for filling ratio of 48% and 30% respectively. The results in Du's work showed an increase over absorption range, and it was concluded to be attributed to lowered reflectance, more supported resonant modes, and broadening of existing resonance [72].

Moreover, ordered arrays were claimed in other works to possess high potential in boosting device performances [80, 81]. Li et al. conducted systematic simulation analysis on the absorption characteristics of silicon thin film with nanopillar arrays. The simulation was performed using full wave finite element method, and the interaction between the incident light field and the structure was realized through infinitely extending the structural units and the dimension equal to the SiNP array periodicity, as indicated by the dash line in Fig. 2-10, in the two-dimensional space by applying the periodic boundary condition. Light absorption was proved to be enhanced significantly with the nanostructure decoration. Fig. 2-10 is the (a) cross-section view and (b) top view of the structure used in Li's study. The thickness of the underlying Si thin film and the height of SiNP are set as 800 and 1000 nm, respectively, and the spacing between two neighboring SiNPs is equal to the SiNP diameter. The

incident light is normal to the Si substrate, same as Du's work mentioned above. The optical information is obtained from the spatial distribution of the energy flux, as a result of the interaction of incident light and the Si structure.

Figure 2-10 Schematics of (a) the cross-sectional view and (b) top view of the 800 nm thick Si film with SiNP array decorated surface. The SiNP length is 1000 nm. The ratio of diameter to periodicity is 0.5. [81]

Silicon nanocones were also studied by Li[82] in another work as shown in Fig. 2-11. The interaction between the incident light field and the studied structure is calculated through infinitely extending the structural unit with the same side length as the array periodicity in the two-dimension space by applying the periodic boundary condition, same as previous work. The schematics and method were similar and the study points out that the optimized base diameter and array periodicity should be set equal. (performance enhancement is discussed in section 2.5.4)

Figure 2-11 Schematic of the cross-sectional views of (a) the SiNC and (b) the top view [82]

Other researches also showed a remarkable enhancement in terms of light absorption. Different period, diameter, and filling ratios of the SiNPs structures were studied and promising results were published shown in Fig. 2-12 [43]. In Hu's work, the effects of wire diameter, length, and filling ratio on the absorptance of nanowire arrays are simulated, as shown in Fig. 2-12a and b. From Fig 2.12a, it is apparent that nanowire arrays with moderate filling ratio have much higher absorptance compared to thin films. In a high-frequency regime, nanowire arrays have higher absorptance than their thin film counterparts. In low-frequency regime, nanowire arrays absorb less but can be designed to approach that of the film by changing the filling ratio ($f=0.5$ curve is designed to approach the absorptance of thin film at low-energy regime).

Figure 2-12 Radiative properties of nanowire structures with various filling ratios, (a) absorptance obtained by TMM and MaxwellGarnet approximation, (b) reflectance of nanowires with diameter of 50, 65, and 80 nm [43]

While most of researches are emphasized on SiNPs and SiNCs, there are other structures designed on improving light absorption in simulation works. Silicon nano-holed thin film was simulated in Wang's work [83]. It could be

regarded as a negative-SiNPs structure where interaction between photons and materials were still maintained, and the structure is shown in Fig. 2-13. It is stated by Wang that the solar energy absorption could be optimized when the nanohole array structure dimension are set as: periodicity of 700nm, depth of 200nm, and the hole diameter versus periodicity ratio of 87.5%.

Figure 2-13 Proposed light trapping silicon nano-holed structures for thin film PV application, the corresponding refractive index is referred to crystalline silicon [83]

To sum up the efforts in designing different morphologies of Si nanostructures for thin film PV application, firstly, both randomised and ordered arrangement of nanostructures have been presented in literature. Most of the theoretical work was focused on regularly arranged nanostructure arrays with square or triangular lattice. Researchers have presented the optimal lattice constant and silicon filling ratio of NW arrays to achieve a high ultimate efficiency (i.e. Li's study [73]). However, randomised structures post fewer restrictions on experimental condition therefore more cost-effective to achieve (i.e. VLS environment where no mask was involved [47]).

Theoretical and experimental studies on randomised nanostructures are largely in silicon nanowires with diameter less than, typically, 100nm, and Du's

work in randomised pillar with diameter in the range of hundreds of nanometers were pioneering. Although Du claimed in his work that additional resonances was introduced by the structural disorder and existing resonances broadening, and that more randomness leads to larger absorption enhancement, there was no experimental support of relevant structures to verify the conclusions. One of the reasons is that the lack of control in dimensions during fabrication, which posts great difficulty in the repeatability of the experiment while the control of filling ratio is explained to be important and needs to be assured [72].

On the other hand, ordered, periodic silicon nanostructures are obtainable with high degree of repeatability with the involvement of mask in experiment. The key importance of maintaining the periodicity is to facilitate researchers' systematic study of the interaction between fine-tuned periodic structures and incident radiations. It is also the common target for researchers to find the optimal dimension of the Si nanostructures with such systematic tuning and analysis[73]. Therefore heavier efforts, compared to randomised structure, have been paid into investigating ordered arrangement of silicon nanostructures (i.e. SiNPs, SiNCs, and etc).

In summary, there is no thumb-rule or universally agreed principle interpreting the differences between these two structures for their potential use in photovoltaic devices. Multiple research publications have shown the enhanced interaction attributable to both structures. Nevertheless, our focus in the research work has been on ordered arrangement because of the excellent repeatability, which provides us comfort and confidence in generating series of

data for comparison and establishing a standard working procedure in fabricating silicon thin film nanostructures.

2.5.3 Experimental Progresses

Experimental attempts in fabricating silicon nanowires were mainly via two routes: bottom-up or top-down mechanism. In other words, the formation is through growth or etching mechanisms. The first proposed and realized Si nanostructures that were integrated into functional devices were SiNWs [42, 48, 51, 84].

Figure 2-14 Schematics and electron microscopy images of the p-i-n coaxial silicon nanowire [42].

The best representative of bottom-up growth of silicon nanowires is the vapor-liquid-solid growth [37, 84]. As shown above in Fig. 2-14, Tian illustrated

the core/shell silicon nanowire structure [42]. Its cross-sectional diagram shows that the photo-generated electrons (e^-) and holes (h^+) are swept into the n-shell and p-core, respectively, by the built-in electric field. The phase diagram of gold (Au)–silicon (Si) alloy on the right panel illustrates that the core is grown by means of the VLS mechanism, whereas the shells are deposited at higher temperature and lower pressure to inhibit further nanowire axial elongation. Fig. 2-14b is the SEM images of the p-i-n coaxial silicon nanowire at two different magnifications (scale bar, 1mm (top), 200nm (bottom)). The nanowire was grown with 100-nm-diameter gold catalyst, and with i and n-shell growth times of 60 min and 30 min, respectively. Fig. 2-14c shows the high-resolution TEM image (spherical-aberration corrected) of the p-i-n coaxial silicon nanowire (scale bar, 5 nm). The work demonstrates successful fabrication of single-crystalline silicon nanowire p-cores by means of a nanocluster-catalysed VLS method, followed by chemical vapor deposition of i- and n-type nanocrystalline silicon shells.

However, VLS faces challenges because most of applications require SiNWs or SiNPs with smooth surface, controllable aspect ratio, and positioning of arrays with high accuracy. VLS silicon growth on glass happens in all sorts of different directions with difficulty in keeping unified crystalline orientation. As a result, VLS method has difficulties in growing SiNPs ordered arrays for further applications.

SiNPs with diameter ranging from tens of nanometers to hundreds of nanometers were successfully obtained by aqueous electroless chemical etching of single crystalline silicon wafers [59, 78, 85]. After cleaning stage, Si wafer was immersed in boiling solution of, for instance, $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:1:5$, for 1 h to achieve the hydrophilic phase [86]. Other solution may also achieve this purpose [79]. Next, close-packed SiO_2 or PS nano-spheres monolayer was

prepared on top of the silicon surface. Subsequently, metal catalyst, e.g. Ag or Au, were evaporated or deposited on top of the nanospheres. The silicon materials standing underneath the nanospheres are protected during further etching stages. The electroless wet etching method attracted huge attentions as it demonstrated a cost-effective way to design device structures in the nano range. By using nano-spheres lithography technique, ordered SiNPs are reported by Huang et.al [59]. The process flow is also well documented as below:

Figure 2-15 Fabrication process flow of SiNPs arrays[78]

Fig 2.15 from Hse's work shows the fabrication process of SiNPs arrays. First, SiO_2 nanoparticles were assembled into a close-packed monolayer on a Si<100> wafer (Fig. 2-15a). Second, the diameter and spacing of the nanoparticles were tuned by selective and isotropic RIE of SiO_2 (Fig. 2-15b). The etching is based on fluorine chemistry using a mixture of O_2 and CHF_3 . This shrinking step also removed the native oxide from the Si substrate,

facilitating further etching. Third, Si nanopillars were formed by Cl_2 based selective and anisotropic RIE of the Si substrate (Fig. 2-15c). The diameter and spacing of the nanopillars were determined by the initial nanoparticle size and both SiO_2 and Si etching times. Finally, SiO_2 particles at the tips of pillars can be selectively removed by etching with hydrofluoric acid.

Furthermore, periodic SiNCs fabrication has also been demonstrated by using dry etching (RIE) [57, 78], or oxidation of SiNPs followed by an oxide-removal step in buffered hydrogen-fluoride acid[85].

Figure 2-16 Demonstration of SiNCs arrays[78]

Fig. 2-16 is also from Hse's work, where demonstration of SiNCs arrays was presented. Following the same steps in fabricating SiNPs (Fig. 2-16a), RIE is controlled to form tapered sidewalls which lead to SiNCs. By controlling the etching time, the combination of anisotropic and isotropic etching can lead to a sharpening of the tips (Fig. 2-16b to d).

To summarize the review of experimental procedures, both VLS bottom-up and etching top-down mechanisms are able to work effectively in obtaining Si nanostructures with promising properties. VLS is advantageous in

growing separated, small-area SiNWs with controlled dimensions. It can be used to obtain single-crystalline Si phase when appropriate growth condition is mastered. However, it encounters great difficulties in being used in PV applications where large-area, uniformed growth of silicon nanostructures (SiNPs or SiNCs) is needed.

Top-down etching has been presented to be more feasible in fabricating even wafer-scale nanostructured Si material for PV device. However complicated and high-cost vacuum equipment (e.g. RIE) or high-temperature annealing processes are needed during the fabrication which poses constraint to their applications. And these limitations will remain the interest of future research works.

With all these fabrication efforts and simulation attempts, the goal, as introduced in previous section, is to demonstrate better light absorption properties and thus make it beneficial to integrate these structures into PV device in order to improve their electrical behaviors.

2.5.4 Performance Enhancement

Optical absorption enhancement is the first target that these nanostructures achieved. With reduced reflectance, absorption of incident light was concluded to increase significantly. As shown in Fig. 2-17, Zhu presented the enhancement, both via experimental and simulation attempts, of optical absorption of the nanostructured Si thin film. Fig. 2-17a shows the total absorption of three different kinds of samples at wavelength $\lambda=488\text{nm}$ for

different angles of incidence. The results of the simulation calculations are shown in Fig. 2-17b. The sample with NC arrays demonstrated the highest absorption. The measured absorption of the NC sample is 98.4% around normal incidence, which agrees well with the calculated value of 97.8%. The high absorption of the NC arrays (~98%) presents a significant advantage over NW arrays (85%) and thin film (75%). In general the simulation agrees well with the experimental data over a wide range of angles. At incident angles close to normal, there appears to be fluctuations of the measured value for thin film and NWs. This is because, at normal incidence, some of the reflected light could escape through the port where the laser beam entered. Differences in the samples' surface roughness also contributed to the difference between experimental and simulated data.

Figure 2-17 Schematic illustration of hemispherical measurement using an integrating sphere (a) Measured results of absorption on samples with a-Si:H thin film, NW arrays, and NC arrays over different angles of incidence (at wavelength λ) 488 nm). (b) Simulated value of absorption on samples with a-Si:H thin film, NW arrays, and NC arrays as a top layer over different angles of incidence (at wavelength λ) 488 nm) [57]

The attractive advantages of utilizing the nanostructures is that it efficiently decouples the light trapping process and photo-generated carrier extraction process [80]. In another word, the SiNPs and SiNCs were believed to effectively trap the light inside the active layers. This promotes the utilization

of lower cost low-grade raw materials to be used as thin film active layers where poor absorption was previously expected.

Furthermore, researches were aiming to optimize the periodicity, diameters of structures, length/height of pillars, and other morphological concerns. Li et al. conducted simulations in which different parameters were optimized for the thin film integrated with SiNPs [73].

Figure 2-18 Performance enhancement of silicon nanostructured thin film, (a) absorption, (b) reflection, and (c) transmission results. Ultimate efficiency is summarized in (d) [73]

Fig. 2-18 shows the optical characteristics of the SiNW arrays with different diameter (D) at a fixed periodicity (P) of 300 nm. The increase in diameter would also shift the absorption edge toward low energy end and thus facilitate the photon utilization in the low energy regime, which is similar to the

case of increasing P. The increase in P shall lead to the D increase due to the fixed D/P ratio of 0.5.

Li's results indicated that light absorption can be significantly varied when modifying the array parameters. It was found that more efficient light trapping could be achieved with periodicity of SiNPs array close to hundreds of nanometers (Fig. 2-18a). The superior ultimate efficiency of a proposed Si thin film cell with the nanostructures was calculated to be reaching 30% [73] (Fig. 2-18d). The simulation results were an important indicative and would facilitate the manufacturing of silicon thin film solar cell with SiNPs.

2.5.5 Making into a Device

Devices fabricated based on these structures were shown in literature, and with different designs of cell structures. However, due to the lack of presentation of silicon thin film solar cell which is integrated with these nanostructures, here we are primarily highlighting the results of wafer-based devices or thin film devices with other nano-patterns.

Devices based on wafer demonstrated enhanced behaviors. The electrical properties of the devices were monitored and reported. Comparisons of devices with and without the nano pattern were shown. Fig. 2-19 shows the I-V curve from Tu's research results. The open-circuit voltage and short-circuit current are measured under AM1.5 simulated spectrum. The patterned SiNPs solar cell shows an efficiency of 6.59% ($V_{OC}= 0.82$ V; $J_{SC}= 14.4$ mA/cm²); fill factor= 55.6%. The flat solar cell has an efficiency of 5.18% ($V_{OC}= 0.83$ V; $J_{SC}= 12.3$ mA/cm²); fill factor = 50.9%.

Figure 2-19 Performance enhancement of silicon device with nano-pattern [87]

The patterned solar cell exhibits a 17% higher J_{sc} than the flat substrate cell, demonstrating increased optical path length and improved short-circuit current.

Special attention was paid to certain electrical parameters, e.g. short circuit current. Wong et.al stated that the boost of short circuit current was achieved after integration of silicon nanopillars [88]. It is proven as well that both dark and light current are increased.

Figure 2-20 Experimentally measured short-circuit density J_{sc} as a function of (a) pillar diameter D , (b) pillar height H [88].

Fig. 2-20 presents the enhanced light absorption as a function of silicon pillar diameter and height. Fig. 2-20a shows that the J_{sc} of SiNP surface textured device is boosted to a maximum of $\sim 31.4 \text{ mA/cm}^2$ with pillar D of 200 nm, which is ~ 1.7 times larger than that of the untextured device (18.1 mA/cm^2). Fig. 2-20b depicts that the J_{sc} increases with increasing pillar H due to the enhanced light trapping. However, it is noted that the J_{sc} of 19.7 mA/cm^2 for the sample with a small pillar height (e.g. 100 nm) shows small difference with that of untextured device (18.1 mA/cm^2). The pillar H should be relatively longer (at least 500 nm) to observe significant improvement in J_{sc} (~ 1.5 times larger than the untextured device).

Until now, we have reviewed researches showing that the nanostructures help to increase light absorption and therefore cell performances. These nano-patterns were mainly fabricated using lithography or etching. Devices fabricated with traditional alkaline-etching mechanism were also in comparison. The results showed that the external quantum efficiency and cell efficiency of nanostructure-patterned devices are both superior than that of KOH-textured devices [89], as shown in Fig. 2-21. Fig. 2-21a shows the EQE enhancement in the long wavelength range resulted from the transmission enhancement due to the nano-structure patterned device, since the absorption takes place at bulk, instead of the surface (e.g. elongated light path to enhance light absorption at long wavelength regime, as discussed at start of this chapter). Fig. 2-21b shows that the power conversion efficiency achieved was 13.39%, showing a 9.13% improvement over the 12.27% of the reference KOH-etched sample.

Figure 2-21 Comparisons between cell with nanostructures and cell after KOH-etch [89]

Besides these wafer based experiments, silicon thin film based devices are also incorporating different nano-engineering ideas for better light absorption behaviors. However, the efforts are mainly in back-reflector engineering and the incorporation of nano-crystals, or even metal nano-particles for plasmonic influences [90-97].

Figure 2-22 The relationship between the J_{sc} enhancement and the silver nanoparticle size of the cells under different coverage densities from 5 to 20% [95].

Chen presented an example of incorporating silver nanoparticles to analyze the influence of the silver nanoparticles on the performances of solar

cells [95]. The J_{sc} is directly related to the sizes of the silver nanoparticles under different coverage densities, as shown in Fig. 2-22. According to the author's analysis, when the 20 nm silver nanoparticles are integrated into the thin-film amorphous silicon solar cells, parasitic absorption in the silver nanoparticles is dominate because the small nanoparticles have larger absorption cross sections than the scattering cross sections in the visible wavelength range, which cannot lead to a substantial enhancement of the absorbance in the amorphous silicon layer [95]. Consequently the integration of 20 nm silver nanoparticles decreases the J_{sc} value significantly as shown in the figure.

2.6 Conclusion

In this chapter, details are discussed regarding silicon thin film solar cells. We analysed the characteristics of sunlight radiations and the capabilities of silicon materials in absorbing them. Energy generation and measuring terminologies are briefly introduced. Next, the specific absorption behaviour of silicon material against sunlight is analysed in the context of solar cell operation.

Different phases of silicon were discussed to highlight their histories and applications. Amorphous silicon thin film is mainly utilized in small-scale multi-purpose devices, because their flexible deposition technology and lower equipment demand. Lower conversion efficiency and comparatively poorer stability are its drawbacks. Poly-Si thin film has its advantage of combining the deposition flexibility of a-Si and material superiority of crystalline Si. However, it is a challenge to create film with pure-and-large grains (e.g. for high

performance) while maintaining the cheap deposition technology compatible with a-Si process (e.g. for low cost).

Nanostructured silicon thin film is one of the interesting topics in third generation solar cells. We reviewed the purpose of creating nanostructures on top of thin film – light trapping for better absorption. In addition, we discussed in detail of the different morphologies fabricated or simulated through literature reviews. VLS bottom-up growth and top-down etching are the two main methodologies utilized in obtain SiNWs. However, only the latter is feasible for fabricating large-scale SiNPs or SiNCs covered thin films with smooth surface (e.g. reduced recombination) and controllable aspect ratio (e.g. optimized light interaction with controlled dimension) of arrays. Top-down etching is able to generate highly closed-packed, ordered, and controlled SiNPs or SiNCs arrays. The fabrication details are observed through SEM images and the results are discussed.

Simulation has attempted one step further than experimental effort – optimizing the nanostructure to boost optical absorption and subsequent device performance, because simulation has no constraint of feasible fabrication processes. Both randomized and ordered nano-arrays are discussed in the review, while researches have been mainly focused on ordered SiNPs and SiNCs arrays. Through integration of these nanostructures, light absorption of the active material has been proved to increase significantly.

Furthermore, both via experiment and calculation, promising results of the electrical device performances have been observed. External quantum efficiencies and short circuit current are two main factors being increased by the

nanostructures, which prove that light absorption is indeed increased (e.g. agree to optical measurement). Further boost of J_{sc} is also researched based on different morphologies of the nanostructures (e.g. wafer based cell).

In summary, undoubtedly, the reduction in reflection and better absorption in a wide spectrum range is the benefit brought by nanostructures. The realization of such structures on silicon thin film may practically help to avoid the cost of making specially designed antireflection coatings. The contribution from nanostructures is mainly in enhancing the absorption in high energy regime while broadening the absorption edge towards the lower energy regime.

Optimized nanostructures with ordered arrangement were proposed by researchers, with calculation of their optical and electrical characteristics. However, experimental realization of such devices (e.g. silicon thin film PV cells with nanostructures integrated on top) was insufficient to provide feedbacks to the theoretical simulations. More research efforts in fabricating the ordered nano-patterns on silicon thin film are in need for better understanding of the benefits of integrating these nanostructures into PV devices. From Chapter 3 to Chapter 5, experimental and supporting simulation efforts towards this research interest will be summarized and discussed.

CHAPTER 3 FABRICATION OF WAFER-BASED ORDERED SI NANOSTRUCTURES

3.1 Introduction

This chapter discusses an electroless chemical etching technique using polystyrene nanospheres as a self-assembled mask to fabricate size-controllable, periodic silicon nanopillars and subsequent nanocones arrays. The SiNCs are obtained based on the SiNPs structure using cost-effective ammonia-related etching chemistry. The diameter, height, and periodicity of the NCs can be systematically controlled. This method is potentially beneficial to many other device applications where nano-fabrication is involved.

Reviews presented in last chapter show that silicon nanostructures have potential benefits in enhancing device's optical and electrical performance. The SiNPs and SiNCs have been actively investigated for enhancing light harvesting of a PV cell [57, 73, 74, 98, 99]. In particular, by tuning the diameter, height, center-to-center spacing (period), Li et al. reported that the SiNCs arrays exhibit superior light absorption as compared to SiNPs arrays [73]. It is thus practically important and of great interests to develop low cost and high yield SiNCs array fabrication technology with excellent process controllability on manipulating their physical dimensions. In this section, we report a novel route of preparing SiNCs arrays with controlled size and period. Ordered SiNPs arrays were firstly prepared by a poly-styrene (PS) nanosphere-masked chemical etching process. SiNCs were fabricated subsequently based on the SiNPs using ammonia (NH_4OH). The chemistry has been well-documented to perform anisotropic silicon etching [100]. With systematically

manipulating the etching condition, desired SiNCs arrays can be successfully achieved. Basic optical measurement was also performed to analyze the light trapping property for future application.

3.2 Experimental Procedures

Single crystalline p-type (boron heavily doped) silicon <100> substrates with resistivity of $\sim 0.1\Omega\cdot\text{cm}$ were sequentially cleaned in acetone, methanol, and de-ionized (DI) water, each for 20mins, in ultrasonic bath. After that, piranha solution which consists of a mixture of concentrated sulfuric acid and hydrogen peroxide was used to modify the cleaned Si sample surface into hydrophilic phase. PS nanospheres dispersed in water (Microparticles, GmbH) with different diameters were thermally treated (e.g. 80°C for 10mins and above) and mixed with pure ethanol (volume ratio $> 3:1$) for the purpose of eliminating island formation during spin coating. After the samples were air dried, a monolayer of PS spheres was spin-coated with rpm 500-1000 for 10sec followed by rpm 4000 for 40sec. The size of the PS sphere was then controllably tuned under oxygen plasma RIE (details in section 3.3.1).

Figure 3-1 Monolayer formation after spin-coating

As shown in Fig. 3-1, the hexagonal arrangement of PS ball can be clearly observed. The size shown in the figure is ~928nm (as purchased from Microparticles). The successfully formation of mono-layer PS balls with closed-hexagonal pattern is crucial for further fabrication of NPs and NCs.

Next, a thin layer of Ag (~15nm) was coated on the PS nanospheres. Silver served as reaction catalyst in later stages. Fig. 3-2 shows the silver-covered PS balls and it can be seen that the hexagonal pattern is not influenced by the silver deposition (i.e. sputtering) process.

Figure 3-2 Nanospheres after silver coating

Thirdly, hydrofluoric acid (concentrated HF ~48% solution) mixed with H_2O_2 (volume ratio HF: $\text{H}_2\text{O}_2 \sim 3:1$) was used as etchant for the formation of nanopillars. The silicon material is etched while immersed in the solution, and the reaction involves firstly Ag atoms on the surface of silicon being oxidized and dissolved in solution to form Ag^+ ions [101]:

Secondly, the Ag^+ ions react with the Si covered by the silver particles. Silicon covered by PS spheres is protected because it is not in contact with silver particles, which catalyzes the formation of SiNWs.

Ag^+ ions can be recovered into the original silver layer again, and repeat reacting with silicon further underneath. After the reaction, remaining silver was removed by boiling aqua regia without damaging silicon materials. Fig. 3-3 shows an image of fabricated SiNPs with silver layer covering on top. From the figure, the hexagonal arrangement of SiNPs underneath silver residues can be

seen again, which validates our fabrication process where PS balls serves as a template for the positioning of subsequent SiNPs.

Figure 3-3 The remaining silver on top of silicon nanopillars after etching

After silver removal, the samples were cleaned using DI water. Until this stage, SiNPs are successfully formed and the morphologies will be discussed in next section. Further formation of SiNCs requires a mixture of ammonium hydroxide (NH_3OH) and hydrogen peroxide (H_2O_2) to be used to convert the SiNPs into SiNCs. Samples were finally rinsed by DI water and dried for characterization.

The schematic process flow of fabrication of SiNPs & SiNCs is depicted in Fig. 3-4. (a) cleaned wafer, (b) coating of poly-styrene spheres, (c) deposition of thin Ag layer, (d) etching of silicon using $\text{HF}:\text{H}_2\text{O}_2$ solution, (e) removal of silver by aqua regia and PS spheres by DI water rinsing, and (f) formation of SiNCs based on the SiNPs structures. A noteworthy point of our fabrication process is that the major controlled procedure for fabricating nanostructures with different morphologies is step (b), where the formation of mono-layer

patterned PS spheres is achieved. This will also be discussed in following section.

Figure 3-4 Process flow of fabrication of SiNPs and SiNCs on wafer based substrate

3.3 Results and Discussions

The formation of SiNPs using PS nanospheres as mask has been shown elsewhere, e.g. [85]. Fig. 3-5 illustrates SiNPs formed in our work. As shown in the figure, the hexagonal arrangement of PS ball has been accurately transferred to the SiNP pattern.

Figure 3-5 SEM image of SiNPs successfully obtained

3.3.1 Morphologies

➤ SiNPs Formation

The SiNPs have a center-to-center distance, which is also known as the period, equivalent to the diameter of PS spheres during spin coating stages. This period is not affected through the whole etching stage because the nanospheres remain stably on top of silicon materials. Long etching time can be applied to obtain SiNPs with larger length, e.g. height.

In order to control the diameters of the SiNPs, we shall master the diameters of PS nanospheres after the coating stage. The spin-coating ensures a close-packed hexagonal pattern where the period of SiNPs is determined. However, further treatment involving O_2 -plasma RIE is able to trim the PS spheres before etching. Fig. 3-6 shows the effect of the O_2 RIE treatment on the size shrinkage of PS spheres.

(a)

Figure 3-6 PS nanospheres size shrinkage before and after O_2 plasma RIE treatment for: (a) before treatment (b) 50s, (c) 100s, (d) 150s and (e) 200s

Plasma generated from oxygen (O_2) carrier gas typically consists of O^+ , O^- , O^{2+} and O^{3+} ions for example. The plasma particles are extremely unstable and often used to react with low energy organic substances. The results show that we can monitor the “separation” between adjacent PS spheres with O_2 plasma RIE treatment. Sample in Fig. 3-6b with 50 seconds treatment shows minimal changes from original monolayer in Fig. 3-6a. The spheres start to “depart” from neighboring ones and the spaces in between are increasing with further treatment time (Fig. 3-6b to e). However, it is the diameter of PS spheres that is affected by the treatment, while the center-to-center distance of adjacent spheres is not influenced. In another word, by applying this oxygen treatment, we are able to modify the diameters of subsequent SiNPs while maintaining the period. It provides a good platform for us to further analyze the effects of different dimensions of SiNPs.

After the treatment, silver was deposited on the surface of the PS spheres, followed by etching process. Hydrofluoric acid mixed with H_2O_2 (as discussed in section 3.2) was used as etchant for the formation of nanopillars.

The silicon material was etched while being immersed in the solution, and the reaction was the same as discussed previously.

The etching time is kept the same for samples described in Fig. 3-6 to obtain SiNPs with same height, same period, but with different diameters. The corresponding top-view SEM images are in Fig. 3-7. Fig. 3-7a is the sample with no oxygen treatment, where the size of PS sphere is original ~590nm as purchased from Microparticles. Fig. 3-7b to 3.7e is related to 50, 100, 150 and 200 seconds of O₂ treatment. We can observe that the space between the pillars is getting larger as we increase the treatment time. The diameters of pillars are reduced as well. The original diameter of 590nm is reduced to less than half, ~270nm as measured from Fig. 3-7e.

(a)

(b)

(c)

Figure 3-7 SiNPs with HF-H₂O₂ etching time 4 minutes but different O₂ treatment duration. (a) before treatment (b) O₂ treatment 50s, (c) 100s, (d) 150s and (e) 200s

The process can be achieved on wafer with large area (e.g. $\sim 5 \times 5 \text{ cm}^2$), while the monolayer of PS spheres are still maintained. Fig. 3-8 shows that for larger area, there are “groups” of pillars within which hexagonal arrangements can be observed. There is an obvious “boundary” between neighboring groups. However, these islands are not jeopardizing the light trapping properties, but actually reported to increase light trapping properties from randomized structure studies [75]. Theoretically, it has been reported that structural disorder can introduce additional resonances and broaden existing resonances [102], for the purpose of broadening absorption range.

Figure 3-8 SEM image of the SiNPs at lower magnification

Next, a longer etching time will generate a “higher” pillar provided that the etching species are sufficient in concentration. For our observation, 1.5 mins etching will create pillars with around 400nm heights, while 8 mins etching can lead to pillars with height over 2 μm . The side-view SEM images are shown in Fig. 3-9, where image a to d are related to etching time of 1.5 mins, 3 mins, 6 mins and 8 mins, respectively. From the figures, it is apparent that longer etching time leads to higher pillar. However, we noticed that the increase of pillar height is not linear with respect to the etching time. A simple plot of height vs. time is shown in Fig. 3-9e and the data is presented in Table 3.1. The figure illustrates that the etching takes place at faster pace in the starting minutes (e.g. first 3 mins) than thereafter. This is due to the diluted concentration of etchant along the etching process where concentrations of HF and H_2O_2 are reasonably decreasing. Furthermore, the etching speed in the first 1.5 mins is observed to be averagely slower than the second 1.5 mins (e.g. 1.5mins – 3 mins). This mechanism can be understood by referring to the etching chemistry mentioned in previous section [101]. Silver atoms will firstly be oxidized and dissolved into the solution before silicon material can be etched. Therefore, the starting stage of the whole etching process experiences a short delay for the SiNPs to be created. Thus the average etching rate in the first 1.5 mins is observed to be smaller.

(a)

(b)

(c)

(d)

Figure 3-9 Cross-section SEM of SiNPs with etching time (a) 1.5 mins, (b) 3 mins, (c) 6 mins,

Etching time 1.5 mins	Pillar height ~ 400 nm
Etching time 3 mins	Pillar height ~ 1 μm
Etching time 6 mins	Pillar height ~ 1.8 μm
Etching time 8 mins	Pillar height ~ 2.2 μm

(d) 8 mins and (e) plot of pillar height against etching time

Table 3-1 Brief summary of SiNPs height under different etching time

Furthermore, the etching is also restricted by the concentration of etching species. Increased HF concentration generally brings a faster etching speed. Nevertheless, high etching rate is not desirable in our experiment because it undermines the stability of nanospheres on top of the silicon materials. Higher concentration of reactive species generates more intensive chemical reactions and therefore more liquidity turbulence. The PS spheres tend to lose their adhesion to the top surface of Si as they are completely immersed in the etching solution. The silicon underneath will then be exposed to etchant attack.

Figure 3-10 SiNPs under attack by etchants when HF concentration increases (e.g. HF:H₂O₂ = 4:1 and above, HF stands for 48% solution as discussed in section 3.2).

The “attacked” silicon is referred as porous silicon as shown in literature [103-106], with potential application in optical sensors. The etching concentration in our experiment has been standardized to be HF:H₂O₂ = 3:1. Different etching behaviors have been documented in other researcher’s work where the purpose of the experiment was not focused on ordered arrays of silicon nanostructures [103-106].

➤ SiNCs Formation

Here we introduced a further etching stage via the use of ammonia solution (NH₃.H₂O ~2.5M, pH ~ 11). The reaction is anisotropic as the etch rate in high Si-binding-energy planes are significantly lower [100, 107]:

As a result, the etching will be suppressed in Si <111> plane and only proceeds in lower binding-energy Si<100> planes [108]. A cone shape with a fixed top angle can be expected. The top angle is determined by the plane angle between <111> and <100>, which is 54.7°. Fig. 3.11 shows the SEM image of

the cones after etching. The shape of SiNCs can be clearly observed and the slant surfaces of all cones are almost parallel with each other, implying a good process control with the effect of “stopping” $\langle 111 \rangle$ plane. The top angle of the SiNCs is estimated to be: $180 - 2 \times 54.7 = 70.6^\circ$.

Figure 3-11 SiNCs after ammonia-based etch

Figure 3-12 SEM image of SiNCs at lower magnification

Fig. 3-12 shows the SEM image of SiNCs at lower magnification. The figure illustrates that the nanostructure is uniformly formed on a large scale on the wafer surface. Since the top angle is fixed, the dimension control of SiNCs will be different from that of SiNPs.

We present the detailed comparisons and summary of dimension control in the following Table 3.2. As shown in the table, diameters of SiNPs are transferred from the diameters of PS spheres before etching. In another word, further oxygen plasma etching is able to trim the size of the PS spheres and control the diameter of subsequent SiNPs. However, diameters of SiNCs are only determined by original diameter of PS spheres. Further O₂ etching shrinks the PS sphere without dislocating them, and further ammonia etching will only experience high resistance when the two stopping planes intersect with each other (shown as inset image in the table). As a result, the base diameter of SiNCs is directly related to the diameter of PS spheres.

Dimension	SiNP	SiNC
Diameter	<p>transferred from PS balls</p> <p>and further controlled by oxygen plasma</p>	<p>transferred from PS balls, further treatment has no effects.</p> <p>..... before PS spheres treatment — After PS spheres treatment</p> <p><111> ~70°</p> <p>Two stopping planes intersect at the bottom of the cones.</p>
Period	Same with PS sphere diameter	Same with PS sphere diameter

Height	Controlled by etching time	Determined by fixed top angle and Diameter. $\text{Height} = \text{half diameter} / \tan(35^\circ)$ PS sphere diameter as base diameter of cone
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Table 3-2 Summary of dimension control of SiNPs and SiNCs

The period of both structures are directly related to the diameter of PS spheres after spin coating, it is because that all subsequent treatment and etching processes will not dislocate the sphere.

Height of SiNPs is dependent on the etching duration in the condition that etchant is not too concentrated to damage the pillar (as discussed in previous part). However, the height of SiNCs is not related to the etching duration, as discussed in the table. Since the formation of cone is directly linked the preferential etching of Si<100> over Si<111>, the top angle of SiNCs is fixed at around 70° and thus the height of the cone is determined by this angle and the predetermined diameter size.

The concentration of etching species, the ammonia solution, needs to be controlled in order to protect the cone surface. With higher concentrations, the cone shape is impaired. Fig. 3-13 shows our results under higher etching concentrations (3.2M NH_3 , pH ~ 12). From the figure, the deformation of cone

morphology is obvious. It manifests that stronger alkaline etching species are able to impact the high-binding-energy silicon plane.

(a)

(b)

Figure 3-13 Comparison of cone morphology under: (a) higher etchant concentration 3.2M NH_3 and (b) lower etchant concentration 2.5M NH_3

In summary, we have described a systematic approach to control the morphologies of SiNPs and SiNCs in this section. In our experiment, the diameters of both structures are directly linked to the original diameter of PS spheres, while the diameter of SiNPs can be further reduced by oxygen treatment. Period is fixed by PS sphere diameter. Height of SiNP is under control via varying etching duration, while the height of SiNC is determined by the inter-plane angle of 70° and the original PS sphere diameter.

3.3.2 The Reflectance Measurement

The reflectance of samples with and without SiNPs and SiNCs are measured by Lambda 950 UV/VIS/NIR spectrometer with integrating sphere from *Perkin Elmer*. The measurement done in this section was not comprehensive because we used it merely as a qualitative analysis to demonstrate the impact of the nanostructures with respect to interaction with

incident light. The optical characteristics will be detailed studied regarding different morphologies in next chapter where the nanostructures are obtained on silicon thin films. Reflectance is measured at 8° incident light. Since the sample is mounted at the rear sample mount of the integrating sphere, all reflected light will be enclosed in the integrating sphere and collected by the detector.

Fig. 3-15 shows the reflectance spectra measurement result. The observation range is from 200 to 1300 nm.

Figure 3-14 Reflectance spectra of nanopillar and nanocones textured (SiNP diameter ~ 250 nm, pillar height $\sim 1.2 \mu\text{m}$, and SiNC diameter ~ 600 nm, height $\sim 1 \mu\text{m}$) silicon wafer and blank wafer

One main interest for solar application is the reduction of reflectance at visible range, and the situation has been significantly improved with SiNPs and SiNCs structure. For light wavelength range of 200-700nm, the sample with SiNCs structure shows reflectance less than 5%, while the sample with SiNPs structure shows a reflectance between 5% and 10%. Furthermore, for the sample with the SiNPs structure, it shows a large reflectance increase at the near infrared range (less than 1100 nm in this case), while the sample with the SiNCs structure shows a reflectance still maintained to well below 10%.

3.4 Summary

3.4.1 Limited Application of Solution-based Etching Methodology

One of the major drawbacks of our solution-based etching process is that it damages the surface of SiNPs and SiNCs. From our SEM images shown, surface roughness of the SiNPs can be comfortably believed to be significant.

Figure 3-15 SEM image of cross section of SiNPs

This is a severe problem as carriers tend to have higher recombination rate at sharp edges, e.g. large roughness. In common practices this is intentionally avoided in cell fabrications.

3.4.2 Morphology Control in Thin Film Application

Another shortcoming of this solution-based approach is attributed to the nature that etching species inside solution tend to reach “deep” into the valley of SiNPs. This means that the formation of SiNCs and well-shaped SiNPs may require a non-intensive etching process in order to protect the morphologies of the nanostructures.

Fig. 3-16 shows the deformation caused by intensive etching species. However, even when we control the concentration of etching species, we still need the high-binding-energy silicon plane to define the shape of the SiNCs

because it practically serves as a stopping layer against the etchants. As we discussed, the height of the SiNCs is factually determined by the top angle and the PS sphere. Therefore, formation of SiNCs will be greatly questioned and failure is highly probable in future application when we fabricate the nanostructures on silicon thin film on glass substrate where no practical high-binding-energy planes exist. These challenges will be addressed in the next chapter as we chose alternative etching methodology to achieve desired structures.

Figure 3-16 SEM image of SiNPs under high-concentration etching

Despite of the limited application of solution-based etching procedure, we successfully demonstrated controlled fabrication of SiNPs and SiNCs arrays on Si substrate using electroless chemical etching with PS nanospheres as self-assembled mask. The etching formation was based on hydrogen fluoric acid and ammonia related chemistry, as presented in their respective sections. The whole process is cost-effective with excellent repeatability, which may be of potential use in silicon based engineering interest.

CHAPTER 4 SILICON THIN FILM NANOSTRUCTURES FOR EFFICIENT LIGHT-TRAPPING

4.1 *Introduction*

Silicon nanostructures for PV applications are one of the key interests in exploration of third generation solar cell [61, 66, 67]. As mentioned in last chapter, two-dimensional silicon nanostructures, especially cone structures, are believed to encounter huge difficulties in thin film fabrication on glass substrate. The preferential etching from ammonia chemistry is dependent on the differential etching capacity in different silicon planes, e.g. $\langle 100 \rangle$ vs. $\langle 111 \rangle$. As a result, it is reasonable to predict the probable obstacle in transferring the etching methodology to thin film fabrication. However, successful integration of Si nanostructures on glass to realize high efficiency thin film Si solar cells cheaply and efficiently remains as our particular interest.

SiNPs can be formed by either bottom-up growth or top-down etching. Chapter 3 represents a good example of top-down etching using solution-based approach with self-assembled PS monolayer masking technique. The process is an electroless and practically “maskless” low-cost method. However, the limitations are pointed out in the summary of Chapter 3, and it shows the difficulties in introducing wet chemistry into thin film based silicon nanostructure fabrications. The problems of solution based etching primarily are roughness and dimension control of nanostructured arrays. There is little work showing fabrication of patterned periodic SiNPs or SiNCs on either a-Si

or poly-Si thin film on glass. The reason is mainly due to the nature of chemical etching. Wet chemical etching is generally isotropic, which makes it difficult to control the aspect ratio and dimensions of the nanostructures. Modern etching techniques provide two most efficient methods in obtaining high-aspect-ratio silicon structures – dry reactive ion etching (DRIE) and inductively coupled plasma etching (ICPE). ICPE is capable of making sub-wavelength patterns (~ 100 nm), but it is comparatively costly. For future generation of solar cells, reasonable cost has to be maintained while pursuing high quality thin films. Hence, RIE stays the most feasible tool to fabricate periodic Si nano-patterns on glass for our case.

In this chapter, we report the preparation of different nanostructures on Si thin film, which are SiNPs and SiNCs arrays with controlled dimension. The ordered arrays are masked by PS nanosphere lithography. By systematically manipulating the treatment condition of PS spheres and the etching conditions, morphologies of the arrays can be controlled accordingly. Further characterizations of their optical properties are conducted in detail, and the key objective remains to enhance light absorption capacity.

Furthermore, simulation works performed by commercial FDTD software *Lumerical* is also summarized in this chapter. The simulation is based on our experimental results where different morphologies have been achieved. As a result, the simulation work serves as a theoretical support of the experimental effort and it also helps to validate our experiments. Our observations from both experiments and simulations give us confidence in

concluding the validity of our results and proceeding to the fabrication of solar cells based on these nanostructures.

4.2 *Experimental Procedures*

Glass substrates were sequentially cleaned in acetone, methanol, and de-ionized (DI) water, each for 30 mins, in ultrasonic bath. The substrates were dried before silicon thin film deposition. The deposition was done by sputtering under vacuum in the order of 10^{-7} mbar. The deposition rate was controlled to achieve a reasonably smooth surface (small roughness as shown in Figure 4-1). The thin film thickness was around $2.5\mu\text{m}$ and it was sent for annealing after deposition.

Figure 4-1 Roughness measurement of the deposited silicon thin film obtained by atomic force microscopy

The smoothness of the glass substrate was not measured. However, the necessary practices, such as extensive cleaning stages, were performed in order to ensure the coating of Si was done on the smoothest glass in our best effort.

The reason for obtaining small roughness is to facilitate the assembly of PS nanospheres. Smoothness of the silicon film is crucial to enable PS spheres to form monolayer on the film. To achieve smooth silicon film, we chose sputtering with slow growth rate rather than comparatively cheaper CVD method for deposition. Furthermore, the crystalline phase is also monitored in order to assure our poly-Si etching processes. Fig. 4-2 shows the Raman spectroscopy measurement of the silicon thin film. As seen from Fig. 4-2b, the crystalline Si peaks around $516\text{--}519\text{ cm}^{-1}$, due to the nanocrystalline phase (centered around 510 cm^{-1}) and polycrystalline phase (centered around 520 cm^{-1}) [109-111]. The presence of amorphous Si phase was initially observable (Fig. 4-2a) when substrate temperature during sputtering is low. After we increased the substrate temperature and introduced a post-annealing stage (550° for 8 hours) right after the deposition, we observed full crystallization.

Figure 4-2 Raman spectra of the silicon thin film (a) before and (b) after annealing

Furthermore, in order to determine the grain size of the thin film. We etched the sample with Secco solution ($\text{HF} + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O}$ in a ratio of $\text{HF}:\text{H}_2\text{O} = 2 : 1$ with 44 g $\text{K}_2\text{Cr}_2\text{O}_7$ dissolved in 1 L of H_2O) and obtained the SEM image of crystalline silicon grains. Fig. 4-3 shows the SEM image and X-ray diffraction (XRD) measurement of the crystalline thin film after Secco etch.

From the SEM and XRD figures, we found that the major grain sizes in the thin film are nano-crystalline Si and micro-crystalline Si, with size ranged around tens of nanometers. The XRD result in Fig. 4-3b states that crystalline Si peaks at $\langle 111 \rangle$ ($d = 3.14\text{\AA}$), $\langle 220 \rangle$ ($d = 1.92\text{\AA}$), and $\langle 311 \rangle$ ($d = 1.62\text{\AA}$) are present after the thermal annealing. The preferred orientations are $\langle 111 \rangle$ and $\langle 220 \rangle$. Although large grains, e.g. in the order of hundreds of nanometers, are missing from our film, the existence of poly-Si thin film on glass is confirmed by the SEM and XRD results.

Figure 4-3 (a) SEM and (b) XRD images of the poly-Si (Secco etched) film.

Next, samples were immersed into piranha solution for the removal of organic components, as described in previous chapter. The solution is able to hydrolyze the Si thin film surface by introducing OH^- group. Next, PS

nanospheres, dispersed in water (Microparticles, GmbH) with a diameter ranging from 600nm to 800nm were mixed with ethanol to avoid island formation during spin coating. Then a monolayer of PS spheres was assembled using spin-coating on the Si thin film surface.

The PS spheres will serve as the mask for the subsequent RIE process. Again, the size of the PS sphere was controllably tuned by O₂ plasma treatment. Arrays of SiNPs and SiNCs were created by halogen-based RIE process with a gaseous mixture of primarily Cl₂ and HBr. After the RIE stage, residual PS nanospheres were removed by ultrasonication in organic solvent, which brings no damage to the silicon structures. Optical measurement was then conducted.

4.3 Results and Discussions

4.3.1 SiNPs Morphologies

Since RIE with chlorinated plasma does not have large loading effect compared to CF₄ plasmas, the chemical reaction during the silicon RIE in Cl₂ plasma is not as intense as in CF₄ plasma [18]. Less chemical attack means the etching is relatively more physical, giving less chance of undercut. The etching process is shown in Fig. 4-4. The diagram primarily intends to show the masking behavior of PS spheres.

Figure 4-4 Process demonstration of PS nanospheres lithography
The corresponding SEM images are shown in Fig. 4-5:

Figure 4-5 SEM image showing the “masking” of PS nanospheres on silicon thin film

As seen from Fig. 4-5, a monolayer of PS spheres with diameter around $0.6\mu\text{m}$ can be observed clearly “sitting” on top of the nanostructures underneath. The silicon underneath is protected by the PS spheres during etching.

The density of reactive species decreases from the top to the bottom of the trench in between pillars during etching process, resulting in a higher silicon etching rate at the top and lower rate at the valley. Therefore each silicon pillar has slightly tapered sidewalls. This can be verified by further cross-section SEM images shown later.

➤ *Investigation on diameters of nanopillars*

The top surface and bottom area of the SiNPs can be controlled by fine tuning the O₂ plasma treatment duration, as shown from Fig. 4-6 to Fig. 4-9. For PS spheres with an original diameter of 600nm and 800 nm, various sets of oxygen treating time were applied. Different diameters of the PS spheres ranging from 200 nm to 800 nm were achieved. Top view images show that the diameters of SiNPs are closely related to the diameters of the PS spheres and O₂ treatment.

Figure 4-6 SEM top and tilt view images of SiNPs with diameter 800nm (without oxygen treatment)

Figure 4-7 SEM top and tilt view image of SiNPs with diameter 600nm (oxygen treatment 50s)

Figure 4-8 SEM top and tilt view image of SiNPs with diameter 400nm (oxygen treatment 100s)

Figure 4-9 SEM top and tilt view image of SiNPs with diameter 200nm (oxygen treatment 150s)

SiNPs with diameter 800nm is fabricated based on PS sphere with the same diameter (refer to diameter control on section 3.3.1), while SiNPs with diameter 200nm, 400nm, and 600nm are all obtained from PS spheres with diameter 600nm. From our observation, while the diameter of original PS spheres determines the “starting” diameter of the SiNPs, oxygen plasma treatment does the fine-controlling job. The largest treatment time in our adoption was 150 seconds, where the size of PS spheres was reduced to close to 200 nm¹. Further reduction of PS spheres was possible to achieve even smaller scale Si nanostructures. However, as the size shrinks, the spheres are losing their geometric symmetry and the obtained silicon nano “pillars” do not possess

¹The O₂ plasma equipment was a new set-up and different from the equipment used in Chapter 3, therefore the etching conditions are different from the results in previous section)

round flat top surfaces. Fig. 4-10 demonstrates the damage of PS spheres where subsequent SiNPs are hindered in terms of geometric dimension.

Figure 4-10 SEM image of SiNPs with diameter smaller than 200nm with distorted top dimension (a) top view (b) tilt view (oxygen treatment more than 200s)

Fig. 4-10 are the SEM images of over-treated SiNPs samples with distorted top surface dimension. Tilt views were also taken in order to confirm the consistent periods while top round area has been deformed.

The controlled fabrication of SiNPs with various diameters has been shown, and the other two parameters, e.g. periods and heights, are kept constant in this section. The periods are 600nm for sample with diameter of 200nm,

400nm and 600nm, while the period is 800nm for sample with diameter of 800nm. The etching time is fixed at 4 minutes where an estimated height of 900 nm is generated (shown in later section).

➤ *Investigation on periods of nanopillars*

Next, the controlled fabrications of SiNPs with various periods were attempted. In pursuit of different periods, we used PS nanospheres with diameters close to 200, 400, 600, and 800 nm. Therefore after being O₂ plasma treated, samples were etched with fixed amount of time, in order to achieve reasonably constant height with comparable SiNPs diameters.

We fabricated all SiNPs with height around 900 nm, and diameter near 200 nm. The reason of choosing 200nm is because it is the largest period value that PS sphere with diameter 200 nm can achieve, as shown in the SEM images below.

Figure 4-11 SEM top and tilt view image of SiNPs with period 800nm (diameter ~200nm, with oxygen treatment 250s)

Figure 4-12 SEM top and tilt view image of SiNPs period 600nm (diameter 200nm, with oxygen treatment 150s)

From these diagrams above, we can see that SiNPs with period 800 nm (PS ball size ~ 800 nm) show morphology distortions clearly because the O_2 treatment time required to reduce its size to 200 nm is long. The PS spheres were damaged by oxygen species in the plasma. Other than this, the periodity of 800 nm is still maintained. Furthermore, it is interesting to note that with increased oxygen treatment, the etching process starts to produce morphologies more like a nano cone, other than pillar. The reason is because top surface offers less protection by PS spheres with the shrinkage of PS spheres. Further details on how to obtain SiNCs will be discussed in later section. Again, the etching time was fixed to 4 mins which generates a pillar height of around 900 nm, which was chosen based on simulations [72].

Figure 4-13 SEM top and tilt view image of SiNPs with period 400nm (diameter 200, with oxygen treatment 80s)

Figure 4-14 SEM top and tilt view image of SiNPs with period 200nm (diameter 200, without oxygen treatment)

From the SEM images, we conclude that the excellent hexagonal arrangement and close-packing pattern are directly transferred from the nanosphere mask. This transfer is performed with adequate accuracy provided that oxygen plasma treatment is not too intense to damage the sphere morphology of the PS mask.

➤ *Investigation on height of nanopillars*

Height of SiNPs can be controlled by etching time, therefore with reasonably higher accuracy compared with control of diameter and periods. In our attempts, we did not manipulate the etching time much because from previous calculation, a combination of 1000nm SiNPs + 800 nm thin film is able to generate promising results [81]. From the calculation, it was found that the light absorption around 2.5 eV, i.e., the high energy density region of the solar spectrum, could be significantly enhanced with increasing the SiNP array periodicity from 100 to 500 nm due to suppressed reflection and transmission. Further increase in the periodicity to 700 nm would decrease the light absorption because of the enhanced light reflection in the energy region above

2.5 eV. The ultimate efficiency calculation shows that, a maximum value, about 27%, could be achieved when the periodicity is around 500 nm.

In our experiments, the observed etching time 4 mins can produce SiNPs with height near to 900 nm. Therefore there will be $2500 - 900 = 1600$ nm of silicon thin film lying underneath the nanostructure. A cross section image can show the height control procedures of SiNPs clearly.

(a)

(b)

Figure 4-15 Cross section SEM image for analysis of the height of SiNPs: (a) 4 mins etch creates height of ~900nm, (b) ~ 8 mins etching etches through the 2.5 μ m Si thin film

The slanted sidewall can be observed in above figures. RIE process eliminates the drawbacks of wet etching described in last chapter and we can conclude that the formation of SiNPs is successful. Three main parameters in controlling the morphologies of the nanostructures are managed manually.

4.3.2 SiNCs Morphologies

The creation of different periods, diameter and height is dependent on the size of the PS spheres and requiring careful control of the etching process. In order to obtain SiNCs, further etching of SiNPs is needed.

The intermediate stage which consists of oxygen plasma treatment is important. This stage is able to further-refine the size of PS nanosphere, without damaging the SiNPs and the thin film underneath. PS spheres shrinks while being exposed to O₂ plasma ambient. The treatment time can be varied to trim PS spheres to various desired diameters. After the plasma treatment, further etching is conducted to etch the top structure of SiNPs. Fig. 4-16 below describes the process flow in simple drawings.

Figure 4-16 Process demonstration of further fabrication of SiNCs

Top exposure of SiNP leads to the shrinkage of top flat surface. However, silicon at the bottom valley of the pillar still remains relatively more-isolated from the etching gaseous environment, and this is the reason that cone shaped is obtained. The diameter of SiNC will stay close to that of SiNP, with possible minor shrinkage. In practice, large amount of trial-and-error and re-attempts are executed to manage the suitable duration for different SiNPs structures. Fig. 4-17 shows a clear working-path on the formation process with presentation of SEM images. The sample is chosen for SiNPs with diameter 800nm. We can observe that the bottom dimensions of the SiNPs are well transferred to SiNCs, with possible minor shrinkage, while the top dimension is being attacked by etchants and its size is reduced. As mentioned in Fig. 4-16,

extended RIE condition will be jeopardizing the cone shape and lead to distortion or shrinkage of base diameter.

Figure 4-17 Process to obtain SiNCs (a) SiNPs with diameter 800 nm and period 800 nm, (b) after 100s O₂ plasma treatment and further RIE, (c) after 200s O₂ plasma treatment and further RIE and (d) after 300s O₂ plasma treatment and further RIE

From the SEM images, it can be observed that the period of the PS sphere array remains unchanged because the bottom foundation of the SiNPs remains intact. Subsequently, the RIE etching will diminish the PS spheres, therefore exposing the silicon at top surface to the etching species. Continuous etching will eventually generate SiNCs.

To summarize the fabrication of SiNCs:

- SiNCs formation is directly linked to the previous stage of fabricating the SiNPs
- The fabrication of SiNCs involves two stages: O₂ plasma treatment to control the size of PS sphere, and further RIE etching of transforming SiNPs into SiNCs by the halogen chemistry.

- The fabricated SiNCs will “inherit” the dimension properties of their related SiNPs with appropriate etching duration, maintaining the period, base diameter, and the height of the structures.

In our experiments, since the SiNCs inherited the dimension from SiNPs, we also obtained a series of SiNCs with various dimensions. Some of their SEMs are shown below.

Fig. 4-18 is the top view of obtained SiNCs nanostructures. Different from SiNPs (Fig. 4-6 to Fig. 4-9), we realized in practice that it is not apparent for observation of the PS spheres on top of the SiNCs (as in Fig. 4-17d as well). It is because the reduced dimension of silicon material underneath the PS sphere decreases its physical support to the PS sphere. As a result, sharp top of cone structure can be observed, as presented in Fig. 4-19a and 4.19b.

Figure 4-18 SEM top view of SiNCs

(c)

Figure 4-19 SEM tilt view of SiNCs (a) SiNPs with diameter 600nm, period 600nm, O₂ 200s and further RIE, (b) SiNPs with diameter 800nm, period 800nm, O₂ 300s and further RIE, (c) low magnification view of the sample from (b)

Fig. 4-19a and b show samples started with PS diameter 600nm and 800nm respectively. The PS sphere was not treated by oxygen plasma before SiNPs etching, to maintain its original diameter and period. After the formation of SiNPs, different O₂ treatment time is used for these samples, while the 800nm PS sphere requires a longer treatment in order to create the subsequent SiNCs. A noteworthy point is that the top angles of SiNCs are mathematically determined by its height and base diameter. Therefore, as discussed, both parameters can be controlled and they are independent of each other, though base diameter is slightly reduced from SiNPs to SiNCs for extended etching time. However, we have standardized our height of SiNPs and SiNCs to be 900nm as shown in Fig. 4-20, thus the influence of this shrinkage of base diameter for different samples will be minimized.

Figure 4-20 SEM cross-section view of SiNCs

Since the fabrication of SiNCs was strictly following their corresponding SiNPs counterparts, a summary of different morphologies are presented below, while the simulation work shown in later part will be an attempt to verify and theoretically support these structures in their measurement of optical properties.

Summary of Fabricated SiNPs and SiNCs (Controlled Height 900nm)	
Controlled Period 600nm	Diameter 200nm, 400nm, and 600nm
Period 800nm	Diameter 800nm
Controlled Diameter 200nm	Period 200nm, 400nm, 600nm and 800nm

Table 4-1 Summary of various structures of SiNPs and SiNCs

SEM images confirm that periods are well preserved based on the diameter of the PS spheres on silicon surfaces. During the whole etching process, we observed that the PS spheres are stably held by the underlying silicon film without being swept off due to the gaseous ambient. This should be attributed to the piranha-soaking procedure of the silicon thin film.

As a result, our nanosphere masking technique is feasible to scale up to large-area Si nanostructures. Furthermore, we also find out that with such high packing density, the sidewalls of the slightly tapered SiNPs remain separated from adjacent pillars, which can facilitate the interaction between the nanostructures and incident light.

In the following sections of the chapter, we shall analyze the optical measurement results of the nanostructures, and followed by the discussion of the simulation results.

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4.3.3 Optical Characteristics

Optical characteristics of the SiNPs and SiNCs on silicon thin film are measured by Lambda 950 UV/VIS/NIR spectrometer with integrating sphere from *Perkin Elmer*. Reflectance is measured at 8° incident light. The sample is mounted at the rear sample holder of the integrating sphere for reflectance measurement, as shown in Fig. 4-21. All reflected light will be enclosed in the integrating sphere and collected by the detector.

Figure 4-1 Measurement configuration of integrating sphere (Perkin Elmer)

For transmittance measurement, normal incident light is shined on the sample surface, which is mounted at the front sample holder of the integrating sphere. All transmitted light will be enclosed in the integrating sphere and collected by the detector as well.

From the measurement configuration, there is one further step to obtain the absorption characteristics of our samples: $\text{Absorption} = 1 - \text{Reflectance} - \text{Transmittance}$. Since total reflectance and transmittance are

captured by the equipment, final absorption spectrum is obtained by mathematical calculations.

➤ *Impact of nanostructures*

Figure 1-2 Measurement results (a) reflectance spectra and (b) absorption spectra (1-R-T) for samples with and without nanostructures

Fig. 4-22 shows the reflectance and absorption spectra of silicon thin films on glass. The diagram clearly shows the optical influence of integrating nanostructures onto thin film. The reflectance diagram shows that the flat silicon thin film on glass exhibited more than 20 % reflectance in the high photon energy range. The reflectance of the SiNPs and SiNCs structured thin

film was less than 10% in the same photon energy range. This low reflectance value is maintained across a large span of energies ranging towards lower energy regime. For photon energy lower than 1.2eV, reflectance starts to increase for SiNCs and SiNPs samples. However their values at this region are still well below that of the control flat thin film sample.

Furthermore, the absorption diagram also shows a significant improvement from controlled flat thin film sample. The absorption is increased from average 60% to near 90% in photon energy larger than 2.5 eV. The broadened absorption edge towards lower energy regime is obvious as well. The absorption is still above 50% for photon energy close to 2 eV where the value of the control sample is remarkably lower. However, the absorption spectrum of our thin film sample shows an absorption drop near 2.5eV (the absorption edge), which is considered inferior with the knowledge of absorption edge of Si material around 1.1eV-1.3eV. This drop in the spectrum probably signifies that the thickness of our sample, 2.5 μ m is insufficient to capture light in lower energy regimes. Due to physical experiment constraints, the improvement in the silicon thin film quality was not performed in our work and is included in Chapter 6 for future use.

According to wave optics, incident light in low energy region (long wavelength) should be able to penetrate through the SiNPs and SiNCs structures, reaching the underlying Si thin film. This phenomenon is clearly shown in the absorption spectra. In the corresponding region, samples with and without nanostructures both show relatively weaker absorption compared to higher energy region. However, it is crucial and interesting to notice that this

absorption edge shifts toward the low energy range with the integration of nanostructures. The “shift” is mainly located in region of photon energy 1.8eV – 2.5eV. Light in this region corresponds to largely wavelength of hundreds of nanometers, the visible light. And these wavelengths are comparable with the size of nanostructures, thus scattering of these lights are enhanced at the sample surface. Light scattered into the active material underneath will have a longer path than the case of thin film sample. For light with lower photon energy (e.g. smaller than 1.5eV), the enhancement from nanostructures is not obvious.

➤ *Effect of various dimensions*

The reflectance and absorption spectra of SiNPs and SiNCs samples with various dimensions are summarized in this section.

Figure 1-3 Reflectance and absorption spectra of SiNPs samples: (a) reflectance of SiNPs with varying diameters and (b) various periods and $d \sim 200\text{nm}$, (c) absorption of SiNPs with varying diameters and (d) with varying periods and $d \sim 200\text{nm}$

Fig. 4-23 shows the reflectance and absorption measurement of various SiNPs samples. The samples were organized base on their morphologies. Fig. 4-23a and b are the reflectance spectra of SiNPs samples. Fig. 4-23a shows for silicon nanopillars with period fixed at 600nm , the lowest reflectance is achieved with diameter 600nm . With the diameter decreasing from 600nm to 200nm , reflectance increases from lower than 5% at high energy regime (e.g. $>2.5\text{eV}$) to over 15% . Fig. 4-23b illustrates the influences of varying periods. As shown in the figure, with diameter fixed at 200nm , reflectance increases as the period increases from 200nm to 800nm . Fig. 4-23c and d depicts the absorption curve for samples with reflectance properties shown in Fig. 4-23a and b, respectively. Following the trend shown in reflectance spectra, the absorption data in Fig. 4-23c shows the increase as diameter increases.

The lowest reflectance is achieved with dimension period of 600nm and diameter 600nm , and the best absorption property is also achieved at this dimension structure. As analyzed in page 91, this is due to the enhanced interaction between nanostructures and incident light at comparable size/wavelength, while light possesses the highest energy density near this region. These enhanced property from thin film control sample is primarily achieved in higher photon energy regime (e.g. $> 2\text{ eV}$). Although the reflectance of low energy photon is still high, it is much lower than flat thin film sample. The broadening of absorption edge towards lower-energy regime is also presented by the SiNPs sample, with absorption maintained above 80% for photon energy $\sim >2\text{eV}$ (compared to control thin film data in Fig. 4-22b).

Next, the reflectance and absorption spectra of SiNCs are presented in Fig. 4-24. Once again the data are organized based on their nanostructure morphologies. The absorption data was manually calculated and recorded by subtracting the reflectance and transmission diagram from 100%.

Figure 1-4 Reflectance and absorption spectra of SiNCs samples: (a) reflectance of SiNCs with varying diameters and (b) various periods and $d \sim 200$ nm, (c) absorption of SiNCs with varying diameters and (d) with varying periods and $d \sim 200$ nm

Observations have been summarized from figures above: for SiNCs nanostructure, the lowest reflectance is again achieved with dimension period of 600 nm and diameters of 600 nm. However, none of the other samples with

SiNCs nanostructures are able to achieve reflectance low than 10%. In the case of SiNPs sample of period 200nm and diameter 200nm, it has shown reflectance of well below 10% for a broad range of photon energy regime. Furthermore, same and following the trend of SiNPs, absorption is significantly enhanced compared to flat Si thin film control sample shown in Fig. 4-24c.

For SiNPs nanostructure, the highest absorption is achieved with period of 600nm and diameters of 600nm. Samples with diameter 200nm and period 200nm as well as 800 nm also have absorption close to 90% for a wide range of energy regime. For SiNCs nanostructure, the highest absorption is achieved with samples of $p = 600$ nm and $d = 600$ nm, and $p = 800$ nm and $d = 800$ nm. Furthermore, samples with diameter of 200 nm exhibit lower absorption than samples with larger diameter, consistent to our group's simulation [75, 81].

We have not monitored any significant differences between SiNPs and SiNCs samples. It is worth noting that the absorptance curve of the nanostructured samples show a large redshift towards the low energy regime, which means that the inefficient absorption in the low energy range ($<1.5\text{eV}$) suffered by thin film solar cells has been alleviated greatly. Additionally, since the absorption is obtained from $1-T-R$, it is the combined effect of low reflection and low transmittance in the high frequency regime that causes higher absorption in SiNPs and SiNCs samples.

The total absorption behavior of nanostructured samples can be well understood from the perspective of wave optics. The wavelength of incident light in low energy region is much longer than the periodicity of the nanostructure arrays (e.g. 200nm-600nm). Accordingly, the incident light wave

can easily penetrate through the sample, reaching the underlying Si layer. This understanding is well evidenced by our measured data where reflectance and absorption behavior of nanostructured samples at low energy show minimal enhancement from control sample (Fig. 4-24c).

Different from the light in low energy regime, the wavelength of incident light in high energy regions is comparable with the dimension of nanostructures. Therefore, light scattering would be remarkably enhanced, resulting in the elongated optical path and thus the enhanced light absorption. An excellent light absorption of over 95% in the energy region above ~2.3 eV for the SiNPs and SiNCs samples with $p = d = 600\text{nm}$ are shown.

However, the energy density is relatively weak in the high energy region within the solar spectrum (Fig. 2-1), and the redshift above mentioned thus is more noteworthy. At photon energy lower than 1.5eV, the light absorption enhancement has become insignificant.

To summarize, the absorption behavior at long wavelength region are originated from the resonant mode enhanced absorption [75] (more details in next section where simulations results show more oscillations in optical behaviors). The absorption enhancement in shorter wavelength region is attributed to significantly lower reflectance in this regime. In addition, all samples with nanostructures show significantly larger absorption in visible wave range compared to the flat silicon thin films. This result is important specifically for solar cell applications.

4.3.4 Simulation Efforts

Besides our experimental processes, efforts were also made in utilizing simulation software to calculate mathematically the optical performances of our designed nanostructures.

The finite-difference time-domain method was employed for all spectra calculation using *Lumerical* FDTD Solutions, a commercial FDTD software package. The schematics we used are shown below.

Figure 1-5 Schematics of SiNPs and SiNCs arrays on Si thin film

All structures are in the x-y plane and surrounded by air, while light irradiation is directly incident from top along z direction. Reflectance, transmittance, and absorption are the main monitoring interests and obtained from Maxwell equation[112, 113]:

$$\left\{ \begin{array}{l} \nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} \\ \mathbf{D} = \epsilon \mathbf{E} \\ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \\ \mathbf{B} = \mu \mathbf{H} \end{array} \right.$$

where $\mathbf{E}$ is the electric field, $\mathbf{H}$ is the magnetic field, ϵ is the complex permittivity, and μ is complex permeability. For the ϵ being a function of the

frequency, the frequency domain equation $\mathbf{D}(\omega) = \epsilon(\omega)\mathbf{E}(\omega)$ should be transformed to the time domain by using the auxiliary difference equation (ADE).

In the two-dimensional space, by applying the periodic boundary condition (modal absorbing boundary conditions), the optical information is obtained from the spatial distribution of the energy flux. It is simulated that spectral irradiance of the normal incident light corresponds to the AM1.5G standard.

➤ *Flat thin film*

Figure 1-6 Spectra of flat Si thin film

Fig. 4-26 shows the reflectance, transmission, and absorption of flat Si thin film of thickness 2.5 μm . It simulates the optical behavior of our flat control sample. As seen from the figure, light absorption concentrates on the higher energy region with photon energy larger than 1.5eV-2eV.

By simulating the behavior after integration of SiNPs and SiNCs, we are able to show the great enhancement of light absorption and make comparisons with our experiments.

➤ *Integration of nanostructures*

Figure 1-7 Reflectance spectra of samples with SiNPs and SiNCs

(a) SiNPs with various diameters, (b) SiNPs with various periods, (c) SiNCs with varying diameters and (d) SiNCs with varying periods

Figure 1-8 Absorption spectra of samples with SiNPs and SiNCs

(a) SiNPs with various diameters, (b) SiNPs with various periods, (c) SiNCs with varying diameters and (d) SiNCs with varying periods

There are large oscillations in the low energy regime for all calculated curves in Fig. 4-26, Fig. 4-27 and 4.28. For low energy incident light, the interference effects with silicon nanostructures exist, resulting in the oscillation of reflection and absorption ($A = 1 - T - R$). In the high-frequency regime, the absorption increases and the interference effect diminishes around 2.5 eV. In the low energy range, each peak of oscillations in the absorptance spectra corresponds to a quasi-guided resonant mode [114] and these modes supported by nanostructures help to enhance absorption [114-116]. From Fig. 4-28, both

the SiNPs and SiNCs arrays support resonant modes that result in stronger absorptance compared to flat thin film. These supported modes assist the stronger coupling of the incoming light in the nanostructures. Therefore we are observing the broadening of absorption edge for both SiNPs and SiNCs sample compared to flat thin film.

The simulation results are in-principle agreeing with our experiments, based on the following observations:

- In both spectra, we did not observe significant differences in the performance of SiNPs and SiNCs.
- The best performing SiNCs samples are $p = 600$ nm and $d = 600$ nm. The reason why SiNPs are different in this best-performing case will be explained in next page.
- In general, samples with diameter 200 nm are inferior to other samples. (corresponding to graphs titled (a) and (c))
- The reflectance in average has been reduced to near 30% in high energy regime (recall that this value is 50%-60% for flat thin film).
- Absorption is greatly enhanced in visible range and the absorption edge is enlarged for nanostructured samples.

However, we did notice some mismatches between our experiment and simulations:

- In absorption spectra, SiNCs are outperforming SiNPs structure. This phenomenon is reasonably expected from literature. SiNCs promotes the gradual change of refractive index as light is coupled

into the active layer. Thus it functions more efficiently in trapping light inside the layer.

Figure 1-9 Gradual change of effective refractive index in structure of SiNCs

However, this is not strictly our case in experiments, since we have observed the sidewalls of our SiNPs to be slightly slanted. It is then not strictly behaving in a perfect “pillar” way.

- For SiNPs samples with $p = d$ (both 200 nm and 600 nm), simulation generates data which are much poorer than our experimental observations. The reason is that simulation takes these two structures differently from what we obtained in experiments. With periods equal to diameters, it practically means that the pillars are “connected” in their top surfaces.

Figure 1-10 pillars with $p = d$ dimension

Therefore the coupling of light is suppressed in simulations. Nevertheless, in our experiment this does not happen because the slanted sidewalls of our pillars are helping to build the desired gradual change in effective refractive index along the light path. Therefore, in actual experiment the measured optical properties would be better than the simulated values.

Despite the mismatches identified above, we would like to state that our simulation work is in-principle in agreement of the experimental measurements. Therefore, it provides us the validation of our experiment and confidences to proceed to cell fabrications.

4.4 Summary

In conclusion, we have developed a self-assembly PS spheres maskless lithography process for fabrication of highly-ordered silicon nanopillar arrays and nanocones arrays on silicon thin films. The important impacts of these SiNPs and SiNCs are well characterized by their morphologies analysis and optical performance measurements.

Experimental efforts primarily utilize the oxygen plasma treatment to control the size of PS nanospheres, reactive ion etching to create the designed nanostructures and characterization technologies to provide feedbacks on experiments and confirmation of the successful routes. On the other hand, simulation efforts were also made to validate our experiment measurements and

provide theoretical support of the results. They agreed in-principle with our experiments.

The SiNPs and SiNCs shown in this chapter has little appearance in literature, thus we believe our effort is pioneering. Furthermore, by using the PS nanosphere lithography, we can practically generate more ideas in designing nanostructures for more efficient light trapping purposes. This investigation effort is potentially beneficial to many other device applications which include nano-fabrication on glass.

CHAPTER 5 NANOSTRUCTURED SILICON THIN FILM SOLAR CELL

5.1 *Introduction*

The successful demonstration of SiNPs and SiNCs on Si thin film and corresponding conforming simulation results have equipped us with the foundation for possible fabrication of solar cells with SiNPs and SiNCs structures.

In order to fabricate the sample device, we started with high-smoothness TCO-coated glass substrate instead of bare glass. Subsequently, 1.5 μm p-Si was sputtered followed by another 1 μm n⁺-Si. Si was DC sputtered in a magnetron sputtering system equipped with multiple magnetron sources and a heated dc biased substrate holder. Chamber pressure was below 1×10^{-5} Pa and the process pressure was around 0.1 Pa (from Pirani Gauge) with argon-flow at 30 sccm/min. The sputtering target has rectangular dimension 400mm x 100mm (p and n type both at 99.99%). Sputtering power density was 1.5W/cm² and deposition was carried out at substrate temperature $\sim 150^{\circ}\text{C}$. The substrate temperature is primarily caused by ion bombardment attributed to the sputtering process. Substrate bias was maintained at 150V and deposition rate was found to be $\sim 10\text{-}20\text{nm/min}$.

Similar deposition methodologies of silicon thin film using sputtering techniques are also documented in literature [117-121]. It has been recognized

as a low cost and pollution-free technology since toxic dopant gases are not utilized (e.g. phosphine).

Figure 5-1 Layout of the fabricated cell

Next, after the formation of SiNPs or SiNCs and removal of residual PS spheres, further growth of Ga doped ZnO (GZO) electrode was introduced using metal-oxide-chemical-vapor-deposition (MOCVD). The homemade MOCVD system utilized trimethylgallium, dimethylzinc, and oxygen as reaction sources, with nitrogen employed as the carrier gas for the metal organics. A 300-nm top electrode GZO was deposited at 300°C with a chamber pressure of 25 torr. The GZO layer possesses high transmittance property and conductivity as presented in our previous work ($3 \times 10^{-4} \Omega \cdot \text{cm}$) [122].

The final structure of the fabricated cell is shown in Fig. 5-1, and Fig. 5.2 shows a cross-section SEM image of the thin film cell (images of SiNCs and SiNPs cells have not been obtained due to physical constraints, and are to be obtained in future works). Subsequently, samples were characterized in series and comparisons were made among nanostructured samples, and control sample which consists of flat thin films was used as reference. Characterization includes the external quantum efficiencies (e.g. EQE) of the cell and the current – voltage (I-V) performances.

Figure 5-2 Cross section SEM image of the control cell

5.2 Impact of the Nanostructures

The external quantum efficiency (EQE) is one of the major interests in application of a solar cell. The nanostructures in a solar cell promote the interaction between incident light and silicon material, and subsequently couple it into active layers. Elongated light path within the active layer facilitates the absorption of light. Furthermore, nanostructures with hundreds of nanometer in size theoretically enhanced the absorption coefficient of the active layers by scattering light photons at comparable and longer wavelength. The EQE measurement in our work used a configuration including a halogen light source, a monochomator, a picometer and an optical power meter. The measurement range was in wavelength of 350-1100nm.

Fig. 5-3 shows the EQE spectra of fabricated cell with and without silicon nanostructures. The control sample is showing a photon-to-carrier efficiency well below that of nanostructured samples. Significant enhancement

of EQE was observed in most cases. Little difference was monitored between SiNCs sample and SiNPs sample.

Figure 5-3 External quantum efficiency of samples with and without silicon nanostructures ($p = 600$ nm, $d = 600$ nm)

From the diagram, it is obvious that enhancement of light absorption as discussed in previous chapter in visible range has greatly improved the number of carriers within the cell. The EQE at light wavelength around 600 nm, which possesses the greatest intensity, has been measured with value close to 90%. In addition, the previous optical data of broadened absorption edges in low energy regime is also re-produced, where the EQE of nanostructured samples at light wavelength larger from 750 nm to 850 nm is observed to be largely enhanced.

Next, after the analysis of quantum efficiency, we monitored the current-voltage characteristics of our samples with and without silicon nanostructures using a solar simulator under AM1.5G illumination with normal

incident light on the GZO side. The significant increase in the EQE between 400 and 800 nm has lead to the boost of short circuit current J_{SC} , as shown in Fig. 5-4. From the diagram, the measured J_{SC} of control sample is 5.58 mA, while the J_{SC} of the nanostructured samples are 14.5 and 14.25 mA for SiNPs and SiNCs respectively.

We would like to state that the dimensional impact of SiNPs and SiNCs are not considered here as we primarily intend to demonstrate the enhanced behaviors. Further details regarding dimension influences will be discussed in later sections. In addition, trend shown in thin film based cells are in agreement of our previous works of wafer based samples [123].

Figure 5-4 Current-voltage characteristics of samples with and without silicon nanostructures ($p = 600$ nm, $d = 600$ nm)

Before we move into the analysis of electrical performances of samples with various nanostructure dimensions, one more point is worthy to be mentioned. There have been multiple publications in literature where researchers stated that the SiNCs coated samples are believed to behave better than SiNPs samples in terms of optical and electrical performances [57, 82].

Researches argued that absorption in SiNCs coated samples is higher than SiNPs samples therefore subsequent PCE of their corresponding thin film cells are higher.

However, from our experimental observations, we did not reach this conclusion as no great difference was monitored in the optical and electrical performances between SiNCs and SiNPs coated samples. Our measurement showed comparable data for these two categories of nanostructures where they both enhanced the light absorption significantly. I-V characteristics were also promising for both these groups since the increases of J_{SC} were remarkable.

The analysis in differentiating SiNCs and SiNPs is not practical in this dissertation because of the lack of experimental support. It will be our main interest to demonstrate, both qualitatively and quantitatively, the performance enhancement via the integration of silicon nanostructures. It will be our target as well to exhibit the important impact of various dimensions of nanostructures with respect to their influences on the optical and electrical performances.

5.3 *Effects of Varying Dimensions*

➤ Control Period

Functional cells with same or similar periods were made into groups for comparisons. Details on the dimensions (period and diameter) can be referred in the optical property session in last chapter.

(a)

(b)

Figure 5-5 EQE of samples with different diameters and similar periods for: (a) SiNPs and (b) SiNCs (p =periods, d =diameters, in nm)

Fig. 5-5 is a presentation of the EQE information of the groups of SiNPs and SiNCs samples. The external quantum efficiency exhibits similar increase from flat thin film sample. However the amount of increment

differs. Sample with diameter 600 nm and period 600 nm shows the largest influence for both SiNCs and SiNPs, while the EQE are measured to behave the best. As shown in previous optical measurement and simulations, dimensions near 600 nm exhibits the largest impact in light trapping and therefore the EQE data here is conforming well to them. Sample with diameter 200 nm behaves the poorest since its interaction with incident light is limited. In addition, sample with periods and diameter both being 800 nm is demonstrating an enlarged absorption range compared to other samples. We can observe that the absorption edge of this sample is extending more towards the low energy (long wavelength) regime.

Furthermore, differences between SiNCs and SiNPs groups are not significant. However, we do observe that the EQE of SiNCs is slightly lower than that of SiNPs. Theoretically this should not be the case since SiNCs were simulated to outperform SiNPs [82]. The explanation for this observation is due to the evaporation of contact GZO. Cones possess relatively sharp corner tips which practically make the contact formation difficult in obtaining good ohmic contact as well as good adhesion, while pillars possess smooth flat top surface. This drawback of SiNCs influentially deteriorate the carriers extracted, therefore EQE and J_{SC} are expected to be smaller.

Furthermore, with consideration of the fact that light irradiation has its maximum intensity near 600 nm region, we can comfortably assume that the sample with $p = 600$, $d = 600$ nm shall provide better results in I-V test. The following table summarizes this information of interest.

Diameter	J_{SC}	V_{OC}	FF	PCE
	(mA/mm ²)			(%)

Period p = 600 nm

d = 200 nm	12.8	0.64	0.39	3.2
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p = 600 nm

d = 400 nm	13.2	0.64	0.41	3.5
------------	------	------	------	-----

p = 600 nm

d = 600 nm	14.5	0.64	0.41	3.8
------------	------	------	------	-----

p = 800 nm

d = 800 nm	14.3	0.65	0.40	3.7
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Table 5-1 Summary of electrical information of SiNPs sample with different diameters and similar periods

Here it has been the first time in our dissertation that the influence on power conversion efficiency PCE is addressed. We understand that the presentation of PCE data needs more consideration and investigations into another two factors of the sample: namely open circuit voltage V_{OC} and fill factor ff . However, we would like to state that for SiNPs sample with various dimensions, they did not present any significant differences in these two factors and thus we will not address them specifically in this section. Any differences among SiNPs, SiNCs and control samples will be analyzed in later sections. In general, the V_{OC} and fill factor ff for SiNPs samples are in the range of 0.64V – 0.65V and 0.39 – 0.41, respectively.

Next, the electrical data of SiNCs samples are summaries in table 5.2. Since a slight underperforming of SiNCs' EQE was observed and introduced

previously, we have monitored the electrical data of SiNCs samples to be slightly poorer than that of SiNPs.

	Diameter	J_{SC}	V_{OC}	FF	PCE
		(mA/mm ²)			(%)
Period p = 600 nm	d = 200 nm	9.8	0.64	0.38	2.4
p = 600 nm	d = 400 nm	11.3	0.64	0.39	2.8
p = 600 nm	d = 600 nm	14.25	0.63	0.39	3.5
p = 800 nm	d = 800 nm	13.3	0.65	0.37	3.2

Table 5-2 Summary of electrical information of SiNCs sample with different diameters and similar periods

The under-performance of SiNCs can be explained by their relatively lower fill factors. The V_{OC} and ff of our SiNCs samples are in the range of 0.62-0.65 V and 0.37 – 0.39. The V_{OC} exhibits little difference from the SiNPs samples since the fabrication processes are maintained at standard level and the Fermi-potential difference at both ends of electrodes determines the open circuit voltage. However, ff is determined by the resistive performance of the whole cell. Resultantly, we conclude that the resistance behavior/contact interfaces inside the SiNCs samples is inferior compared to SiNPs case. The reason was mentioned previously as the sharp tips of SiNCs are practically inconvenient for GZO layer to be evaporated on. Thus good ohmic contact and adhesion is more difficult to be achieved in SiNCs situation.

➤ Control Diameter

Samples with controlled diameters and various periods were fabricated. The morphologies have been presented in previous chapter. The following diagram presents the EQE data of the groups of SiNPs and SiNCs samples.

(a)

(b)

Figure 5-6 EQE of samples with different periods and same diameter for (a) SiNPs and (b) SiNCs (p=periods, d=diameters)

From Fig. 5-6a, the differences between different periods are not significantly shown as in the increases of EQE. However, the largest increase, which are believed to be $p = 800$ nm and $p = 600$ nm in this case (SiNPs with $p = 800$ nm and $d = 200$ nm stands for the inter space between pillars to be 600 nm), is still representing the nanostructures with dimensions closest from the light wavelength with the greatest intensity. The higher EQE from sample $p = 600$ nm is coming from the enhanced absorption of light intensity near this wavelength, while the larger absorption range of sample $p = 800$ nm is attributed to its greater ability to interact with lower energy photons.

In the case of SiNCs shown in Fig. 5-6b, we have monitored remarkable differences. Different from SiNPs, we observe that the enlargement of absorption edge which previously belongs to sample with $p = 800$ nm is diminishing (as indicated by the arrow in 5.6a). Practically the differences among samples of periods 200 nm, 400 nm and 800 nm are very limited. The phenomenon is obviously different from what we observed in our optical measurement and simulation results. Furthermore, the EQE data is not showing as great improvement from control sample as that of SiNPs. The reasons might be due to the poor contact formation on top of SiNCs which introduces large resistance behavior and defects.

Additionally, the electrical data is also recorded and shown in the following table. With lower periods, our observation concludes that the increase of J_{SC} is smaller. The data is conforming to the EQE performance.

Periods	J_{sc} (mA/mm ²)	V_{oc}	FF	PCE (%)
	p = 200 nm	8.8	0.63	0.38	2.1
	d = 200 nm p = 400 nm	10.2	0.64	0.38	2.5
	d = 200 nm p = 600 nm	12.8	0.64	0.39	3.2
	d = 200 nm p = 800 nm	12.7	0.63	0.39	3.1

Table 5-3 Summary of electrical information of SiNPs sample with various periods and same diameters

Table 5.3 summarizes the data for SiNPs samples. Since we are expecting a better performance compared to SiNCs devices, it will be more meaningful to compare with other SiNPs samples in previous sections. Based on the results, it is obvious that devices with various diameters and comparable periods of 600 nm and 800 nm are outperforming the devices with diameter $d = 200$ nm and various periods ranging from 200 nm to 800 nm. The reasons have been summarized in previous sections being the better interaction (enhanced resonant mode) with lower energy photons, leading to lower reflectance thus higher absorption in high energy regime.

	Periods	J_{sc} (mA/mm ²)	V_{oc}	FF	PCE (%)
Diameter d = 200 nm	p = 200 nm	7.6	0.62	0.36	1.7
d = 200 nm	p = 400 nm	8.1	0.63	0.37	1.9
d = 200 nm	p = 600 nm	9.8	0.64	0.38	2.4
d = 200 nm	p = 800 nm	7.7	0.63	0.37	1.8

Table 5-4 Summary of electrical information of SiNCs sample with various periods and same diameters

Shown in Table 5.4, the electrical performances of the SiNCs based samples with various periods and diameter $d = 200$ nm are comparably low. This is expected as the EQE for this group is poorer. The results are also conforming to our optical measurement where this group of sample showed absorption level remarkably lower than other groups.

In conclusion, we have shown the measured electrical performance of our control cell as well as the cells with nanostructures. Enhanced electrical behaviors are apparent and their relationships with different morphologies are presented. More discussions will be presented in the next section.

5.4 Summary

Parameters Groups	J _{sc} (mA/mm ²)	V _{oc} (V)	FF	PCE (%)
Flat Control Sample	5.58	0.64	0.44	1.6
SiNPs Control Period	14.5	0.64	0.41	3.8
SiNPs Control Diameter	12.8	0.64	0.39	3.2
SiNCs Control Period	14.25	0.63	0.39	3.5
SiNCs Control Diameter	9.8	0.64	0.38	2.4

Table 5-5 Summary of electrical information of various groups of the devices

The data summarized above are presenting the devices with the best electrical performances in their respective groups. There are several comparisons we would take note:

- All our samples showed poor blue response (e.g. high photon energy regime). This is because we didn't have appropriate passivation stage in our fabrication therefore large front surface recombination exist in our samples. This recombination affects carrier from being absorbed into external circuit.
- The performance enhancement via the integration of SiNPs and SiNCs nanostructures is significant. Compared to flat thin film sample with the PCE of 1.6%, the nanostructured samples are showing an increase of PCE to 3% and above.

- The best performance is presented by SiNPs sample with $p = 600$ nm and $d = 600$ nm. It may mislead the readers of this dissertation that the structure of this sample is showing a pillar-to-pillar distance of 0. However, as presented in previous chapter, the sidewalls of pillars are actually slanted slightly; therefore they are practically separate from each other, as shown in Fig. 5-7. The reason why 600nm behaves as the “optimal” dimension is believed to be attributed to its promoted interaction with photons at comparable wavelength (e.g. 500-700nm), where light possesses higher energy density than other wavelength regions.

Figure 5-7 SEM image of pillars with slanted sidewalls

- SiNPs devices are outperforming the SiNCs devices with same nanostructure dimensions. The reason behind shall be due to the contact formation stage where SiNCs device exhibits poorer resistive performance, denoted by the smaller J_{SC} and lower fill factor. The V_{oc} for NPs and NCs is comparable which suggests there is little difference between surface recombination in the

two. However, ff is generally lower in NCs which means the series resistance for NCs samples are generally larger than that of NPs samples because of poorer GZO contact.

In summary, this chapter presents the electrical data of organized samples in different groups of nanostructures. The main key performance indices are the external quantum efficiencies and the I-V characteristics of the samples.

Devices with nanostructure dimension close to 600 nm exhibit the best behavior under illumination of AM1.5G. This data is conforming to the optical measurement where device with period and diameter both 600nm shows the largest absorption. Besides, this data agrees to the simulation result of $p = d = 600\text{nm}$ as well.

Thus, until this chapter, we have successfully step-by-step demonstrated (a) the fabrication of SiNPs and SiNCs based solar cells on crystalline silicon thin film and (b) performance enhancement via the integration of these nanostructures. The influences of this integration and the impact of various structures are presented and discussed.

CHAPTER 6 CONCLUSIONS AND FUTURE WORKS

6.1 *Summary of Dissertation*

In this dissertation, a series of simulation and experimental studies were carried out in order to fabricate nanostructured silicon thin film solar cells. The nanostructures were designed, fabricated and characterized for the purposes of enhancement of light trapping within the active layer and electrical performances of the PV devices.

Silicon nanostructured thin film solar cell is achieved and its performance is enhanced by the utilization of light trapping technology which enhances light absorption within the thin film material. In this dissertation, processes in fabricating silicon nanostructures were developed. We firstly summarizes an electroless chemical etching technique using polystyrene nanospheres as self-assembled mask to fabricate the size-controlled, periodic silicon nanopillars (SiNPs) and subsequent silicon nanocones (SiNCs) arrays. The nanocones were obtained based on the nanopillar structure using ammonia-related etching chemistry. With solution-based processes, the cost of the procedures is limited. The diameter, height, and period of the nanopillars and cones are systematically controlled. Optical measurement suggests that the involvement of nanostructures promotes light absorption significantly. An excellent light absorption of over 95% in the energy region above ~2.3 eV for the SiNPs and SiNCs samples with $p = d = 600\text{nm}$ are shown.

Furthermore, we transferred this technology onto silicon thin film and demonstrate the accomplishment of silicon thin film nanostructures. SiNPs and SiNCs on glass were obtained by conventional reactive ion etching technique. The etching was masked by PS nanospheres again, and different morphologies of these patterns are obtained with different masking condition and etching parameters. Optical properties such as reflectance and absorption of these nano-patterned silicon-on-glass structures were characterized. With the integration of SiNPs and SiNCs, a significant reduction in reflectance (e.g. from 20% of the control sample to less than 10% for nanostructured sample) and increase in absorption (e.g. from ~60% to more than 90% at certain wavelengths) were observed. Meanwhile, simulation efforts were also made in analyzing the optical effect of our nanostructures. Satisfactory results were achieved as simulations agreed well with experimental results, thus serving as a theoretical support of our work.

Furthermore, solar cells were fabricated subsequently. Enhanced performances (e.g. PCE from 1.6% of control cell to 3.8% of SiNP cell) were observed. The external quantum efficiency and short circuit current of the cells based on these nanostructures demonstrate a remarkable increase. The impact of various nanostructures and dimensions of them are investigated ranging from 200 nm to 800 nm.

In summary, this dissertation addresses the development and characterization of nanostructured polycrystalline silicon thin films. Further performance influences of subsequent PV devices are investigated. The work done will offer opportunities and approaches to further improve the PV device

performances for potential implementation in commercial PV practices. This investigation effort is also potentially beneficial to many other device applications involving nano-fabrications on glass.

6.2 Innovations

The novelties of this dissertation are primarily experiment-based, and they shall be summarized as follows (in the order of decreasing significance):

- SiNPs and SiNCs structures have been extensively researched. Other published works show little report on approaches of their formation on silicon thin film. Our work is believed to be pioneer in developing maskless fabrication technology in obtaining nanostructured silicon thin film solar cells.
 - The morphological control over thin film based SiNCs and SiNPs is believed to be for the first time reported in literature. The idea of using PS self-assembled mask and its stability during oxygen plasma and RIE treatments enable us for such accomplishments.
 - Plenty of simulation results are published in literature defining the “best” morphology or dimension of nanostructures for silicon thin film solar cells. However, experiments are missing in practical support of all these theoretical analysis. Our achieved results from both experiments and simulations are in-principle agreeing with each other. Thus our experimental efforts are theoretically supported and our simulation attempts are practically

verified. Although there are distinctions between the results of these two groups, reasonable explanations have been provided accordingly.

- It is believed to be for the first time that we showed the accomplishment of SiNCs on silicon wafer by using the ammonia-related etching chemistry. The alkaline chemistry has been well-established in Si industry. However it is mainly used to create anti-reflection randomized roughness shown in other publications. Our approach in using it to create ordered SiNCs arrays is worth the interest because it provides an innovative route to systematically obtain controlled and ordered silicon nanostructures for wafer applications.
- The spin coating of PS nanospheres is not detailed highlighted in this dissertation. However, it involves several stages of modifying the as-purchased PS spheres, such as diluting, heating, and mixing with different concentrations of alcoholic solutions. The reasons why we conducted this investigation was to avoid island formation during spin coating of monolayer and to promote the adhesion of PS spheres on to silicon surfaces even when there are a slight amount of roughness (thin film case) and even when they are being under etchants attacks.

6.3 *Future works*

Besides the results obtained in our experiments, there are other areas where we find future potential for research efforts.

➤ Other morphologies of silicon nanostructures

SiNPs and SiNCs were demonstrated in this dissertation with detailed fabrication procedures. Furthermore, there are other structures available for experimental endeavors. In literature, these structures include silicon nano-holes, nano-coneholes, or inverted SiNPs and SiNCs structures. In order to achieve these structures experimentally using the PS nanosphere lithography, more efforts in controlling the spheres are needed. There have been active efforts where these efforts showed preliminary results [75, 124-126]. Hole structure, or inverted SiNPs have been shown in these referred documentations with comparable properties to standing SiNPs. Experimental approach in obtaining inverted coneholes is more difficult to be achieved with cost-effective maskless methods. However, attributed to the proposed gradual change in refractive index which leads to subsequent coupling interaction with incident light, and potential easier contact formation with top transparent electrode, inverted SiNCs is potentially promising in achieving good performances.

Furthermore, by using the PS lithography we can design even more complicated structures, Fig. 6-1 gives a pyramid design of the nanostructure. It requires a “step-by-step” etching to finely modify the dimension of the structure. The idea was to create even more resonant mode (as discussed in Chapter 4) for better interaction with photons. However, more thoughts on the etchant species need to be taken.

Figure 6-1 one possible more complicated nanostructure (a) design cross-section, (b) SiNPs coated by size-reduced PS spheres

However, to achieve such structures, more accurate control of the PS sphere needs to be investigated. Fig. 6-1 (b) shows our effort to demonstrate such control, with redefining the size of PS spheres after the formation of SiNPs. It is obvious that the PS spheres are still maintaining their position even when they have lost their morphology. In another word, the position of the PS sphere in next step of etching is unaffected. Still, such more complicated structure requires higher accuracy of the process control.

➤ Different allocation of nano-units

SiNPs and SiNCs are located hexagonally with respect to each other, which means the angle between neighboring center-to-center connections is 60° . Further effort can be worth research to obtain square-lattice arrangement of the nanostructure arrays.

Figure 6-2 Hexagonal-lattice and square lattice

In addition, randomly located nanostructures are also shown in literature. We have discussed on this point in section 2.5.2. In our experiment, the concentration of PS solution can be controlled by adding in ethanol. Lower concentration of PS solution can help to form randomly located arrays (as shown in Fig. 6-3) because they tend to be dispersed and spread-out unevenly during spin coating. The details of spin coating are thus important. We did not proceed with this structure in our dissertation because of its poor repeatability and controllability.

Figure 6-3 Randomized locations of silicon nanostructures achieved

➤ Cell fabrication

The technology in fabricating the silicon thin film solar cell in our experiment was immature. Although we successfully demonstrated the effect of integration of SiNPs and SiNCs into Si solar cells to boost their optical and electrical performances, a more decent route in fabricating silicon thin film solar cell will be in great deal helping to achieve better behaviors.

To conclude, all potential attempts that might affect the light-trapping capability of the device should be made in the pursuit of better device performances. With better light absorption, silicon nanostructured thin film solar cell has the potential to cut down cost while maintaining its performance

at competitive level. Theoretical efforts have been made in designing different nanostructures to achieve the target of higher PCE, and experimental attempts have also been taken in pursuit of this target. Benefited from the mature fabrication technology in silicon industry, deep insight in optimizing the device can be shared in scientist community more freely and openly. The work in optimizing the optical and electrical enhancement shall be significantly beneficial to silicon PV industry, and potentially for the exploration of alternative energy sources for human beings.

Journal Publications

Publications directly related to dissertation:

1. **Yang, M. F.**, HongYu Yu, Xiaowei Sun, (2011). "Periodic silicon nanocone arrays with controllable dimensions prepared by two-step etching using nanosphere lithography and $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ solution." Solid State Communications**151**(2): 127-129.
2. **Yang, M. F.**, Xiao Wei Sun, Hong Yu Yu, Junshuai Li, Junhui Hu (2011). "Low temperature polycrystalline silicon film formation by metal induced crystallization with nickel salt derived by ultrasonic spray pyrolysis." Crystal Research and Technology**46**(9): 935-938.
3. Wang, F., Hong Yu Yu, Xincai Wang, Junshuai Li, Xiaowei Sun, **Mingfei Yang** (2010). "Mask less fabrication of large scale Si nanohole array via laser annealed metal nanoparticles catalytic etching for photovoltaic application." Journal of Applied Physics**108**(2).
4. Wong, S. M., Yu, H.Y., Li, Y.L., Li, J.S., Wang, F., **Yang, M.F.**, Singh, N., Lo, P.G.Q., Kwong, D.L. "Boosting Short Circuit Current with Rationally Designed Periodic Si Nanopillar Surface Texturing for Thin Film Solar Cell." 2010 International Electron Devices Meeting, DOI: 10.1109/iedm.2010.5703456
5. Li, J. S., HongYu Yu, Yali Li, Fei Wang, **Mingfei Yang**, and She Mein Wong (2011). "Low aspect-ratio hemispherical nanopit surface texturing for enhancing light absorption in crystalline Si thin film-based solar cells." Applied Physics Letters**98**(2).

Publications from other collaborative work:

6. Lai, S. C., **Ming Fei Yang**, Dolmanan, Surani Bin, Ke, Lin, Xiao Wei Sun (2010). "Efficiency Optimization on Dye-Sensitized Solar Cells With Low-Frequency Noise Analysis." Ieee Transactions on Electron Devices**57**(9): 2306-2309.
7. Zhihui Jiao, Jinmin Wang, Lin Ke, Xuwei Liu, Hilmi Volkan Demir, **Mingfei Yang**, Xiao Wei Sun, (2012). "Electrochromic properties of nanostructured tungsten trioxide (hydrate) films and their applications in a complementary electrochromic device." ElectrochimicaActa**63**: 153-160.

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