Light management in nanostructures for solar cell application

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2013

Du, Q. (2013). Light management in nanostructures for solar cell application. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/54802>

<https://doi.org/10.32657/10356/54802>

LIGHT MANAGEMENT IN NANOSTRUCTURES FOR SOLAR CELL APPLICATION

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A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2013

Acknowledgements

First I would like to express my sincere gratitude to my supervisor Prof. Kam Chan Hin for his guidance and direction during my pursuit of Ph.D at NTU. Following his guidance, I entered the field of light management in nanostructures. He encouraged me and provided strong support at each stage of my entire four years of Ph.D research life. I would also like to express my greatest thanks to my co-supervisor Prof. Sun Xiaowei. I have benefit a lot from his enthusiasm for science, expert knowledge and wide vision in the research field. His unselfish help and guidance made me have an open mind towards ideas on my research work. I would like to thank my co-supervisor Dr. Alagappan Gandhi and Dr. Zhang Liping from the Institute of High Performance Computing for their valuable comment, discussion and constructive suggestions. I would also like to express my special thanks to Prof. Hilmi Volkan Demir for his valuable suggestions and discussions.

I would like to take this opportunity to thank all the staffs and students at the Nanoelectronic Lab I, II and *Luminous!*. I would like to express my special thanks to Prof. Yu Hongyu, Dr. Tan Swee Tiam and Dr. Liu Xuewei for their insight views and fruitful discussion. I would like to thank the rest of the group members and friends: Dr. Wang Jianxiong, Dr. Dai Haitao, Dr. Ye Jiandong, Dr. Divayana Yoga, Dr. Zhao Junliang, Dr. Li Junshuai, Dr. Chen Jing,

Dr. Luo Dan, Dr. Zhao Dewei, Dr. Ling Bo, Dr. Aung Ko Ko Kyaw, Dr. Yan Fei, Wang Ye, Jiao Zhihui, Zheng Ke, Ji Yun and all other friends from the Nanoelectronics Lab and *Luminous!* for their friendship, encouragement, inspirational discussions, and various assistance they provided me.

Finally, I wish to express the most gratitude to my parents Du Chengen and Zhang Guizhen, my wife Xia Yin, my daughter Du Yuxuan, my parents-in-law Xia Youxue and Qiao Chunlan. Without their invaluable love, understanding and support, I would not have completed my Ph.D study.

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Abstract

Solar cells have received great interest and tremendous efforts have been devoted in the last few decades. However, the main problem of the conventional solar cell is that the cost is too high to achieve relatively high efficiency. In order to make the solar cell affordable to public, scientists are now focusing on the design of the third generation solar cells named as nanostructured solar cell. By texturing the front, back surface or the active layer itself, the light absorption and thus the efficiency can be largely improved. The other way to improve the light absorption is to directly texture the active layer into nanostructures which is also promising to achieve high efficiency and low cost solar cells. Transparent electrodes are essential part of the solar cell device. Indium tin oxides (ITOs) are the most widely used transparent electrodes for solar cell nowadays. However, the price of indium mineral has soared to rocket high due to the huge demand and limited mineral reserves. Thus, scientists are now trying to seek for alternative materials to replace ITO electrodes.

The work of this thesis mainly focuses on the design and investigation of three types of nanostructures: anti-reflective coating, metallic nanostructure electrodes and nanostructured active layer.

Nanostructured anti-reflective coatings achieved by front surface texturing have been studied intensively. Zinc Oxide (ZnO) nanowire and

nanohole structures are presented in this work. The designed nanostructures can act as an anti-reflective coating in the visible range and also serves as a UV blocking layer simultaneously. The important structure parameters such as period and filling ratio are varied and optimized to achieve high transmittance in the visible range and high absorptance in the UV range. The optical properties of nanowire and nanohole structures, as well as the angular response properties are investigated in detail.

A nanopatterned aluminum thin film electrode is also presented. With the optimized parameters, the nanopatterned aluminum thin film exhibits a high transmittance in the range from 300 – 1000 nm and has a low sheet resistance, which makes it a potential electrode to replace ITO. In this work, the key parameters such as period and filling ratio are optimized to increase transmittance and in the meantime reduce sheet resistance. The optical properties are analyzed in detail and the role of surface plasma polariton (SPP) in the influence of transmission spectrum is particularly discussed. Hole filling materials, substrate materials and angular response are also taken into consideration in the nanopatterned aluminum electrode design. Several commonly used metals are optimized respectively aiming to obtain high performance nanostructured metallic electrodes.

In order to further increase the absorption in the active layer, a new type

of nano-cone-hole (NCH) array was brought into study. With the optimized NCH array, the absorptance is largely enhanced compared to the thin film and the optimized nanohole (NH) array. The absorptance enhancement is attributed to the lower surface reflectance; more supported resonant modes and enhanced modes interaction. The angular dependences of ultimate efficiency of transverse electric (TE) and transverse magnetic (TM) polarizations are also studied.

The influence on absorptance by introducing randomness into nanowire (NW) arrays is also investigated. The absorptance in the active layer can be improved by randomizing the regular arranged NW array. The ultimate efficiency of the optimized position random case is improved by 15% as compared to the regularly arranged one. According to electric field distribution at two different wavelengths, the absorption enhancement of random structure is due to a better anti-reflective performance, additional resonances introduced by the structural disorder and existing resonances broadening.

In summary, this dissertation addresses three types of nanostructure designs, including the nanostructured ZnO anti-reflective coating, the nanopatterned metallic electrode and the nanostructured active layer. The work done here will help to understand better the design rules for light management in nanostructures and the know-how can be applied to new type nanostructure design for solar cells.

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Abbreviations

ASTM	American Society for testing and Materials
c-Si	Crystalline silicon
PV	Photovoltaic
AM	Air mass
TMM	Transfer matrix method
FDTD	Finite difference time domain
FEM	Finite element method
EM	Electro-magnetic
1D	One dimensional
2D	Two dimensional
3D	Three dimensional
PML	Perfect Matched Layer
ZnO	Zinc oxide
NW	Nanowire
NH	Nanohole
ITO	Indium tin oxide
NCH	Nano-cone-hole
Al	Aluminum
ARC	Anti-reflective coating
FOM	Figure of merit
TiO ₂	Titanium oxide
SiO ₂	Silica
AlN	Aluminum nitride
a-Si	Amorphous silicon
PC	Photonic crystal

VLS	Vapor-liquid-solid
Si ₃ N ₄	Silicon nitride
TE	Transverse-electric
TM	Transverse-magnetic
PS	Polystyrene
LED	Light emitting diode
EBL	E-beam lithography
DBR	Distributed Bragg reflector
TIR	Total internal reflection
IQE	Internal quantum efficiency
EQE	External quantum efficiency
CVD	Chemical vapor deposition
NC	Nanocone
F-B	Forouhi-Bloomer
TCs	Transparent conductors
TCO	Transparent conducting oxide
SPP	Surface plasmon polariton
IR	Infrared
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)
Ag	Silver
Au	Gold
Ni	Nickel

Chapter 1 Introduction

1.1 Motivation

With the rapid economic development and improving standard of living across the developed and of developing countries, energy consumption has increased tremendously over the past few decades. Today, most of the consumed energy is generated by burning fossil oils, natural gas and coals, which generates a number of air pollutants such as carbon dioxide, sulfur dioxide, nitrous oxides, particulate matter (soot), and toxic materials such as mercury. These pollutants has significantly polluted the earth and caused serious environmental issues, for example, global warming, sea level rising and increasing natural disasters. On the other hand, recent forecasts estimate that the limited resources such as fossil oil, nature gas and coals supplies can only last up to 100, 275 and 2000 years respectively [1]. As a result, the limited reserve of these resources will definitely post critical risk to both environment and society.

The solar spectrum has a broad wavelength band range from infrared to ultraviolet. The energy of our sun is mainly released as the visible light. However, visible light only represents a portion of the total spectrum of radiation, while infrared and ultraviolet lights are also significant parts of the solar spectrum. In order to improve the solar cell efficiency, we need to use the

solar energy with wavelength as broad as possible. There are several benefits of using the solar energy. The energy from the sun is abundant and free to use, if we could harvest it. Solar cell technologies have as little impact on the environment by converting solar energy to electricity consumed by us. As it quietly generates electricity from light, solar cells do not generate air pollution or hazardous waste. Every year, the solar power striking the earth is 1.52×10^{21} KWh, which is 10,000 times the global power consumption. Thus, solar cell systems can guarantee to be a candidate of clean energy in the future.

As discussed previously, power generated from solar cells can become an important part for our power supply. Unfortunately, solar cell commercial market at today seems to reach a saturation point. One of the main reasons is that the price of the power generated by the solar cell modules remains high as compared to that from conventional fuels. In order to beat the mainstream energy, the price of the solar cell modules needs to reach \$1/W, where we are still far away from. Currently the solar cell market is still dominated by silicon-based solar cells and the price of the solar cell modules is mostly determined by the price of the raw silicon material, which is approximately 50% of the cost of a silicon solar cell module. Thus, there are still rooms for improvement in order to reach the \$1/W target.

1.1.1 Needed light trapping techniques in solar cells

As mentioned earlier, the solar cells made of silicon are still high in cost,

which has prevented it from further penetrating the market. It is worth to mention that the light trapping techniques are beneficial to the conventional thick solar cells to increase its efficiency as well. In wafer-based thick cells, light trapping is usually considered in the regime of ray optics where structures are large compared to the wavelength of the light, and light rays with different history do not interfere. For bulk weak absorption semiconductor materials with Lambertian scattering front surface and lossless back reflector, the average optical path length was increased by $4n^2$ compared to the planar one with a single path. Here, n is the refractive index of the absorption semiconductor. This was the geometric optics limit called Yabolonovitch limit [2-5]. The input of the light from external sources must be in balance with the light absorbed by the semiconductor and the light reflected through the escape cone. For a semiconductor solar cell of thickness L with a surface area A , when the emission of photons within the semiconductor was neglected, the photon current balance can be written as [5]

$$(1-r)I_{\gamma,inc} = I_{\gamma,esc} + I_{\gamma,abs} \quad 1.1.1-1$$

$I_{\gamma,inc}$, $I_{\gamma,esc}$ and $I_{\gamma,abs}$ are the photon current of the incident, escaped and absorbed light respectively. The photon current density per solid angle is $j_{\gamma,\Omega}$. r is the reflectivity from the surface. The absorbed photon current in $V = AL$ is

$$I_{\gamma,abs} = 4\pi\alpha V j_{\gamma,\Omega} \quad 1.1.1-2$$

Here, α is the absorption coefficient of the semiconductor. The photon current

of the escaped light from the surface is

$$I_{\gamma,esc} = A(1-r) \frac{\pi}{n^2} j_{\gamma,\Omega} \quad 1.1.1-3$$

The absorptivity for perfect Lambertian light trapping can be written as

$$a_{trap} = \frac{I_{\gamma,abs}}{I_{\gamma,inc}} = (1-r) \frac{I_{\gamma,abs}}{I_{\gamma,esc} - I_{\gamma,abs}} \quad 1.1.1-4$$

$$a_{trap} = (1-r) \frac{4\pi\alpha L}{(1-r)\pi / n^2 + 4\pi\alpha L} \quad 1.1.1-5$$

$$a_{trap} = \frac{1-r}{(1-r) / 4n^2\alpha L + 1} \quad 1.1.1-6$$

For small absorption coefficient α , the absorptivity $a_{trap} = 4n^2\alpha L$ which is $4n^2$ greater than the absorptivity without light trapping. For Si with $n = 3.5$, the absorptivity is 50 times larger than the bulk planar one.

Recently, research is being directed towards reducing the thickness of conventional thick silicon solar cells (normally 200-300 μm) by an order of magnitude or more. Those solar cells (also known as ultrathin solar cells), with the thickness of only hundreds of nanometers or a few of micrometers have caught much attention from both of the research and commercial community. This is because of the reduction of the cell thickness could translate to lower material costs, enhanced cell flexibility and reduced effects of light-induced degradation. However, the main drawback of these ultrathin solar cells is the reduction of the light absorption and thus inefficient in capturing light. For

example, crystalline silicon (c-Si) have an indirect band gap, which gives rise to weak absorption of light in the near infrared, with an absorption length that increases from just over 10 μm for $\lambda = 800 \text{ nm}$ to over 1mm for $\lambda = 1108\text{nm}$ [6]. However, that range of wavelengths contains 36.2% of solar photons with energies above the band gap of c-Si [6]. Thus, solar cells made from c-Si thin films will fail to absorb a significant portion of photons that could otherwise be used to generate power in the cell. The essential parameter determining whether or not high efficiency can be achieved in thick Si based solar cell devices is the minority carrier lifetime. However, when the active layer thickness is less than 50 μm , high conversion efficiency depends on light absorption ability. Similarly, for organic solar cells, the thickness of the active layer is also limited to few hundred nanometers owing to the poor carrier mobility in the organic active layer. The light trapping effect is more obvious for thin film solar cells. For thin film solar cells with proper designed textured nanostructures, the Yablonovitch limited for bulk materials can be achieved and even exceeded which make the nanostructured solar cell to be more competitive in the future. In order to increase the cell efficiency when the cell thickness reduces, different kinds of light trapping techniques have been developed recently. In structures with micrometer scale feature sizes, light should be treated as coherent and interference. In such systems, classical ray tracing methods are no longer valid, and the photogeneration rate can only be deduced from the gradient of the

Poynting vector. As such wave optics is widely used in the design of the light trapping techniques.

1.1.2 Main Parameters used in designing high efficiency thin film solar cells

For designing a high efficiency thin film solar cell, several parameters need to be considered in numerical simulation, such as solar spectrum, active layer absorption, ultimate efficiency, current density and optical generation rate and so on. Here, we mainly focus on the first three parameters.

Figure 1-1 Schematic of AM 1.5 reference spectral conditions

1.1.2.1 Solar spectrum

Solar spectrum distribution has a broad wavelength range and is

different in various places on the earth due to the different latitude and environment. In order to make a standard criterion reference for the photovoltaic (PV) industry to evaluate the PV performance, in 1999, the American Society for testing and Materials (ASTM) and government research and development laboratories developed and defined two standard terrestrial solar spectral irradiance distributions [7].

Figure 1-2 ASTM G-173 Reference spectra

Air mass is usually used for solar spectrum description and is defined as the relative path length of the direct sun beam through Earth's atmosphere. As shown in Figure 1-1(a), Air mass zero (AM 0) is defined as the sun light intensity distribution just outside the Earth's atmosphere which is also called extraterrestrial spectral irradiance. AM 1 is the solar intensity distribution on the Earth's surface when the sun is directly overhead. When the angle of the sun increases to 48° or 60° , the solar intensity distributions are called AM 1.5 and AM 2.0 respectively. Among them, AM 1.5 is most intensively used for PV cell

performance testing by the industry and laboratories. For AM 1.5, there are also two types of standards named as Direct-Normal and Global. Direct means that only the solar radiation from sun and the forward scattered radiation from the around of the sun disk are considered. Normal refers to the sun light that is perpendicular to the receiving device which is shown in Figure 1–1(b). Direct-Normal is commonly used when the PV cells equipped with focusing or concentrating components. Global means that both the direct radiance from the sun and the radiance from the sky and ground-reflected are considered as shown in Figure 1–1(c) which normally used for flat plate PV cells. The solar spectral irradiances of extraterrestrial (AM 0), AM 1.5 Global and AM 1.5 Direct-Normal are shown in Figure 1–2 respectively.

1.1.2.2 Absorption in active layers

Absorption in the active layers is one of the important parameters to quantify the performance of the nanostructured solar cells [8]. Only the light absorbed in active layer can contribute to the electron-hole pairs generation and hence converted to current. In the design of nanostructures, we need to ensure the absorption happen mostly in the active layer by tuning the parameters of the nanostructures. Based on the Poynting theorem, the time-averaged power being absorbed in the active layers can be calculated from

$$Absorption = \frac{1}{2} \sigma \cdot \int_V |\vec{E}|^2 \cdot dV \quad 1.1.2-1$$

Where $\vec{E}$ is the steady-state electric field, V refers to the volume of the active layer and $\sigma = \omega \cdot \text{Im}(\epsilon)$ is the product of the frequency of the oscillating electric field and the imaginary part of the dielectric constant of the active layer materials. Normally, the dielectric constant is a wavelength-dependent parameter, and it varies with the change of the wavelength. In order to have a better absorption, the structure of solar cells is designed in such a way that the electric field is concentrated in the active layer in order to further enhance the light absorption in the active layers.

1.1.2.3 Ultimate efficiency η

Numerically, when benchmarking the performance of the solar cells, the parameter called ultimate efficiency is widely used. For any devices employing a photoelectric process which has a single cut-off frequency ν_g , there will be an ultimate efficiency [9]. The ultimate efficiency calculation is for ideal solar cell at zero cell temperature, it assumes that (1) photon with energy greater than bandgap photon energy $h\nu_g$ (ν_g is bandgap frequency of semiconductor) produces the same effect as photon of energy $h\nu_g$, (2) photon with lower energy than $h\nu_g$ produces no effect.

Assuming each photon with energy larger than the band gap energy $h\nu_g$ absorbed by active layer can generate an electron-hole pair, the ultimate efficiency, η , can be written as

$$\eta = \frac{\int_0^{\lambda_g} I(\lambda) A(\lambda) \frac{\lambda}{\lambda_g} d\lambda}{\int_0^{\infty} I(\lambda) d\lambda} \quad 1.1.2-2$$

where $I(\lambda)$ is the solar intensity of the Air Mass 1.5 direct normal and circumsolar spectrum, $A(\lambda)$ is the absorptance, λ is the wavelength, λ_g is the wavelength corresponding to the band gap.

In practical, the cell temperature cannot be zero and the radiative recombination can never be removed for any non-zero cell temperature. Shockley and Queisser also calculated the maximum efficiency with this limitation and obtained the so-called Shockley-Queisser limit. For example, for the cell illuminated by a black body source of 6000K and assuming the cell temperature is 300K, the upper bound of Si solar cell is 32.8% without concentration.

In simulation work, the ultimate efficiency is commonly and widely used by all the researches. In this thesis, we only discuss the ultimate efficiency of the nanostructured solar cells.

1.1.2.4 Simulation methods

During the nanostructure designing, both experimental and theoretical methods are important, here, we mainly focused on the theoretical methods used in nanostructure design and optimization.

Various methods such as transfer matrix method (TMM), finite difference time domain (FDTD), finite element method (FEM), scattering

matrix method, multiple expansion method and compact finite-difference frequency-domain method are used in studies of nanostructured solar cells. In this chapter, we only introduce the FDTD method.

- Finite Difference Time Domain Method (FDTD) [10-12]

Figure 1-3 Three dimensional (3D) Yee cell grids used for FDTD

Finite-difference time-domain (FDTD) is a popular computational electrodynamics modeling technique. It is widely used in solving electro-magnetic (EM) wave problems, such as propagation and scattering of EM wave, electron circuit and antenna analysis. In general, TMM is used to simulate the behavior of steady state EM wave and FDTD can be used to modeling the behavior of non-steady state EM wave. The time-dependent Maxwell's equations (in partial differential form) are discretized to the space and time partial derivatives. By using this method, we can get the transient distribution of EM field in spatial or time domain. In linear and homogeneous materials, the Maxwell equations can be written as

$$\frac{\partial \vec{H}}{\partial t} = -\frac{1}{\mu(\vec{r})} \nabla \times \vec{E} \quad 1.1.2-1$$

$$\frac{\partial \vec{E}}{\partial t} = \frac{1}{\varepsilon(\vec{r})} \nabla \times \vec{H} - \frac{\sigma(\vec{r})}{\varepsilon(\vec{r})} \vec{E} \quad 1.1.2-2$$

$\varepsilon(r)$, $\mu(r)$, $\sigma(r)$ are permittivity, permeability and conductivity respectively which are functions of positions.

By using the method proposed by Yee, the Maxwell equations can be discretized in spatial and time domain. The 3D Yee cell grids are shown in Figure 1-3. In Cartesian coordinate system, the components of Maxwell equation can be written as

$$\frac{\partial H_x}{\partial t} = \frac{1}{\mu(x, y, z)} \left(\frac{\partial E_y}{\partial z} - \frac{\partial E_z}{\partial y} \right) \quad 1.1.2-3$$

$$\frac{\partial H_y}{\partial t} = \frac{1}{\mu(x, y, z)} \left(\frac{\partial E_z}{\partial x} - \frac{\partial E_x}{\partial z} \right) \quad 1.1.2-4$$

$$\frac{\partial H_z}{\partial t} = \frac{1}{\mu(x, y, z)} \left(\frac{\partial E_x}{\partial y} - \frac{\partial E_y}{\partial x} \right) \quad 1.1.2-5$$

$$\frac{\partial E_x}{\partial t} = \frac{1}{\varepsilon(x, y, z)} \left[\frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z} - \sigma(x, y, z) E_x \right] \quad 1.1.2-6$$

$$\frac{\partial E_y}{\partial t} = \frac{1}{\varepsilon(x, y, z)} \left[\frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x} - \sigma(x, y, z) E_y \right] \quad 1.1.2-7$$

$$\frac{\partial E_z}{\partial t} = \frac{1}{\varepsilon(x, y, z)} \left[\frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y} - \sigma(x, y, z) E_z \right] \quad 1.1.2-8$$

By using the central difference method,

$$\frac{\partial}{\partial x} f(x) = \frac{f(x + \Delta x / 2) - f(x - \Delta x / 2)}{\Delta x} \quad 1.1.2-9$$

the 3D FDTD discretized equations can be expressed as

$$H_x|_{i,j,k}^{n+1/2} = H_x|_{i,j,k}^{n-1/2} - \frac{\Delta t}{\mu_{i,j,k}} \left(\frac{E_z|_{i,j+1,k}^n - E_z|_{i,j,k}^n}{\Delta y} - \frac{E_y|_{i,j,k+1}^n - E_y|_{i,j,k}^n}{\Delta z} \right) \quad 1.1.2-10$$

$$H_y|_{i,j,k}^{n+1/2} = H_y|_{i,j,k}^{n-1/2} - \frac{\Delta t}{\mu_{i,j,k}} \left(\frac{E_x|_{i,j,k+1}^n - E_x|_{i,j,k}^n}{\Delta z} - \frac{E_z|_{i+1,j,k}^n - E_z|_{i,j,k}^n}{\Delta x} \right) \quad 1.1.2-11$$

$$H_z|_{i,j,k}^{n+1/2} = H_z|_{i,j,k}^{n-1/2} - \frac{\Delta t}{\mu_{i,j,k}} \left(\frac{E_y|_{i+1,j,k}^n - E_y|_{i,j,k}^n}{\Delta x} - \frac{E_x|_{i,j,k+1}^n - E_x|_{i,j,k}^n}{\Delta y} \right) \quad 1.1.2-12$$

$$E_x|_{i,j,k}^{n+1} = \frac{\varepsilon_{i,j,k} - \sigma_{i,j,k} \Delta t / 2}{\varepsilon_{i,j,k} + \sigma_{i,j,k} \Delta t / 2} E_x|_{i,j,k}^n + \frac{\Delta t}{\varepsilon_{i,j,k} + \sigma_{i,j,k} \Delta t / 2} \left(\frac{H_z|_{i,j,k}^{n+1/2} - H_z|_{i,j-1,k}^{n+1/2}}{\Delta y} - \frac{H_y|_{i,j,k}^{n+1/2} - H_y|_{i,j,k-1}^{n+1/2}}{\Delta z} \right) \quad 1.1.2-13$$

$$E_y|_{i,j,k}^{n+1} = \frac{\varepsilon_{i,j,k} - \sigma_{i,j,k} \Delta t / 2}{\varepsilon_{i,j,k} + \sigma_{i,j,k} \Delta t / 2} E_y|_{i,j,k}^n + \frac{\Delta t}{\varepsilon_{i,j,k} + \sigma_{i,j,k} \Delta t / 2} \left(\frac{H_x|_{i,j,k}^{n+1/2} - H_x|_{i,j,k-1}^{n+1/2}}{\Delta z} - \frac{H_z|_{i,j,k}^{n+1/2} - H_z|_{i-1,j,k}^{n+1/2}}{\Delta x} \right) \quad 1.1.2-14$$

$$E_z|_{i,j,k}^{n+1} = \frac{\varepsilon_{i,j,k} - \sigma_{i,j,k} \Delta t / 2}{\varepsilon_{i,j,k} + \sigma_{i,j,k} \Delta t / 2} E_z|_{i,j,k}^n + \frac{\Delta t}{\varepsilon_{i,j,k} + \sigma_{i,j,k} \Delta t / 2} \left(\frac{H_y|_{i,j,k}^{n+1/2} - H_y|_{i-1,j,k}^{n+1/2}}{\Delta x} - \frac{H_x|_{i,j,k}^{n+1/2} - H_x|_{i,j-1,k}^{n+1/2}}{\Delta y} \right) \quad 1.1.2-15$$

Superscript n is the number of time step length, subscript i, j, k are the lattice positions in x, y, z directions respectively. Δt is the step length of time, $\Delta x, \Delta y, \Delta z$ are the distances between two adjacent points respectively. The sampling in time is selected to ensure numerical stability of the algorithm. The time step is determined by the Courant limit [13]

$$\Delta t \leq \frac{1}{c \sqrt{(\Delta x)^{-2} + (\Delta y)^{-2} + (\Delta z)^{-2}}} \quad 1.1.2-16$$

c is the speed of light in vacuum.

In the calculation of FDTD, the calculating area is finite. The setting of boundary condition is important for the accuracy of calculation. In general, we use the second Mur absorption boundary condition or the Perfect Matched Layer (PML) boundary condition. The source setting is also very important for the calculation. Different sources are needed for different calculation. The Gaussian source, pulse source and plane wave source are commonly used in FDTD calculation.

All the information obtained from FDTD calculation is time domain information. In nanostructures, the dispersion relation and energy band are relation between frequency and wave vector, in order to get these relations, the Fourier transform is needed.

$$u(\omega) = \int_0^{N_t} u(t)e^{i\omega t} dt \approx \sum_{n=0}^{N_t} u(n\Delta t)e^{i\omega n\Delta t} \quad 1.1.2-17$$

N_t is the total number of time step.

With calculated electric field distribution, the absorption in the active layer can be easy obtained from Eqn. 1.1.2-17 .

1.2 *Objective*

This thesis addresses the design of high efficiency thin film solar cells with nanostructures. In order to improve the solar cell efficiency, planer thin film solar cells need to be nanostructure engineered at the front surface, back surface and even the active layer itself. By designing and optimizing the

parameters of the nanostructures, it is able to achieve low reflectivity from the front surface, high absorption in the active layer and further improve the efficiency of the solar cells. In this thesis, three types of nanostructures are presented and optimized to achieve different setting purposes. The first part is focused on the design of zinc oxide (ZnO) nanostructured anti-reflective layer with nanostructures and the second part is to design 2D metallic nanopatterned thin film to achieve high transmittance and low resistance simultaneously, the last part discusses the design of nanostructure active layer to further increase the efficiency.

In the first part of anti-reflective layer design, normally the anti-reflective layer is only focused on the visible wavelength range. However, it is also very important to improve the absorption of the anti-reflective layer in the UV range to protect the optoelectronic devices. Here, two types of ZnO nanostructures are presented and studied including ZnO nanowire (NW) and nanohole (NH) structures to achieve high absorption in UV and low reflection in the visible light. Through the parameters such as lattice constant, filling ratio optimization and anti-reflective layer with high absorption in UV, low reflection in the visible light can be obtained.

Secondly, there are some drawbacks of commonly used ITO electrode such as the brittleness of the ITO layer and the relatively high price of ITO thin films. It is necessary to design a new type of electrode with lower cost and

higher flexibility. Here, a new type of nanopatterned Al transparent electrode is presented to address this potential need.

Besides using the anti-reflective layer to improve the light absorption in the active layer, directly texturing the active layer into nanostructures has been widely used to improve the absorption and reduce the amount of active materials simultaneously. The third goal of the thesis is to design a new nanostructure to further increase the light absorption in the active layer and improve the solar cell efficiency. Although the light absorption of thin films with nanostructures such as NW and NH structures has been greatly improved compared to that of the unpatterned thin films, there is still scope to further improve the absorption with other types of nanostructures. A new type of nano-cone-hole (NCH) structure has been presented to obtain higher absorption compared to NW and NH structures. The influence of randomness on absorption properties is not clearly understood till now. In order to take into account the randomness of the nanostructures, the influence of randomness has also been studied.

1.3 *Major contributions*

- ❖ An efficient UV blocking anti-reflective coating made of ZnO NW and NH array structures are presented. Compared to ZnO thin films, both NWs and NHs have improved performance with optimized lattice constant a , ZnO filling ratio f and nanowire heights h . The optical

properties of the nanostructures are less dependent on the incident angle of light, which enables them to be used as wide angle anti-reflective coatings with UV blocking.

- ❖ The designed aluminium NH hexagonal structure shows high transparency in the whole wavelength range from 0.3 μm to 1.0 μm and low sheet resistance which makes the designed Al NH thin film to be a competitive candidate to replace ITO. The transmission dip can be moved out from the visible range by manipulating the lattice constant. Angular response of the nanopatterned metallic film is excellent even for large incident angles.
- ❖ A new type of NCH array nanostructure was presented. The ultimate efficiency of the optimized NCH array is enhanced by 23.11% as compared to an optimized NH array of the same thickness. The absorptance enhancement of the NCH arrays is attributed to its lowered reflectance, more supported resonant modes, and enhanced mode interaction.
- ❖ The proposed optimized position random Si NW array solar cell showed better absorption compared to regularly arranged one. The result shows that position randomization with a filling ratio larger than 36% renders better absorptance over a broadband ranging from 300 to 1130 nm compared to regular structures. The ultimate efficiency of a

48% filling ratio position randomized nanowire structure is 13.4% higher than the optimized regularly arranged NW structure with the same thickness.

1.4 *Organization*

This thesis consists of 7 chapters.

Chapter 1 is the introduction part of the thesis which states the motivations and the importance of light trapping techniques for the thin film solar cells. The basic parameters for nanostructure solar cell designation and optimization are introduced. The motivation, the objective of this thesis and finally the major contribution of this thesis has also been discussed.

Chapter 2 introduces the recent progresses of nanostructures for solar cells application which are reviewed in detail with different category.

Chapter 3 reports a realization of a ZnO nanostructure anti-reflective coating. The optical properties of the NW and NH ZnO thin film structures are discussed in detail. ZnO structure shows better anti-reflective ability in visible wavelength range and better absorption in UV wavelength range compared to ZnO thin film with the same thickness. Optimized structure parameters are obtained by FDTD simulation. The optical properties of NW arrays are slightly better than those of NH arrays. The angular response of both NW and NH structures are also studied.

Chapter 4 presents a two dimensional nanostructured aluminum thin

film with nanohole patterned in hexagonal. The influence of lattice constant on transmittance, reflectance and absorptance are presented. By manipulating the lattice constant, the transmission dip in the transmission spectrum can be moved out from the visible range. The origin of the transmission dips is discussed in detail. When the sheet resistance is kept constant, the influence of parameters on the transmission spectra is studied. Angular responses for incident light with different polarization are also analyzed in detail. The optical properties of some commonly used metallic materials (silver, gold and nickel) are studied, and compared to other nanopatterned metallic films, nanopatterned Al thin film yields the best transmission spectrum in the visible wavelength range.

Chapter 5 demonstrates a novel design of NCH structured thin film silicon solar cell. Before doing optimization of the NCH structure, we optimize the NH structure first to obtain the optimized parameters first. Structure parameters of NCH such as filling ratios and lattice constant are then optimized to achieve high light absorption in nanostructured silicon active layer. The absorption performance of NCH structures are compared with optimized NH structures and thin film silicon with one optimized anti-reflective layer. The reasons of the absorption enhancement are analyzed in detail. The ultimate efficiency of NCH and NH structures are simulated and compared. Angular responses of both nanostructures are presented simultaneously.

Chapter 6 discusses the influence on the absorptance in NW silicon active layer if some sorts of randomness are introduced into the regularly arranged NW silicon arrays. Three different random structures are randomly generated by computer. The absorptances of different cases are compared and investigated. With comparable filling ratio, more randomness leads to larger absorption enhancement. Better absorption performance of random structure is owing to better antireflective performance, additional resonances introduced by the structural disorder, and existing resonances broadening. Electric field at two different wavelengths are plotted to further explain the absorption enhancement and ultimate efficiency of all regular and random cases are compared.

Chapter 7, the conclusion and future works of this thesis are presented.

Chapter 2 Review of light management in nanostructured solar cells

Light management in nanostructures has been intensively studied recently. In order to have a good understanding of the necessities and benefits of the nanostructures, a review of recently published papers is discussed in this part. With different types of nanostructures, the reflected light is reduced, light can be largely reflected back from the back surface and redirected which lead to a light trapping in the active layer hence enhance the light absorption in the active layer and the solar cell efficiency.

2.1 *Anti-reflective (AR) structures*

The anti-reflective coating (ARC) is an essential part for optoelectronic devices especially for solar cells. With properly designed ARC, the light reflected back from the front surface can be reduced which means more light can propagate through and absorbed by the active layer.

Figure 2-1 One layer anti-reflective coatings

The layered ARC has been developed for a long time since 1930's. The one layer ARC is simple and easy way to achieve as shown in Figure 2–1. For one certain designed wavelength, the reflectance can be reduced to zero

theoretically. It is well known, the reflectance at the interface of two different materials is [14]

$$R = \frac{1}{2} \left\{ \left(\frac{\sin(\theta_2 - \theta_1)}{\sin(\theta_2 + \theta_1)} \right)^2 + \left(\frac{\tan(\theta_2 - \theta_1)}{\tan(\theta_2 + \theta_1)} \right)^2 \right\} \quad 2.2.1-1$$

Where θ_1 is the incident angle of light from upper material, the refractive index is n_1 , θ_2 is the refractive angle in the lower materials with refractive index n_2 . When the refractive index (n_r) of the ARC layer is the geometric mean of the indices of two material which means $n_r = \sqrt{n_1 * n_2}$, and the thickness (d) of the ARC layer is a quarter of an optical wavelength which means $d = \frac{\lambda}{4n_1}$, the reflectance from the top surface is zero. For example, for silicon solar cell, the refractive index of silicon is 3.5, the refractive index of the ARC need to be the geometric mean of the refractive indices of silicon and air. With this desired refractive index, the silicon nitride with refractive index ($n = 1.91$) is commonly chosen as an ARC layer. The thickness of the silicon nitride layer is 70 nm if the reflectance zero is design at 535 nm where the solar intensity is high in the whole wavelength spectrum. Obviously, one layer ARC is not suitable for solar cell application, because solar spectrum is a broadband spectrum and the one layer ARC can only have near zero reflectance at certain designed wavelength.

In order to address the problems of the single layer ARC, multilayer ARC have been designed and studied [15-24]. In 1947, the three layered ARC

has been studied in detail both theoretically and experimentally by L. B. Lockhart and P. King [15]. More works have been done to achieve broadband multilayer ARCs. A design and simulation of ARC for application to silicon solar cells are presented by D. Bouhafs's group in 1998 [18]. Single-, double-, triple-layer ARC are designed with different materials such as Ta_2O_5 , ZnS , Al_2O_3 , MgF_2 . Short-circuit current and cell efficiency have been improved by the ARCs.

In 2009, a group from MIT gives a global optimization ARCs for silicon solar cell especially for thin film silicon solar cells [20]. Multilayer ARCs are optimization according to the performance of the solar cells. Figure of merit (FOM) of the short circuit current is employed to do the ARC optimization. With the global optimization, the parameters of the two layers can be easily obtained. Detailed absorption spectra of the solar cells with different ARCs in the active silicon layer are studied. According to the simulation result, the absorption and the efficiency of the solar cell are improved by the ARCs with optimization.

One special kind of layered ARCs is that the refractive index of the ARC layer is gradually changed from the top to bottom. Early in 1970's, one layer gradient refractive index films have been successfully fabricated, the reflectance is effectively reduced from about 8% to $< 0.5\%$ in the wavelength regime $0.35\ \mu\text{m} - 2.5\ \mu\text{m}$ [21]. The gradient refractive single layer ARC is

fabricated with a porous, skeletal silica layer by a chemical etch/leach process applied to glasses sensitized by a phase-separating heat treatment.

The ARC reflective performance has been further improved. A group from RPI reported that they have fabricated an extremely low refractive index multilayer ARC which can eliminate Fresnel reflection over a broad wavelength and angle-of-incident range [24]. The graded-index coating is consisting of three titanium oxide (TiO_2) nanorod layers and two silica (SiO_2) nanorod layers. The refractive index of the bottom layer of the thin film layered structured is 2.03 which is close to the index of the aluminum nitride (AlN) substrate. The refractive index of the top layer is 1.05 which is very close to air. The reflectance from the top surface of the graded-index coating is 0.1% which is very low compared to reflectance from any bulk materials' surface. The graded-index coating also shows very good angle response. Even for incident angle close to 90° , the reflectance keep in a very low stage.

Similar graded-index coating by using different material has been optimized theoretically and achieved experimentally [22]. With the graded-index coating inserting into the ITO and amorphous silicon (a-Si), the average reflectance of thin film a-Si solar cell structure with the graded refractive index structure has been suppressed by 54% at normal incidence compared to the thin film a-Si solar cell structure without the graded refractive index structure.

Front surface texturing is the other widely used surface technology to achieve reflectivity reduction [25-65]. Additionally, with the front surface texturing, light incident on the surface can be refracted in large angles and trapped in the active layer, hence, the absorption in it can be improved.

One effective way to do the front surface texturing is to texture the front surfaces in the PC structures including 1D (grating) and 2D structures. Many groups have done tremendous work to show that PC structure can be used to improve light absorption in active layers [25-30]. It is reported by Y. Lee's group that the light absorption can also be improved in thin film silicon solar cells with two-filling-factor patterned 1D PC structures [26]. The asymmetric 1D PC formed as a guided-mode resonance notch filter which can couple the incident light to a leakage mode guided in the silicon active layer. The absorption has been enhanced for 3 fold in the asymmetric 1D PC patterned thin silicon solar cell compared to that of the planar one with the same thickness within spectral range from 920 nm to 1040 nm. Good angular response also maintained even when the incident angle of near infrared broadband light increase up to 40° . Most recently, a 1D patterned ZnO transparent structure was reported [28]. The supported optical resonance of the 1D patterned ZnO structure can be used to concentrate unpolarized sunlight or to effectively couple it to guided and diffracted modes. Assisted with an optimized 1D patterned ZnO structure on a 300 nm thick a-Si, the short circuit current density

was enhanced from 19.9 mA/cm² to 21.1 mA/cm².

2D PC structure also has been widely used in thin film solar cells to enhance to light absorption in the active layer. With the 2D patterned PC structure, both broad band light absorption and solar cell efficiency were improved significantly both experimentally and numerically [29]. The performance improvement is mainly due to the diffractive and light trapping effects.

Except the 1D and 2D PC front surface modification, texturing the front surface into different types of nanostructures such as triangular gratings, nano-pyramid structures, nanorods, nanoholes, nanocones and moth-eye structures have been investigated intensively [31-60].

One simple way to make the ARCs is to texture the front surface in triangular diffraction gratings as reported in [57]. The parameters such as depth-to-period ratio and period are numerically optimized which showed excellent anti-reflective performance for a broad wavelength range. One type of top-flat pyramid structure is numerically examined [42]. With proper designed parameters such as period, depth and shape of the pattern, the top-flat pyramid showed very good anti-reflective performance.

Nanorod structures which are treated similar to PCs are also employed in the ARC design. The widely used material of nanorod ARC fabrication is ZnO. In 2004, it is reported by Zhonglin Wang's group that a ZnO nanorod was

fabricated on a alumina substrate by using a catalyst template produced by self-assembled monolayer submicron spheres and guided vapor-liquid-solid (VLS) growth[45] . With the development of the nanostructure fabrication methods, the ZnO nanorod with a sharp tip grown by solution-based method showed an efficient broadband anti-reflective performance [59]. The weighted global reflectance was achieved to be 6.6% which is better than an optimized single silicon nitride (SiN) one layer ARC.

ZnO nanorod ARC was also fabricated on Cu(In,Ga)Se₂ thin film solar cells by a cheap and simple electrochemical approach [58]. The weighted global reflectance of the solar cell decreased from 8.6% to 3.5% compared to conventional MgF₂ ARC. Most recently, a syringe-like ZnO nanorod was obtained with hydrothermal method on a quantum well solar cells [56]. The sharp tip can further suppress the reflectance compared to the top flat nanorod. The conversion efficiency of the quantum well solar cells with syringe-like nanorod had been improved by 36%. The reason of the improvement was attributed to the flatness of the refractive index profile at the air device interface which caused further light trapping effect in the solar cell device.

Other materials such as InP, GaP and Si were also successfully used in nanorod structure fabrication by VLS method [39]. The reflectance was largely reduced due to the nanorod caused significant coupling mismatch with the incident light due to multiple scattering. The other distinctive ITO nanorod

obtained by glancing-angle deposition was reported to be an efficient ARC for solar cells [40]. For both transverse-electric (TE) and transverse-magnetic (TM) polarization, the nanorod ITO structures showed excellent anti-reflective performance for a broad wavelength range of 350 nm to 900 nm even when the incident angle of the light went up to 70° .

Texturing the front surface with a nanocone is the other way to achieve an efficiency ARC layer. It was reported that broadband reflectance reduction and the light absorption enhancement were simultaneously achieved by ZnO nanocone structure with optimized parameters [31]. Optimized parameters for ZnO nanocone structure on crystalline Si were obtained. Corrugated Si nanocone arrays fabricated on Si wafer by two polystyrene (PS) sphere monolayer etching steps also showed high anti-reflective performance [34]. The reflectance was reduced to 0.7% in a broad wavelength range of 400 nm to 1050 nm and the nanocone structure showed a unique super hydrophobic properties with a water contact angle of 164° .

Moth-eye nanostructure is another promising candidate ARC for solar cells. Optimized structure parameters were obtained numerically in [52]. The designed moth-eye predicted a better anti-reflective performance compared to the ideal layered ARCs.

An interesting design of ARC was to coat a monolayer of dielectric silica nanospheres on the top of the a-Si layer [46]. Except the normal

anti-reflective performance, an additional whispering gallery modes was excited which can significantly increase the light absorption in the a-Si active layer. Even for large incident angles, the light absorption was still high.

Randomly texturing the front surface in the nanostructure can efficiently couple the light into solar cell [61-65]. Light trapping in thin film solar cell with randomly textured ZnO nanostructure front coating was analyzed both experimentally and theoretically [65]. Best light trapping performance was predicted for filling up the deepest craters. ZnO randomly textured nanostructure by nanoimprinting on glass substrate was reported experimentally [63]. This report opened a possibility to fabricate large area nanotextured ZnO structures for solar cell application. Detailed numerical study was presented in designing and optimizing randomly textured structures [62]. A simple criterion was presented to show the reason that why certain textures operate more efficient than others.

2.2 Alternative TCO layers

ITO is the widely used transparent electrode for opto-electron devices such as solar cells and light emitting diodes (LEDs). ITO shows good properties such as high transparency and high conductivity to act as an excellent transparent electrode. But the source of the element indium is limited on earth which caused a relatively high price of ITO. Simultaneously, the ITO film is brittle that makes the device based on ITO easily break down when it is bent or

when the substrate is flexible [66]. Because of the mentioned drawbacks of ITO, scientists are now searching alternative candidate to replace of ITO. Nanostructured metallic electrode is the mainly focus of this thesis. Here, only the development of the nanostructure metallic electrode such as nanogrid, nanomesh and NH are reviewed here.

It is reported by L. J. Guo's group from Michigan University that metal wire electrodes fabricated by nanoimprinting lithography can be used to replace ITO for solar cell application [67]. The fabricated metallic electrodes showed both high transmittances in the visible range and low resistance. With properly designed geometry, organic solar cell fabricated on the metallic nanopatterned electrodes showed the same performance as that made on high quality ITO electrodes. Silver nanowire electrodes were successfully fabricated on flexible substrate by using a transfer printing technique by the same group. The enhancement of the conversion efficiency of the organic solar cell with silver nanowire electrodes attributes to both surface plasmon resonance and waveguide modes. The short circle density was enhanced 40% compared to that of the conventional ITO integrated organic solar cells.

Y. Cui's group from Stanford University reported random silver nanowire mesh fabricated with solution process showed excellent optical and electrical performances which exceed those of commonly used metal oxides such as ITO [68]. Organic solar cells based on the random silver nanomesh

electrodes showed 19% higher photocurrent than the ITO based solar cells. After that, it is reported by the same group that large area and low cost silver nanowire electrodes were fabricated by roll-to-roll process [69]. Two types of silver nanowire electrodes were achieved with low resistance and high transmittance in visible range which had better performance than most ITO electrodes on plastic substrates and carbon nanotube or graphene network electrodes.

Detailed theoretical work of the optical properties of the nanopatterned transparent metallic electrode is report by Shanhui Fan's group of Stanford University [70]. According to the numerical result, it showed that the optical properties of optically thin metallic films were quite different from those of the optically thick metallic films. For one dimensional nanopatterned metallic films, when the resistance of the film remained unchanged, better optical performance can be obtained of taller and narrower nanopatterned structures. According to the design rules, a novel nanopatterned metallic electrode was successfully fabricated by a group from Iowa State University [71]. The metallic electrode was fabricated by combination of two-polymer microtransfer molding, oblique metal deposition, and argon ion milling techniques. Both of high transmission and low sheet resistance were achieved simultaneously. The transmittance was 80% in the visible range. Different types of metallic nanopatterned electrodes were fabricated which can be used in different types of devices.

Most recently, a periodic two dimensional silver nanowire network with different pitches and wire diameters was obtained by e-beam lithography (EBL) [72]. A systematic numerical work showed that the optical transmission was determined by four types of physical mechanisms. The optimized nanopatterned metallic networks showed both better transmittance and lower resistance than an 80 nm thick ITO layer sputtered on glass substrate.

Metallic films with randomly patterned holes are the other candidate for the transparent electrodes. NH patterned metallic films was obtained by island lithography [73]. Transmission spectra of NH patterned metallic film with different hole densities were measured. The performance of the disorder NH patterned metal films is similar to the hexagonal lattice patterned one. The increasing of the sheet resistant was originated from the surface roughness and scattering from grain boundaries. The optical and electrical of disorder NH patterned thin metallic film achieved by colloidal lithography was also reported in [74]. For the disordered NH patterned films, the electrical conductivity was still very good for hole coverage up to 0.4. If the hole coverage was larger than 0.4, ordered NH array should be used in order to retain conductive pathways. The surface plasmon effect was used to explain the transmission enhancement.

2.3 Patterned active media enabling light trapping

Instead of texturing the front and back surface to trapping light, many researches had been done on the directly nanopatterning the active layer. Except

the enhancement of the absorption, there are other benefits. For example, it is obvious that the used amount of materials is reduced which makes it possible to fabricate ultrathin film solar cells with the same efficiency as the bulk materials, thus the low quality materials such as a-Si can be used to fabricate nanopatterned thin film solar cells and due to the reduced film thickness, the charge collection efficiency also will be increased.

PCs also can be used as texturing in active layers [75-77]. Numerical studies of the group of C. Seassal have shown the absorption in a thin amorphous silicon layer was increased significantly. The absorption enhancement originates from the coupling of the incident light into slow Bloch modes by the patterned 1D photonic structure. For both S and P polarization, the absorption in an amorphous silicon layer with 100 nm thickness have been improved by 45% and 33% respectively. Experimental results was reported by the same group , the absorption in the 100 nm thick amorphous silicon with patterned 1D PC structure was improved 50% in the range from 380 nm to 750 nm compared to the planar ones.

The mostly widely investigate nanopatterned structure is the NW and NH structures which is similar to 2D PCs reviewed earlier. Early in 2007, it was reported that the NW silicon arrays could be used as a potential candidate to make NW solar cells due to the enhanced absorption in the NW arrays [78]. The optical properties such as absorptance and reflectance were numerically studied

of silicon NW arrays with different NW diameters. Even without the specially designed ARCs, the reflectance was suppressed in a wide wavelength range compared to unpatterned thin films. The absorption enhancement in the high frequency range was improved significantly due to the reduced reflectance. The absorption enhancement in the low frequency range was not as significant as in high frequency which can be overcome by applying other light trapping techniques or using longer silicon nanowires. In this paper, the diameter of the NW was relatively small, it was reported that if the diameter and period of the NW arrays were relatively large, the absorptance can be further enhanced especially in the long wavelength range [79]. The guided resonant modes were used as a mechanism to explain the additional absorption enhancement for large lattice constant. Even for large incident angles, the absorption still kept very large in a broadband wavelength range. Similar optimization work for silicon NW arrays and silicon NW arrays on the silicon substrate were also discussed in detail by other group [80, 81].

Because of the promising results of numerical work, researchers did numerous experimental researches on the fabrication of the NW arrays by different methods [82-91]. It was reported that a large area radial p - n junction Si NW arrays solar cell on stainless steel substrate was fabricated by standard chemical vapor deposition (CVD) process [82]. The optical reflectance of the silicon NW array was reduced by one to two orders of magnitude compared to

planar silicon film. Si NW based solar cells on glass substrates was reported by a different wet electroless chemical etching method [86]. Different from the radial p - n junction solar cells, the reported NW solar cell was made with a layered p - n . Experimental results showed that the reflectance was lower than 10% in the range of 300 – 800 nm and the absorptance was also improved within a broadband wavelength range and achieved more than 90% at 500 nm. The highest conversion efficiency of the NW array solar cell was 4.4% which made it to be the potential low cost solar cells. It was reported that further improvement of the absorptance in NW solar cells was achieved [89]. The peak absorption was more than 96% even when the arrays had less than 5% areal fraction wires and the absorption of day-integrated was achieved up to 85% under normal incident of sunlight. The overall absorption had exceeded the ray-optics light trapping absorption limit for a randomly textured planar Si with the same volume. Broad band near unity internal quantum efficiency for carrier collection through a radial semiconductor/liquid junction at the surface of each wire was also observed. With the big improvement of the absorption and collection efficiency, the nanowire array solar cell geometry used only 1/100th of the material of the traditional wafer-based solar cells. The NW array solar cells with other materials were also reported [85]. The GaAs core-shell NW solar cell was grown by the vapor-liquid-solid process in a molecular beam epitaxial system.

The influence on the optical properties of the randomness of the NWs was reported by Ruan and Bao in [92]. Slight absorption enhancement of NW arrays with random position was observed. For those NWs with random diameter and length, the absorption enhancement mainly originated from the strong optical scattering in the random structure. Similar numerical results showed that if the sizes of NW was in the range of 300 – 700 nm, the absorption was enhanced compared to that of the periodic structures [93].

The interesting results of a nanohole (NH) array structures was reported by Gang Chen's group from MIT [94]. The optical absorption of NH arrays was better than that of the NW array with the same parameters such as period and filling ratio. To achieve the same efficiency as the 300 μm bulk silicon solar cell, the material needed for the NH arrays was twelve times less than the bulk one which made the NH array had a great potential for high efficiency thin film nanostructure solar cells. The optical parameters optimization for NH arrays with a thickness of 2000 nm was achieved with in [95]. Numerical studies showed that two vertically stacked NH arrays with different hole filling ratios can further enhance the absorption. Optimization parameters for both NH arrays were obtained [96]. Experimental results of the NH arrays showed that a efficiency of 9.51% was achieved which was higher than that of the Si NW, planar Si and pyramid-textured Si solar cells [97].

Following the design trend of NW and NH arrays, the nanocone (NC)

structures which take both of the advantage of the ARCs and NWs were induced as an obvious high performance structure as anticipated. A ordered silicon nano-conical-frustum array solar cells were fabricated by self-powered parallel electron lithography [98]. The nano-conical-frustum structure showed an excellent optical performance with a high absorption of ~99% in the wavelength range from 400 nm - 1100 nm by a thickness of 5 μm silicon. The fabricated solar cell demonstrated a very high conversion efficiency of 10.8%. a-Si NC solar cell on glass was demonstrated with a efficiency improvement up to 40% compared to planar solar cells with 150 nm thickness [99]. The NC a-Si solar cell was fabricated from glass substrates patterned via self-assembled Sn nanosphere masks. A hybrid silicon NC-polymer solar cell was studied [100]. With optimized aspect ratio (height/diameter of the NC) less than two, the NC arrays showed both excellent anti-reflection and light trapping properties. The reported conversion efficiency was 11.1% which was the highest among hybrid Si/organic solar cells till now. The proposed NC structure was also used for hybrid Si/polymer solar cell application. Absorption enhancement in ultrathin silicon solar cell with double-sided NC patterned structure was demonstrated [101]. The optimized structure showed a photocurrent of 34.6 mA/cm^2 with a silicon thickness of 2 μm which was close to the Yablonovitch limit. A review paper has discussed the nanostructured photon management for high performance solar cells in detail [102]. High efficiency and low cost solar cell

devices can be achieved through the light management of the nanostructures. From the review above, the absorption properties of NC and other nanostructures are similar to each other, but the total performance such as photo current and solar cell efficiency for NC reported here is better than the other nanostructures. It seems that the NC integrated thin film solar cells show better performance compared to other types of nanostructures.

2.4 *Novel back reflectors*

In order to increase the light absorption in the active layer, except the front ARCs, additional back reflector arise also a necessary part of the solar cell device. Light can be redirected by the back surface and be trapped in the active layer. In early days, metal mirror was commonly used as back reflector. The light is reflected back by the back metallic surface and passes the active layer twice. But only with the metal back reflector, the light trapping effect is very limited. Also, because of the large imaginary part of the refractive index of the metal, an amount of light is lost by the absorption of the metal. Many efforts have been made in designing different new types of back reflectors.

One promising way to trap light in the active layer is to introduce a grating structure at the rear surface [103-116]. Light is diffracted into large angles and is trapped in the active layer owing to the total internal reflection (TIR). The optical properties of the rectangular and blazed gratings have been studied in detail in 1995 [103]. The blazed gratings had more effective light

trapping effect compared to rectangular gratings. Zero order diffractive waves of the blazed gratings were suppressed compared to rectangular gratings which made the blazed gratings more effective. The influence of the rear surface texturing on the cell efficiency and optical properties were discussed in detail in [105]. A simple numerical mode was established and the influence of the depth-to-period ratio in the internal reflectivity was analyzed. The optical performance of saw-tooth grating was excellent which made it to be a candidate of the black reflector. Both rectangular and triangular sub-wavelength gratings were also achieved experimentally [104]. Numerical studies on the influence on the light trapping ability of back side surface grating integrated with front grating were studied in detail by a Germany group [107, 108, 110]. By both texturing the front and back surface, the short-circuit current was further increased. The physical insights of the enhancement were also presented. Structure parameters of front and back surface grating were optimized individually.

Because of the severe absorption caused by the metal reflector, with the development of PCs, researchers are now seeking of using 1D PC (DBR) structure to replace of metal reflector. The absorption loss in the metal reflector can be suppressed by the dielectric DBR. It is reported that with the help of DBR, the conventional Yablonovitch limit for bulk solar cell can be exceed [111]. The absorption enhancement was theoretically examined. Typically,

theoretical analysis showed that the cell internal quantum efficiency (IQE) was enhanced by about 26.98% under the multiple light pass simulation in the wavelength range from 900 – 1100 nm [112].

Normally it is necessary to integrate both grating and DBR structures. Both theoretical and experimental studies had shown the optical absorption enhancement. It is reported that even for bulk convention solar cells, the grating and DBR integrated structure showed enhanced conversion efficiency [113]. The external quantum efficiency (EQE) was significantly enhanced up to 135 times in the wavelength range of 1000 – 1200 nm. Detailed optimization of the integrated structure were also discussed by the same group for very thin silicon solar cells [114]. It is reported that the absolute cell efficiency of 12% was achieved for a 2.0 μm thick solar cell. Experiment results of a 5 μm thick solar cell was achieved with the short-circuit current density increased by 19% compared to a theoretical prediction of 28% [116]. Applying integrated structure on both single and multiple junction thin film silicon solar cell was also reported [115]. The grating was made by directly etching the back DBR structure. Theoretical analysis showed that the integrated structure of grating and DBR was an effective approach to light trapping in both single and multiple junction solar cells.

The influence of random grating were reported in [106]. Numerical results showed that the random grating can improve the light diffraction and

trapping effect and for optimized random gratings, the integrated QE was improved 29% over that of planar solar cells and 9% over that of the optimized periodic gratings.

Compared to conventionally presented back reflectors such as gratings and DBRs, a PC based light trapping technique was proposed to achieve much better light trapping performance [6, 117-124]. Detailed studies of integrating a PC structure as the back-reflector to enhance light trapping in thin solar cells was reported in [117]. Numerical FDTD calculations revealed that the PC back-reflector light trapping was mainly owing to that the PC act as a perfect mirror, and the surface of the PC diffracts light into large angle to undergo total internal reflection at the front surface of the wafer. Experimental results on the 3D PC integrated dye-sensitized solar cell were demonstrated [121]. It was also reported that the absorption was enhanced by 14% for P3HT:PCBM organic solar cells with 2D PC integrated back reflector owing to the excitation of the quasiguided modes [118]. Experimental results of the same architecture were achieved by the same group [119] by using the print process. It was reported that the absorption of an organic solar cell integrated with a PC back reflector was enhanced by 3 fold compared to the planar one. The conversion efficiency was improved of about 70% owing to the absorption and electrical enhancements. Similar 2D PC integrated back reflector was also reported in [120].

Chapter 3 UV-blocking ZnO nanostructure anti-reflective coatings

3.1 *Introduction*

According to the review of anti-reflective (AR) structures in the previous chapter, the researches of the AR structures are mostly focused on the high transmittance in the visible wavelength range. In practice, it is also very important to block the UV part of the incident light because this part of the incident light is harmful to opto-electronic devices especially the active layers in it leading to a breakdown of the devices. UV blocking AR structures are not only an essential part for opto-electronic devices, it is also very useful for artistic work (e.g. prevent paintings being damaged by the UV light). It is necessary to design an AR structure with high transmittance in the visible wavelength range and high absorptance in the UV wavelength range which is seldom studied till now.

ZnO has the intrinsic properties with high transparency in the visible range and high absorptance in the UV range, so it is widely used in ARCs. [45, 59, 63, 125-127] With the rapid growth of research interests in solar cell area, ZnO nanostructure ARCs have been successfully applied for solar cells. [45, 59, 63, 127] For some organic solar cells, most of the absorption of the active layer occurs at visible range, the UV absorption of ZnO can protect the active layer

from damage by the unused UV light. Element (Al, Ga and so on) doped ZnO results in high conductivity property which makes the ZnO a good candidate to substitute the expensive ITO as the transparent conducting layer for solar energy applications. According to these two properties, ZnO nanostructures can be used as conductive layer and UV blocking anti-reflective layer simultaneously. However, the influences of nanostructure parameters such as lattice constant and filling ratio on optical properties have not been studied systematically and the UV blocking property has never been considered.

3.2 *Structure and Simulations setup*

We apply ZnO nanostructures to design UV blocking ARCs. The nanostructures considered here are ZnO NWS and ZnO NHs. The FDTD [128] method is used for the absorptance and reflectance calculation. Commercial software package FDTD Solution was used for absorptance and reflectance calculations. The simulation region in x and y direction is one periodic length of the period structures. The x and y simulation regions are ranged from $-a/2$ to $a/2$, here a is the lattice constant. For all the simulations, the simulation region in z direction for all different cases is fixed from $-1.25\ \mu\text{m}$ to $1.25\ \mu\text{m}$. PML boundary condition is used in z direction and periodic boundary condition is used in both x and y directions. The location of the incident field is at $z = 1.0\ \mu\text{m}$. Two line power monitors are placed on the top and bottom of the NH and NW at $h/2\ \mu\text{m}$ and $-h/2\ \mu\text{m}$ respectively, h is the length of the NW or NH.

The transmission function gives the amount of power transmitted through the power monitor. The absorption is calculated from the subtraction of the transmitted power of the two power monitors.

In order to increase the simulation accuracy and simulation speed, non-uniform mesh is used for all the simulations. In the whole simulation region, the mesh size is set at 100 nm. In the material region and at the interface of different materials, smaller meshes are used to increase the simulation accuracy which can override the mesh size set at the beginning. In the materials region from $-h/2$ μm to $h/2$ μm , the mesh size is set with a smaller one at 10 nm in all directions, and at the interface of two different materials, the mesh size is even smaller at 1 nm with a width of 4 nm equally distributed in each side of the two power monitors in z direction and 5 nm in x and y directions. For all of the sub meshes, the width in x and y directions is the same as the width of simulation region in x and y directions.

The inset of Figure 3–1 shows the schematic of the NW and NH structures. The NWs and NHs are both arranged in square lattice in x - y plane with the same lattice constant a and height h . The filling ratio f is defined as the ratio of ZnO area over one unit cell area. Light is normally incident on x - y plane.

Figure 3-1 Real (n) and imaginary (k) part of ZnO refractive index calculated with F-B dispersion relationship. Inset is the schematic of ZnO nanowire and nanohole structures arranged in square lattice and their corresponding unit cell with lattice constant a .

In the simulation, we use Forouhi-Bloomer ($F-B$) dispersion formula [129, 130] to determine the refractive index of ZnO. The real (n) and imaginary (k) part of the refractive index calculated according to the $F-B$ model are shown in Figure 3–1. The solid line and the short-dashed line represent the real and imaginary part of refractive index of ZnO respectively. It is clearly shown that the imaginary part of the refractive index of ZnO is almost equal to zero for wavelength exceeding 400 nm which is in agreement with measured data [131].

3.3 Results and discussion

The comparison of ZnO NW structure and thin film is shown in Figure 3–2. Both of them have the same thickness of 1 μm . The NW structure has the parameters of $a = 200$ nm and $f = 0.3$. Comparing with ZnO thin film, ZnO NW has lower reflectance in the entire simulated range owing to the surface texturing of the NW. In the visible range, ZnO NW has lower absorptance than

ZnO thin film which means ZnO NW has better transmittance in the visible range. In the UV range, almost 100% the absorptance is achieved for ZnO NW which is also much better than ZnO thin film layer. The filling ratio of ZnO is 0.3 which means better performance can be achieved with only 30% materials.

Figure 3-2 Absorptance and reflectance of ZnO nanowire and thin film with the same thickness (1 μm). For nanowire structures, $a = 200 \text{ nm}$, $f = 0.3$.

3.3.1 Structure optimization of ZnO NW structure

Figure 3–3 (a), (b), (c) and (d) show the absorptance and reflectance spectra of ZnO NW for various of a , f and h respectively. In Figure 3–3 (a), (b) and (c), the absorptance and reflectance are calculated with $a = 100 \text{ nm}$, 200 nm and 400 nm respectively. The height h of the NW is fixed at $1 \mu\text{m}$. In Figure 3–3 (a), the absorptance and reflectance of different f 's are compared for $a = 100 \text{ nm}$. With the decrease of f , reflectance decreases simultaneously for the entire simulated wavelength range which means that less ZnO material is used, the lower reflectance of the NW structures. The absorptance in the visible range

also decreases with the decrease of f . The absorptance in the UV range increases when f decreases from 0.7 to 0.5 and then increases when f reaches 0.3. In Figure 3–3(b), lattice constant a is increased to 200 nm, the reflectance is still very low for different f 's and has similar trend as in Figure 3–3 (a). The enhancement of absorptance of nanowire structures in the UV range can easily be seen from this figure. When f decreases from 0.7 to 0.3, the absorptance increases accordingly and almost all UV light is absorbed by the NW. In the visible range, the absorptance trend is similar to that of Figure 3–3(a). Additionally, we can see that when $f = 0.3$, the absorptance drops faster from UV to visible range compared to the other two filling ratios which means that UV absorption has lower influence on active layer absorptance. In Figure 3–3 (c), the absorptance and reflectance are plotted for $a = 400$ nm. Clearly, when lattice constant is large (400 nm in our case), the reflectance and absorptance in the visible range are large which makes it not suitable for ARCs. From Figure 3–3(a), (b) and (c), $a = 200$ nm and $f = 0.3$ are optimized parameters. In Figure 3–3 (d), we also show the influence of different heights ($h = 200$ nm, 500 nm, and 1 μm) of NW structures with $a = 200$ nm and $f = 0.3$. Obviously, the reflectance does not have large change with various heights. Thinner NW has lower absorptance both in visible range and UV range. When $h = 1$ μm , we can get an efficient nanowire ARC with excellent UV blocking. According to

effective refractive index theory, the effective refractive index (n') of the NW array can be written as

$$n' = n_{air} + f(n_{ZnO} - n_{air}) \quad 3.3.1-1$$

Here, n_{air} and n_{ZnO} are the refractive index of surrounding air and bulk ZnO respectively. f and a are the filling ratio of ZnO NW and the lattice constant. According to the definition of the filling ratio f , when f increases, the NW radius r increases correspondingly. From Eqn. 3.3.1-1, when f increases, the effective refractive index (n') increases simultaneously which leading to a large reflectance as shown in Figure 3-3 (a), (b) and (c). When f increases from 0.3 to 0.7, the reflectance in the whole wavelength range from 0.2 μm to 0.7 μm also increases correspondingly.

Figure 3-3 Absorbance and reflectance of different filling ratio f at fixed nanowire height $h = 1 \mu\text{m}$ with lattice constant (a) $a = 100 \text{ nm}$, (b) $a = 200 \text{ nm}$, (c) $a = 400 \text{ nm}$. (d) Absorbance and reflectance of different heights of nanowire with lattice constant $a = 200 \text{ nm}$ and $f = 0.3$.

3.3.2 Angular response of the designed ZnO nanostructure

Figure 3-4 Influence of different incident angle on absorptance and reflectance of ZnO nanowire. (a) the absorptance of TE, (b) the reflectance of TE, (c) the absorptance of TM, (d) the reflectance of TM, (e) absorptance of thin film (TF), (f) Reflectance of thin film (TF).

For many applications, the ARCs are needed to have lower reflectance in visible range and large absorptance in the UV range even when the light is lunched with a large incident angle. The absorptance of different incident angles for wavelength range from 0.2 μm to 0.7 μm of TE mode is shown in Figure 3-4(a). The absorptance in the UV range is very high even for large incident angles up to 70° and the absorptance in the visible range is quite small

for the incident angles examined. The reflectance of different incident angles is shown in Figure 3–4 (b). It is clear that the reflectance is also very low for both broad wavelength range and large incident angles. The absorptance and reflectance in a broad wavelength range and for different incident angles of TM mode are shown in Figure 3–4 (c) and (d) respectively. Similar results are also obtained for TM mode. From above discussion, large light incident angle only has slight influence on absorption and reflection properties of ZnO NW. The angular dependence of bare thin film (TF) is shown in Figure 3-4(e) and (f) for reference. It is clear that the absorptance of TF is lower in UV and higher in visible range (Figure 3-4(e)) and the reflectance is also very high in the whole wavelength range compared to the NW arrays (Figure 3-4(f)).

3.3.3 Structure optimization of ZnO NH structure

Similar analyses of NH structures are shown in Figure 3–5(a), (b), and (c). In Figure 3–5(a), the influences of different f 's on absorptance and reflectance are studied with $a = 200$ nm and $h = 1$ μm . From Figure 3–5 (a), when $f = 0.3$, the NH structures show better anti-reflectance with better UV blocking. The absorptance and reflectance of different a 's with $f = 0.3$ and $h = 1$ μm are obtained in Figure 3–5 (b). It is clear that the NH structures show better UV blocking anti-reflectance when $a = 200$ nm. For different h 's with $a = 200$ nm and $f = 0.3$, the absorptance and reflectance are plotted in Figure 3–5 (c). Better UV-blocking anti-reflective performance are obtained when $h = 1$ μm .

The absorptance and reflectance of NH and NW structures are compared in Figure 3–5 (d). These two structures have the same behavior in the reflectance. Both of them have good reflectance in the entire simulation wavelength range. For the absorptance, the two nanostructures are also similar to each other in the UV range. The only difference is that the NW structure has lower absorptance in the visible range compared to the NH structure, which indicates that ZnO NW structure is slightly better compared to ZnO NH structure.

Figure 3-5 Absorptance and reflectance of nanoholes of (a) different f with $a = 200 \text{ nm}$, and $h = 1 \mu\text{m}$, (b) different a with $f = 0.3$, and $h = 1 \mu\text{m}$, (c) different h with $a = 200 \text{ nm}$, and $f = 0.3$. (d) Absorptance and reflectance of ZnO nanowires and nanoholes with the same parameters.

According to our simulation, the optical properties of ZnO NH and NW arrays are similar with each other. It is easy to achieve ZnO NW arrays by bottom up fabrication process but when the ZnO NW array is used as a transparent conductor, the electrode is hard to be integrated with the NW

array film. Meanwhile, the NH array can be fabricated by top down fabrication process which is more expensive compared to the bottom up process, but it is easy to integrate the NH array film with the electrode. From this point of view, if the nanostructure is made to be a transparent conductor, the NH array is preferred and if the nanostructure is only used as a high transparent layer with UV absorption, it is better to use the NW array for the purpose.

3.4 *Conclusions*

In conclusion, an efficient UV blocking ARCs is demonstrated using FDTD method. Different lattice constant (a varying from 100 nm to 400 nm), filling ratio ($f = 0.3, 0.5, 0.7$) and height ($h = 200$ nm, 500 nm, 1 μm) are considered in the simulation. According to our simulation, the best parameters for an efficient UV blocking ARCs are $a = 200$ nm, $f = 0.3$, $h = 1$ μm . The optical properties of nanostructures are less dependent on the incident angle of the light. The comparison of ZnO NW and NH structures is also presented in this work, the ZnO NWs are slightly better than NHs.

Chapter 4 A two-dimensional nanopatterned thin metallic transparent conductor with high transparency from ultraviolet to the infrared

4.1 *Introduction*

Transparent conductors (TCs) are essential components of modern optoelectronic devices including solar cells, flat panel displays and light emitting diodes (LEDs). The transparent conducting oxide (TCO), primarily indium tin oxide (ITO), is the most commonly used TC in the commercial market. Most of the optoelectronic devices having a transparent conductor are fabricated on ITO coated substrates because of the relatively high transparency of ITO in the visible range and its low sheet resistance. However, ITO is costly because of the limited source of indium [66]. Moreover, ITO is brittle for devices on flexible substrates [66]. Due to these disadvantages of ITO, researchers are now seeking alternatives, which include metallic nanogratings [67, 71, 132, 133], metallic nanomeshes [68, 134], ultra thin metallic films [135, 136], carbon nanotube networks [137, 138] and graphenes [139-141].

It is known that, thanks to surface plasmon polariton (SPP), the transmission enhancement of optically thick nanopatterned metal films can be realized [142, 143]. However, the enhancement is only in a narrow wavelength

range. This cannot be applied to optoelectronic devices that need high transparency in a wide wavelength range such as flat panel displays and solar cells. When the film thickness of nanopatterned metallic films is within a few or tens of nanometers, the optical properties become quite different from those of the optically thick metallic films. One-dimensional (1D) nanopatterned thin metallic film has been studied both theoretically and experimentally [67, 70, 71, 132, 133]. For the two-dimensional (2D) case, the studies are mainly focused on the transmission suppression in a narrow wavelength range where high optical transmission is anticipated [144]. At certain wavelengths, the transmission of such nanopatterned thin films can be worse (even close to zero) than the uniform one [145, 146]. The transmission suppression is a result of the absorption enhancement due to the coupling of the SPP excited at both interfaces between the metallic thin film and the dielectric surroundings. In these studies, the 2D nanowire or nanohole patterned thin films are commonly arranged in a square lattice. There already have a few experimental papers trying to fabricate 2D nanopatterned metallic electrodes.[73, 147] Unfortunately, the transmittance is not high enough in a wide wavelength ranged. Till now, there is no theoretical analysis on the optical properties of 2D nanopatterned metallic thin films that can be used as a potential candidate for TC over a wide spectral region. In this letter, we report that high transparency in a wide wavelength range from ultraviolet (UV) to infrared (IR) with a relatively low

sheet resistance can be achieved in metal thin films with a hexagonal lattice NH array.

4.2 Structure and simulation set up

Figure 4–1 shows the schematic of the 2D NH patterned metallic thin film for the study. The nanopatterned metallic thin film structure is arranged in the x - y plane with a hexagonal lattice and surrounded by air. Light is directly incident on the film along the z direction.. The top view of the unit cell is shown in Figure 4–1 (b). The lattice constant is indicated as a , the radius of nanohole is represented by r , and the film thickness is h .

Figure 4-1 Schematics of 2D nanohole patterned metallic thin film arranged in hexagonal lattice. (a) 3D view and (b) top view of the nanopatterned structure. Simulation area of one unit cell is indicated with the red dashed line.

The finite-difference time-domain (FDTD) method is employed for all spectra calculations using Lumerical FDTD Solutions, a commercial FDTD software package. The simulation region in x and y direction is one periodic length of the period structures. The holes in Al thin film is arranged in triangular lattice, in one simulation region, the x simulation region is ranged

from $-a/2$ to $a/2$ and the y simulation region is ranged from $-a\sqrt{3}/2$ to $a\sqrt{3}/2$.

Here, a is the lattice constant. For all the simulations, the simulation region in z direction for all different cases is fixed from -75 nm to 75 nm. PML boundary condition is used in z direction and periodic boundary condition is used in both x and y directions. The location of the launched incident field is at $z = 50$ nm. Two line power monitors are placed on the top and bottom of the NH and NW at $h/2$ nm and $-h/2$ nm respectively, h is the thickness of the Al thin film. The transmission function gives the amount of power transmitted through the power monitor. The absorption is calculated from the subtraction of the transmitted power of the two power monitors.

In order to increase the simulation accuracy and simulation speed, non-uniform mesh is used for all the simulations. In the whole simulation region, the mesh size is set at 100 nm. In the material region and at the interface of different materials, smaller meshes are used to increase the simulation accuracy which can override the mesh size set at the beginning. In z direction of -15 nm to 15 nm, the mesh size is set with a smaller one at 3 nm in x and y directions and 1 nm in z direction. For all of the sub meshes, the width in x and y direction is the same as the width of simulation region in x and y directions.

4.3 Characterization of electrical and optical properties of the nanopatterned electrodes.

4.3.1 Electrical properties of the nanopatterned electrodes

Before analyzing optical properties of the nanopatterned metallic thin film, the other important parameter which should be considered is the sheet resistance because a good candidate for TCs needs both high transparency and low sheet resistance. The sheet resistance of a uniform metallic thin film is given by $R_{sh} = \rho/h$, where ρ is the metal resistivity and h is the film thickness, with a unit of Ω/sq . In the case of a 2D nanohole array structure given in Ref. [144], the sheet resistance is modified to $R_{sh} = \rho/h (1/(1-f))$, where f is the nanohole filling ratio in one period defined as $f = 2\pi r^2 / \sqrt{3}a^2$, the area ratio of void region and the whole unit cell. Larger f benefits a higher average transparency level, but if f is too large, the sheet resistance will suffer. To obtain a reasonable sheet resistance, in this study we constraint $f = 0.8$, which means that the sheet resistance of our nanopatterned metallic thin film is allowed to be five times larger than that of the uniform metallic thin film. Without loss of generality, we choose aluminum (Al) commonly used metallic electrodes for the study here. With the film thickness $h = 20$ nm, and the resistivity of Al $\rho = 2.9 \times 10^{-8} (\Omega \cdot m)$, the sheet resistance of 2D nanopatterned metallic thin film is thus $R_{sh} = (2.9 \times 10^{-8}) / (20 \times 10^{-9}) \times 5 = 7.25 \Omega/sq$, which is low enough for an electrode.

4.3.2 Optical properties of the nanopatterned electrodes

4.3.2.1 Influence of lattice constant on optical properties

Figure 4-2(a) Transmittance and absorbance, and (b) reflection spectra of the nanohole Al thin film for various lattice constants with $f = 0.8$ and $h = 20$ nm.

Figure 4–2 (a) shows the transmittance and absorbance spectra and Figure 4–2 (b) depicts the reflectance spectra separately for clarity, all over the spectral range from 300 nm to 1.0 μm for various lattice constants when the incident light is normal to the metallic thin film along the z direction. As shown in Figure 4-2(a), the transmittance is above 80% over a wide wavelength range. From the patterned structure, the filling factor is about 0.8, which means that a significant amount of light energy falling on the Al region is transmitted through it. The main reason of the enhanced broadband transmission is

originated from the excitation of the localized surface plasmon effect [72]. The interference of the incident light and the excited localized surface plasmon forms the transmission dip and the broadband transmission enhancement respectively. The transmittance changes with variation of the lattice constant from 600 nm to 200 nm. The highest transmittance for all different lattice constants is larger than 85% and close to unity at some specific wavelength for $a = 600$ nm. The longer periodicity supports long range surface plasmon polariton (SPP) as it suffers less scattering loss due to a fewer number of holes exposed during propagation. In the wavelength range shorter than 500 nm, there is a transmission dip. When the lattice constant is larger (for example, $a = 600$ nm), the dip is in the visible range in which we are most interested, and the transmission in the long wavelength range is relatively higher than in the other ranges. When the lattice constant decreases, the dip is blue-shifted, and the transmission in the long wavelength range only decreases slightly.

By manipulating the lattice constant, we can move the dip out of visible range, although the transmission in the long wavelength range also drops. Two reasons are attributed to the transmission dips at short wavelengths. One is the enhanced reflectance around the dip, which can be verified by the reflectance in Figure 4–2 (b). The reflectance at the transmission dip is larger than that of other wavelengths. The other one is the absorptance enhancement when two SPP modes are excited at both air-metal interfaces coupled with each other [70,

144]. For a 2D array, the SPP mode excitation condition is given by

$$\vec{k}_{spp} = \vec{k}_0 \sin \theta + i \vec{G}_x + j \vec{G}_y \quad 4.3.2-1$$

$\vec{k}_{spp}$ is the SPP wave vector, $\vec{k}_0$ is the free space wave vector, θ is the incident angle, $\vec{G}_x$ and $\vec{G}_y$ are the reciprocal lattice vectors, and i and j are integers [148]. For uniform metallic thin film, the SPP modes cannot be excited due to the SPP wave vector $\vec{k}_{spp}$ being larger than the free space parallel wave vector $\vec{k}_0 \sin \theta$. When light is incident on periodic structures, the SPP mode can be excited with the additional momentum of $\vec{G}_x$ and $\vec{G}_y$. For a hexagonal lattice array with normal incident light, the excited position of SPP is given by

$$\lambda_{spp} = a \left[\frac{4}{3} (i^2 + ij + j^2) \right]^{-\frac{1}{2}} \left(\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m} \right)^{\frac{1}{2}} \quad 4.3.2-2$$

λ_{spp} is the wavelength of the excited SPP, ϵ_d and ϵ_m are dielectric constants of surrounding materials [148], which are air and metal film respectively in our case.

Additionally, for all the films of different lattice constants, there is a continuous transmittance drop after the maximum transmittance and reaches the next lower level at around 830 nm. This is due to interband transition absorption of Al [68]. Furthermore, this absorption peak is found to be slightly blue-shifted when the lattice constant is decreased. The wide high transparency wavelength range makes the 2D nanohole patterned metallic thin film arranged in hexagonal lattice more suitable for TC applications.

Figure 4-3 Transmittance spectra of the nanohole films with different thicknesses, while keeping their sheet resistance constant.

4.3.2.2 Optimization of structures with fixed resistance

From the sheet resistance perspective, if the volume of Al film in one unit cell remains unchanged, the sheet resistance also will not change. Either thinner films (shorter h) with smaller nanoholes (smaller f) or thicker films (longer h) with larger nanoholes (larger f) will have the same resistance. To study the effects of h and f on the transmittance, the spectral relationship of transmittance for 4 different thicknesses ($h = 10$ nm, 15 nm, 20 nm, 25 nm) of the thin films is plotted in Figure 4–3 with the volume of Al kept unchanged. Here, the lattice constant is fixed at $a = 400$ nm. The transmittance is lowest for $h = 10$ nm, here small h and small f do not lead to better transparency level. The transmittance is better for large h and large f when the optical wavelength is longer than 450 nm. For the wavelength shorter than 450 nm, the transmittance first increases with the increasing h (up to 20 nm), and then decreases slightly

(up to $h = 25$ nm). The maximum amplitude transmission in this range is achieved when the thickness of the metal film approaches SPP skin depth, which is given by

$$\delta = \frac{1}{\text{Im}(k_z)} = \frac{c}{\omega} \frac{1}{\text{Im}(\sqrt{\epsilon_m})}, \quad 4.3.2-3$$

where k_z and ϵ_m are the imaginary refractive index and dielectric constant of the metal respectively, and c is the velocity and ω is the frequency of the light [149]. For example, the calculated SPP skin depth at the surface plasmon resonance frequency 856.55 THz is 23 nm. The imaginary value of the complex refractive index of Al at 856.55 THz is 4.274. As the thickness of the Al layer is close to the skin depth, SPP modes that are excited on both air-metal sides of the Al film are coupled via evanescent waves and form coupled SPP modes, which boost the total transmission significantly. Besides, an increased absorption peak at this wavelength is observed due to the interaction of the front and back SPP waves within the metal medium during SPP propagation. The 25 nm thick Al film shows slight a decrease in the transmission as there is no efficient coupling between SPP modes that are excited on the either side of the Al film due to the fact that its film thickness is greater than the skin depth.

4.3.2.3 Influence of hole filling materials

Filling the air holes with some commonly used dielectrics and organics (e.g. silicon oxide (SiO_2), silicon nitride (Si_3N_4) and

Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS)) is studied. Figure 4–4(a) shows the transmittances filled Al electrode. The transmittance of a thin film with 20 nm thickness is also presented as a reference. All the filled nanostructures have the same lattice constant, filling ratios and thicknesses as the optimized unfilled metal nanostructures. For nanostructure filled with SiO₂, the transmittance is higher than that of the air hole filled nanostructure in long wavelength range from 500 nm, but in the short wavelength range, the transmittance is lower. For nanostructure filled with Si₃N₄ with refractive index larger than SiO₂, there is a significant drop in the short wavelength range. The transmittance of PEDOT:PSS is similar to that of the nanostructure filled with SiO₂. The transmittance of the Al thin film is extremely low and most of the light has been reflected. The influence of the substrate is also studied for holes filled with SiO₂. The transmittances of Al films with hole filled with SiO₂ only, with substrate only and with both hole filled with SiO₂ and substrate are shown in Figure 4–4(b). When the substrate is considered, the transmittance in short wavelength range is further dropped, but the transmittance in the long wavelength range is little influenced and still kept high.

Figure 4-4 (a) Transmittance of the nanohole Al thin film for various filling materials (SiO_2 , Si_3N_4 and PEDOT:PSS) (b) Transmittances of the nanohole Al thin film with air hole, with SiO_2 filled holes only, with SiO_2 substrate only and with both SiO_2 filled holes and substrate respectively. Structure parameters are fixed at $a = 400$ nm, $f = 0.8$ and $h = 20$ nm.

4.3.2.4 Angular response of the nanopatterned electrodes

The angular dependence of the transmittance of the nanopatterned Al thin film is shown in Figure 4–5. The structure parameters are fixed at $a = 400$ nm, $f = 0.8$ and $h = 20$ nm. The average transmittance spectra from 300 nm to 1.0 μm of transverse-magnetic (TM) and transverse-electric (TE) polarization are studied separately. Here, the TM polarization is as the case when the

magnetic field is in the x direction unchanged and TE polarization is defined as the case when the magnetic field is always in the y direction. For TE polarization, the average transmittance remains high even when the incident angle is increased to 60 degrees, while the average transmittance of TM polarization drops to 60 percent. The enhanced transmission of the perforated metal film is due to localized surface plasmon and surface plasmon polariton, in addition to direct light transmission through the hole. Surface plasmon will be excited once the momentum between incident photon and surface plasmon is matched. The required additional momentum for the incident photon to match the momentum of surface plasmon will be provided by the period of the structure. From the graph it is clear that for both TE and TM polarization, the total transmission is almost the same for normal incidence. In other words, both polarizations excite SPs and their contributions to the total transmission are almost same for the zero degree incident beam. The reason is due to symmetric arrangement of the holes in metallic film. However, the total transmission for the TM polarization excitation is found to be reduced as the angle of incidence is increased. This is due to the change in the k vector of the incident photon from the surface plasmon resonance angle defined by Eqn. 4.3.2-1, whereas there is no change in the total transmission in the case of TE polarization as there is no change in the orientation of the incident beam polarization with respect to the metal surface.

Figure 4-5 Average transmittance for TE and TM polarizations vs. the incident angle. The structure parameters are fixed at $a = 400$ nm, $f = 0.8$ and $h = 20$ nm.

Detailed relationship between transmittance spectrum and incident angle is shown in Figure 4–6. For clearance, only the transmittance of 10, 30 and 60 degrees of incident angle are plotted. For TE polarization, the transmittance decreases in short wavelength range and increases in long wavelength range simultaneously when the incident angle increases resulting in a steady average transmittance as shown in Figure 4–5. The transmittance of TM, the transmittance drop in the whole wavelength range when the incident angle increases especially in the long wavelength range. In the visible, when the incident angle is 60 degree, the transmittance is still high that is a benefit for solar cell applications.

Figure 4-6 Transmission spectra for TE and TM polarizations with incident angle of 10, 30 and 60 degrees. The structure parameters are fixed at $a = 400$ nm, $f = 0.8$ and $h = 20$ nm.

4.3.2.5 Optical properties of several metal materials

For some applications, we may need to vary the work function of the TC.

As such, we studied the transmittance of 2D hexagonal lattice NH arrays made of different metals (aluminum (Al), silver (Ag), gold (Au), and nickel (Ni)), as shown in Figure 4–7. For different metals, the optimized parameters are the same, i.e., $a = 400$ nm, $f = 0.8$, and $h = 20$ nm. Detailed spectra optimizations for different metals are not shown here. For Ag and Au nanopatterned thin films,

the transmission dip cannot be moved out from the visible range because the dip tends to have a red shift when the lattice constant is reduced [70]. However, the transmittance in the long wavelength range is much better compared to other metals. The Ni film has a flatter transmission spectrum for the wavelength range from 300 nm to 1.0 μm but the average transmittance is relatively low. Al nanostructure has the best transmittance in the visible range among the four.

Figure 4-7 Transmission spectra for the structures made of metal materials Al, Ag, Au and Ni. The structure parameters are chosen as $a = 400$ nm, $f = 0.8$ and $h = 20$ nm for all metal materials here.

Experimentally, it is also worth to note that this nanostructure can be fabricated by electron beam lithography (EBL) which has been used to fabrication one dimensional metal nanowires and nanowire networks. The drawback is that it is costly and not efficient to fabricate large area metallic transparent electrode. The nanosphere lithography also can be used to do the nanostructure fabrication which is much cheaper compare to EBL but it is hard to control the morphology of the nanopatterned structures and the transmittance

and sheet resistance is still not good enough compare with those of ITO. The mainly challenge is how to fabricate low cost, large area nanostructured metallic transparent electrode with high transparency and low sheet resistant in the future.

4.4 Conclusion

In conclusion, the 2D patterned Al thin film with a hexagonal lattice enables a high transparency for a wide wavelength range from UV to IR. By manipulating the lattice constant a , the transmission dip can be moved out from the visible range. The transmission dip results from the reflectance enhancement and the absorption enhancement of the coupling of the SPP modes at the two air-metal interfaces. The continuous transmittance drop following the maximum transmittance stems from the increasing evanescence of the light. When the sheet resistance is kept constant, larger h and larger f lead to a higher transmittance level over the wide spectral region. TE polarization allows for a better angular transmittance compared to TM polarization. Compared to other nanopatterned metallic films, nanopatterned Al thin film yields the best transmission spectrum in the visible wavelength range.

Chapter 5 Enhanced Optical absorption in nanopatterned silicon thin films with a nano-cone-hole structure for photovoltaic applicaitons

5.1 Introduction

Silicon solar cell is presently dominating the solar cell market owing to the abundant supply, nearly ideal band gap and mature fabrication process. Most commercial silicon solar cells are made from bulk silicon with the thickness of a few hundred microns, i.e., a large amount of silicon is consumed, leading to a higher cost of the final product [150]. Thin film silicon solar cell with the thickness in the range of a few microns is a promising way to reduce the cost. However, the weak absorption, especially in the long wavelength side near the band gap edge of silicon, remains a challenge. To address this need, light trapping techniques including randomly textured structures [2, 151], periodic gratings [152], photonic crystals [6, 96, 113], and plasmonic structures [150, 153, 154] have recently been developed.

Instead of texturing front and back surface of solar cells, it is possible to texture the active layer into nanostructured arrays such as nano-wire (NW)[89, 155-158] nano-cone (NC) [158] and nano-hole (NH) [97] arrays. Theoretical studies [78, 79, 94, 95, 159] show that there is a large enhancement of optical absorption due to efficient anti-reflection of the incident light and effective optical

coupling between nano arrays and incident light. It is further demonstrated that NH arrays [94] exhibit stronger optical absorption compared to NW arrays [78, 79] with the same filling ratio and thickness. In this paper, to further increase the optical absorption, we proposed and numerically demonstrated a new nanostructured architecture of nano-cone-hole (NCH) array that enables significantly enhanced absorption, surpassing those of the previously reported arrays.

5.2 Optical properties optimization of NH arrays

In order to give a more fair comparison of optical properties of NH and NCH arrays, instead of take the optimized parameters of NH array from literature. We do the optimization process by ourselves and compare those with the optimized NCH array.

5.2.1 Structure and simulation setup of NH arrays

Figure 5-1 (a) Schematic of silicon nanohole arrays. (b) Top view of one unit cell

Figure 5-1 (a) shows the schematic of the NH array used for the study. It can be seen that the NH array is arranged in square lattice in x - y plane and surrounded by air. Sunlight is directly incident on the top of the structure along

z direction. The two-dimensional top view is shown in Figure 5-1(b). The lattice constant (period) of the square lattice is indicated as a . The radius of air hole is r . The air filling ratio f is defined as the ratio of the air hole surface area with the unit cell surface area ($f = \pi r^2 / a^2$). In our analysis, the thickness of the NH arrays is fixed at 2.33 μm .

The silicon dielectric function used is taken from [160]. The finite-difference time-domain (FDTD) method was employed for all simulations using Lumerical FDTD Solutions, a commercial FDTD software package. The simulation region in x and y direction is one periodic length of the period structures. The x and y simulation regions are ranged from $-a/2$ to $a/2$, here a is the lattice constant. In z direction, for all the simulations, because of the thickness of the NH is fixed at 2.33 μm , the simulation region in z direction for all different cases is fixed from $-2 \mu\text{m}$ to $2 \mu\text{m}$. PML boundary condition is used in z direction and periodic boundary condition is used in both x and y directions. The location of the launched incident field is at $z = 1.8 \mu\text{m}$. Two line power monitors are placed on the top and bottom of the NCH at $1.165 \mu\text{m}$ and $-1.165 \mu\text{m}$ respectively. The transmission function gives the amount of power transmitted through the power monitor. The absorption is calculated from the subtraction of the transmitted power of the two power monitors.

Non-uniform mesh is used for all the simulations. In the whole simulation region, the mesh size is set at 100 nm. In the material region and at

the interface of different materials, smaller meshes are used to increase the simulation accuracy which can override the mesh size set at the beginning. In the materials region from $-1.165\ \mu\text{m}$ to $1.165\ \mu\text{m}$, the mesh size is set with a smaller one at 10 nm in all directions, and at the interface of two different materials, the mesh size is even smaller at 2 nm with a width of 10 nm equally distributed in each material in z direction and 5 nm in x and y directions in one simulation period.

5.2.2 Characterization of the optical properties of NH arrays

The absorptance of silicon NH array of different f with fixed $a = 700\ \text{nm}$ is shown in Figure 5–2(a). In our simulation, f is varied from 0.3 to 0.7 corresponding to air hole size changing from small to large. The absorptance is various for different f . From Figure 5–2(a), we can see that smaller air hole (more absorption materials) does not guarantee larger absorptance. It is found that when $f = 0.5$, best absorption performance is obtained which can be further verified by the ultimate efficiency in Figure 5–6(b). As shown in Figure 5–2(b), the enhanced absorptance is mainly because of reduced reflectance of the large f . The absorptance of silicon NH array of different a with fixed $f = 0.5$ is shown in Figure 5–2(c). a is varied from 300 nm to 700 nm. From Figure 5–2(c), with the increasing of a , the absorptance decreases in the short wavelength range and increases in the long wavelength range. There is a trade-off between these two. Absorption enhancement in long wavelength range will be suppressed by the

energy loss in the short wavelength range. The optimal lattice constant obtained in our simulation is 700 nm according to the ultimate efficiency calculation in Figure 5-6. Corresponding reflectance is shown in Figure 5-2(d) for reference.

Figure 5-2 (a) Absorbance (b) reflectance of NH array of different air filling ratio f with fixed lattice constant $a = 700$ nm. (c) Absorbance (d) reflectance of NH array of different lattice constant a with fixed air filling ratio $f = 0.5$.

5.3 Optical properties optimization of NCH arrays

5.3.1 Structure and simulation setup of NCH arrays

Figure 5-3(a) shows the schematic of the proposed NCH array. It can be seen that the NCH array is arranged in a square lattice in the x - y plane and surrounded by air. Sunlight is directly incident on top of the structure along the z direction. The two-dimensional (2D) side and top views are shown in Figure 5-3(b) and (c), respectively. Considering the fabrication tolerance, the tip of the

NCH is not exactly at the bottom surface; instead, a small hole with radius of 20 nm is left on the bottom surface [Figure 5–3(b)]. The lattice constant (period) of the square lattice is indicated as a . The radius of the air hole at the top surface is r , and the thickness is h . The air filling ratio (f_{MAX}) is defined as the ratio of the top-surface air hole area to the unit cell surface area, given by $f_{\text{MAX}} = \pi r^2 / a^2$. Here the NH array has the same lattice constant a as NCH array and the air filling ratio f of the NH array is defined as in [94]. In our analysis, the thickness h of the NCH and NH arrays is fixed at 2.33 μm , the same as in [78, 94], for easy comparison.

Figure 5-3 (a) Schematic of the nano-cone-hole (NCH) array. (b) Two-dimensional side view and (c) top view of the NCH array.

The optical absorptions of silicon NCH arrays are analyzed in detail by using finite difference time domain (FDTD) method similar as in NH arrays. Periodic boundary conditions were adopted in the x and y directions, and a perfectly matched layer boundary condition was used in the z direction. All detailed setting of the mesh size, location of the launched field and the position of the line power monitors are set as the same as those in NH array simulations.

5.3.2 Optical Characterization of NCH arrays

Figure 5-4(a) Absorptance, (b) Reflectance and of NCH array of different

f_{MAX} with $a = 800$ nm and $h = 2.33$ μm. (c) Absorptance, (d) Reflectance of NCH array of different a with $f_{MAX} = 0.7$ and $h = 2.33$ μm.

The absorptance and reflectance optimization is shown in Figure 5-4. It is clearly shown in Figure 5-4(a) and (b), with larger f_{MAX} , the absorptance is higher and the reflectance is lower. The influence is more pronounced in the short wavelength range. The enhancement of the absorption is mainly caused by the reduced reflectance for large f_{MAX} similar as in the NH arrays. The absorptance and reflectance spectra of different a with $f_{MAX} = 0.7$ are depicted in Figure 5-4(c) and (d), respectively. With the increased a , the absorptance decreases in the short wavelength range and then increases in the long wavelength range. The resonant modes are mainly contributing to the absorption in the long wavelength range, and anti-reflection property dominates in the short wavelength range. There is a

trade-off between these two, especially for a larger lattice constant. It is worth noticing that for wavelengths ranging from 600 nm to 800 nm, the absorptance and reflectance exhibit a non-monotonic dependence on the lattice constant. For $a = 600$ nm, a better anti-reflective performance can be obtained in this wavelength range, which is larger for $a = 800$ nm. Performance comparison of NH and NCH arrays

5.3.3 Optical properties of the optimized NH and NCH arrays

In Figure 5–5, the absorptance and reflectance of the optimized NCH and NH arrays are presented. The absorptance nonpatterned thin film with an optimized antireflective (AR) coating is also presented for reference. From Figure 5–5(a), the absorptance of the NCH array is significantly enhanced across the whole wavelength range investigated, except for a narrow range around 0.8 μm . This implies that the NCH array exhibits a better light trapping property compared to the NH array. In addition to the enhancement of absorptance in the short wavelength range, it is worth noting that the absorptance curve of NCH array shows a large red shift towards the long wavelength which means that the inefficient absorption in the long wavelength range ($> 0.8 \mu\text{m}$) suffered by thin film solar cells has been alleviated greatly. In the long wavelength range, each peak in the absorptance spectra corresponds to a quasi-guided resonant mode [96], and these modes supported by nanostructures help to enhance absorption [79, 94, 96]. From Figure 5–5(a), both of NCH and NH arrays support resonant modes that

result in stronger absorptance compared to non-patterned thin film layers. The NCH array supports more modes compared to NH array. For the sake of easy visualization, the inset in Figure 5–5(a) shows a zoomed-in absorptance spectra of the NCH and NH arrays in the wavelength range from 0.90 μm to 0.95 μm (indicated by the purple-dashed line) in Figure 5–5 (a). It is clear that more modes (peaks) are supported by the NCH array compared to the NH array, contributing to the further enhancement of the absorptance in the case of the NCH arrays. Besides, the overall absorptance of NCH arrays is also improved compared to the NH arrays, which is resulted mainly from a stronger coupling between the incoming light and the supported modes in the NCH structure. The reflectance spectra of the NCH and NH arrays are compared in Figure 5–5 (b). Thanks to the better gradual changing of the effective refractive index of the NCH arrays [21], it is clear that the reflectance of the NCH array is much lower than that of the NH array in the whole wavelength range, especially for short wavelengths.

Figure 5-5 (a) Absorbance of the optimized NCH array and NH array. Inset is the enlarged spectra from 0.9 to 0.95 μm. (b) Reflectance of the same NCH array and NH array.

5.3.4 Ultimate efficiencies of NH and NCH arrays

In order to have a better understanding of the absorbance enhancement of the NCH arrays, the ultimate efficiency of both NH and NCH are calculated according to the absorbance spectra of both nanoarrays.

Assuming that each photon absorbed by the active layer can generate an electron-hole pair, the ultimate efficiency, η , can be written as [9]

$$\eta = \frac{\int_0^{\lambda_g} I(\lambda) A(\lambda) \frac{\lambda}{\lambda_g} d\lambda}{\int_0^{\infty} I(\lambda) d\lambda} \quad 5.4.2-1$$

where $I(\lambda)$ is the solar intensity of the Air Mass 1.5 (AM1.5) direct normal and circumsolar spectrum [7], $A(\lambda)$ is the absorptance, λ is the wavelength, λ_g is the wavelength corresponding to the band gap. The efficiency of the NCH array (NH array) is calculated for various a and f_{MAX} (f), while keeping $h = 2.33 \mu\text{m}$ for easy comparison.

Figure 5-6 (a) Ultimate efficiency of the NCH array for different lattice constants, a , and maximum filling ratios, f_{MAX} . (b) Ultimate efficiency of the NH array for different lattice constants, a , and filling ratios, f .

The ultimate efficiencies of the NCH and NH arrays are shown in Figure 5-6. In Figure 5-6 (a), we observe that a larger f_{MAX} promises a higher efficiency

regardless of the lattice constant for all NCH arrays. With the increased f_{MAX} , the change of effective refractive index across the thickness of the NCH arrays in z direction is more gradual which results in a better anti-reflection characteristic, further enhancing the absorption. This can be verified by the absorptance and reflectance spectra for different f_{MAX} with $a = 800$ nm in Figure 5-4(a) and (b). The efficiency increases with the increasing of the lattice constant up to $a = 800$ nm, after which the efficiency begins to drop with further increasing a . More modes are supported for a larger a [79, 94], and simultaneously, the reflectance in the short wavelength range increases[95] as shown Figure5-4 (c) and (d). When a is smaller than 800 nm, more supported modes help to bring up the efficiency. When a is larger than 800 nm, the mode enhancement will be suppressed by the energy loss in the short wavelength range resulting from an increased reflection. The optimized ultimate efficiency is achieved at 32.65% when $a = 800$ nm and $f_{\text{MAX}} = 0.7$ (Figure 5-6 (a)). The optimized ultimate efficiency of the NH arrays is shown in Figure 5-6 (b). The relationship between the ultimate efficiency and the design parameters a and f for the NH array has been clearly explained [94]. The trend of the ultimate efficiency is similar to the NCH array we discussed here. The highest efficiency is 26.52% with $a = 600$ nm and $f = 0.5$ for the NH array (indicated by black arrow) in Figure 5-6(a). Comparing to NH arrays, the ultimate efficiency of NCH arrays is enhanced by 23.11%, surpassing the feasible enhancement using the NH structure.

Figure 5-7 2D cross-section of (a) NCH and (b) NH structure with anti-reflective coating.

For thin film structure, the efficiency can be significantly improved by an AR coating. One layer of AR coating is deposited on the optimized NCH and NH structures. 2D cross-section views of NCH and NH structures are shown in Figure 5-7. The thickness of the AR coating is indicated as t . For example, with an optimized 70 nm Si_3N_4 , the ultimate efficiency of AR thin film solar cell is increased to 21.21% which has been enhanced by 36.84% compared to that of thin film without AR coating (15.50%). Here, we also investigate the influence of the AR coating for the optimized NCH and NH arrays. The dielectric function of Si_3N_4 is taken from ref. [113]. The efficiency of the NCH and NH arrays is increased to 34.23% and 28.83% respectively with an optimized AR coating thickness of 73 nm and 63 nm respectively. The efficiency of the NCH array is enhanced by 18.73%

compared to the NH array, which is still significant. The AR coating mainly contributes to the improvement of absorptance in the short wavelength range. The modes supported by the NCH and NH arrays are not influenced by the AR coating.

Figure 5-8 Angular dependence of ultimate efficiency of (a) TE and (b) TM mode of the optimized NCH and NH arrays respectively.

In Figure 5-8(a) and (b), we show the angular dependence of the ultimate efficiency for the optimized NCH and NH arrays respectively. For both NCH and NH arrays, transverse-magnetic (TM) polarization has higher ultimate efficiency compared to transverse-electric (TE) polarization. For incident angles up to 60 degree that we simulated, the NCH array always shows a better efficiency than the

NH array.

5.4 Conclusion

In conclusion, we presented a new NCH array structure with highest ultimate efficiency of 32.65% which is much larger than that can be obtained by NH array. The structure parameters of both NH and NCH arrays are optimized. The optical properties of NH and NCH arrays are analyzed in detail. Lower surface reflectance, more supported resonant modes and enhanced modes interaction are main reasons for the significantly enhanced absorption of NCH array. The NCH array has better ultimate efficiency than that of the NH array even for large incident angles up to 60 degrees.

Chapter 6 Broadband absorption enhancement in randomly positioned silicon nanowire arrays for solar cell applications

6.1 *Introduction*

Silicon solar cell is presently dominating the solar cell market owing to the abundant supply, nearly ideal band gap and mature fabrication process. Most commercial silicon solar cells are wafer based ones with thickness of a few hundred microns, which consume a large amount of silicon, leading to a high cost of the final product [150]. However, the weak absorption, especially in the long wavelength range near the band gap edge of silicon, remains a problem. Silicon nanowire (NW) structures are promising to achieve thin yet efficient solar cells and have been studied intensively owing to the large enhancement of absorption and improvement of carrier collection [39, 78-80, 82, 84, 86, 89, 90, 155-157]. Besides, other nano structures such as nano hole[94, 95], nano cone [98] and nano cone hole [161] have also been proposed for photovoltaic applications. Thus far, most of experimental and theoretical work are focused on regularly arranged nanostructure arrays with square or triangular lattice. Optimal lattice constant and silicon filling ratio of NW arrays have been obtained to achieve a high ultimate efficiency [79, 80]. On the other hand, randomly positioned NW arrays are of much lower cost as it is difficult and costly to maintain the large area regularity with a few hundreds of nanometers' registration. A few

experimental works on NW arrays with random orientation, length, size and position show increased reflection [39, 162]. Theoretically, it has been reported that structural disorder can introduce additional resonances and broaden existing resonances [163]. Recently, it has been reported by Bao and Ruan that optical absorption could be enhanced with disordered vertical silicon NW arrays in the wavelength range from 410 nm to 775 nm [92]. The random structure considered in ref. [92] is generated by randomly placing the NW within its unit cell while keeping the unit cell position fixed, which is a special case of position random structures. The influence of a general case position randomization on the optical properties has not been studied yet. In this paper, we investigate the optical properties including absorptance, reflectance and transmittance of general case position randomized NW structures.

6.2 Structure and simulation set up

Figure 6–1 shows the schematics of the NW arrays for the study. All considered structures are arranged in 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 square lattice is shown in Figure 6–1(a).

According to the optimal parameters [79], the lattice constant (period) is chosen as 500 nm, and the filling ratio (defined as the ratio of the NW top surface area to the unit cell top surface area in one unit cell) is 0.5, which means the radius of the NW is about 199 nm, which is used for all structures in this paper for easy comparison. Figure 6–1(b) shows the position random structure as ref. [92] with

the NW randomly placed within the unit cell containing it (i.e. the largest displacement of any NW is 40 nm from its original position in the regular structure), which is called random NW contained in regular unit cell NW array. Figure 6–1(c) shows a general case position randomized NW array. For the general case position random NW array, the filling ratio is generally lower than the regularly arranged one. In our case here, the filling ratio is 48%; the structure is called 48% position random NW array. A general case position randomized NW array with a 30% filling ratio is shown in Figure 6–1(d) and named as 30% position random NW array for short. In the process of generating position random NW arrays, the NW overlapping cases were excluded. In our analysis, the thickness of all NW arrays is fixed at 2.33 μm similar to ref. [78] For all random NW structures in Figure 6–1(b), (c), and (d), four different structures are simulated and then averaged to avoid any small probability event. The silicon dielectric function used is taken from ref. [160].

The finite-difference time-domain (FDTD) method is employed for all spectra calculation using Lumerical FDTD Solutions, a commercial FDTD software package. The simulation region in x and y direction is 2.5 μm by 2.5 μm , which means 5 periods are considered in the simulation. The x and y simulation regions is ranged from $-1.25 \mu\text{m}$ to $1.25 \mu\text{m}$. In z direction, for all the simulations, because of the thickness of each NW is fixed at 2.33 μm , the simulation region in z direction for all different cases is fixed from $-2 \mu\text{m}$ to 2

μm . Periodic boundary conditions are used in x and y directions and PML boundary condition is used in z direction. The location of the launched incident field is at $z = 1.8 \mu\text{m}$. Two line power monitors are placed on the top and bottom of the NCH at $1.165 \mu\text{m}$ and $-1.165 \mu\text{m}$ respectively. The transmission function gives the amount of power transmitted through the power monitor. The absorption is calculated from the subtraction of the transmitted power of the two power monitors.

Figure 6-1 Schematics of silicon NW arrays with a (a) regularly arranged square lattice, (b) random NW contained in regular unit cell used in Ref. [92], (c) 48% position random, and (d) 30% position random structure

A non-uniform mesh is used for all the simulations. In the whole simulation region, the mesh size is set at 100 nm . In the material region and at the interface of different materials, smaller meshes are used to increase the simulation accuracy which can override the mesh size set at the beginning. In

the materials region from $-1.165\ \mu\text{m}$ to $1.165\ \mu\text{m}$, the mesh size is set with a smaller one at $10\ \text{nm}$ in all directions, and at the interface of two different materials, the mesh size is even smaller at $2\ \text{nm}$ with a width of $5\ \text{nm}$ equally distributed in each side of the two line monitors in z direction and $5\ \text{nm}$ in x and y directions. For all of the sub meshes, the width in x and y direction is the same as the width of simulation region in x and y directions.

Detailed generation codes of the position random NW arrays are shown as follows. The codes are written with the embedded language of the software which is similar to the C language. By doing the loop, position randomness NW arrays are generated without overlap with each other. Each section of the codes are explained in detail with a start of **/*.

```
selectall;
delete;
num = 24; */number of loop times.
px=matrix(num); */set up three matrix with the same length of num.
py=matrix(num);
d = matrix(num);
r = sqrt(a^2/2/pi); */ radius of the NW.

*/set the initial values of the matrix.
for (i=1:num){
d(i)=2*end;
}
x = (star+r) + ((end-r)-(star+r))*rand;
y = (star+r) + ((end-r)-(star+r))*rand;
px(1)=x;
py(1)=y;
addcircle; */ add the initial random NW in to the simulation region.
set("x",x);
set("y",y);
set("radius",r);
```

**/do a loop to generate the position randomness NW arrays without overlap with each other.*

```
i=2;
for (0;i<=num;0){
x = (star+r) +((end-r)-(star+r))*rand;
y = (star+r) +((end-r)-(star+r))*rand;
for (j=1:i-1){
d(j) = sqrt((x-px(j))^2 + (y-py(j))^2);
}
dmin = min(d);
if(dmin < 2*r){
i=i;}else {px(i)=x;
py(i)=y;
addcircle;
set("x",x);
set("y",y);
set("radius",r);
i=i+1;}

}
*/set up the material properties of all the NWs.
selectall;
set("material",material);
material == "Si(Silicon)-Palik";
set("z min",-h/2);
set("z max",h/2);
```

6.3 Characterization of random NW array

6.3.1 Absorption properties of random NW array

Figure 6–2(a) shows the absorptance spectra of four different 48% position random NW arrays. The four NW structures are randomly generated by the computer. The corresponding random structures of the four cases are shown in the figure inset. From Figure 6–2, the absorptance spectra of the four cases are close to each other with little deviation. Similar results were also obtained for position

random NW arrays with other filling ratios we have tested. Thus it is meaningful to use the average (or any one) of the absorptance spectra of the 48% position random NW arrays to compare with the standard regular structure and other filling ratio position random NW arrays.

Figure 6–2(b), (c) and (d) shows the optical properties of the four structures shown in Figure 6–1. Each absorptance peak in the spectra corresponds to a guided resonant mode [79, 94]. From Figure 6–2(b), the absorptance of random NW contained in regular unit cell NW array is close to that of the regularly arranged one in the wavelength range considered here, i.e. this random structure does not have much influence on the absorptance. Small deviations from the origin position do not lead to obvious increase in supporting modes and mode broadening, which is consistent with the analysis in ref. [92]. The reflectance (Figure 6–2(c)) and transmittance (Figure 6–2(d)) are also similar to those of regularly arranged one. As shown in Figure 6–2(b), the absorptance of 48% position random NW array is significantly higher and flatter compared to both the random NW contained in regular unit cell and regularly arranged NW arrays in long wavelength range from 800 nm to 1.13 μm where the absorption is very weak, a problem suffered by thin film silicon solar cells. The corresponding reflectance and transmittance are also shown in Figure 6–2(c) and (d). In the short wavelength range, the absorptance is mainly determined by the reflectance owing to the high material absorption of silicon in this range. The lower the reflectance, the higher the absorptance is. From

Figure 6–2(c), the reflectance is similar for all NW arrays which result in a similar absorption in the short wavelength range. The transmittance (Figure 6–2(d)) is close to zero in the short wavelength range. In the long wavelength range, the absorptance is determined by both reflectance and the supported guided resonant modes. From Figure 6–2(c), the reflectance of 48% position random NW array is lower than the random NW contained in regular unit cell and the regularly arranged ones which are confirmed by the transmittance in Figure 6–2(d). Besides, the structural disorder introduces additional resonances and broadens existing resonances leading to an absorption enhancement [163]. More modes are induced for larger position randomness. The flatter absorption spectrum of position random NW array indicates that the resonances are more broadened. The optical properties of NW array as a function of the filling ratio is further investigated for general case position random NW array. Even when the NW filling ratio is 30%, the absorptance is only slightly lower than that of the regularly arranged one. From Figure 6–2(c), the 30% position random NW array has better anti-reflection performance. The reflectance is lower than that of the regularly arranged one. The drop of absorptance is mainly coming from the less supported resonant modes when the filling ratio becomes lower. With less supporting modes, light can not be trapped in NW structures long enough to enhance absorption. Hence a larger transmittance in all considered wavelength range is expected compared to others (Figure 6–2 (d)).

Figure 6-2 (a) Absorptance of four different 48% position random NW arrays. (b) Absorptance, (c) Reflectance and (d) Transmittance of regular, random NW contained in regular unit cell, 48% position random and 30% position random silicon NW arrays respectively.

6.3.2 Electric field distribution of random NW array

In Figure 6-3, we plotted the electric- (E-) field intensity distributions in the regular structure and 48% position random structure at two wavelengths of $\lambda = 899.1$ nm and $\lambda = 916.0$ nm. These two wavelengths were chosen as 899.1 nm is one absorptance peak and 916.0 nm is the next adjacent absorptance trough for the regularly arranged NW array (Figure 6-2(b)). It is clear by comparing Figure 6-3(a), (b) with Figure 6-3 (c), (d) that, the resonance corresponding to 899.1 nm wavelength has been broadened by introducing the randomization. Moreover, we can also see from Figure 6-3(d) that additional mode appears at 916.0 nm. The broadening of resonance can also be understood from the quality factor (Q factor). The sharp peaks in the absorptance spectrum of regularly arranged structure

correspond to guided resonant modes with high Q factor (Figure 6-2(b)). The higher the Q factor, the longer the light will be trapped in the structure attributing to a higher absorptance peak. With randomization introduced to the regular structure, the Q factor is reduced. The reduction of the Q factor leads to a broadening of the resonance, hence broadening of the absorption spectrum.

Figure 6-3 E-field distributions in regularly arranged NW array at (a) $\lambda = 899.1$ nm and (b) $\lambda = 916.0$ nm. E-field distributions in 48% position random NW array at (c) $\lambda = 899.1$ nm and (d) $\lambda = 916.0$ nm.

6.3.3 Ultimate efficiency of random NW array

Table 6-1. Ultimate efficiency of various NW arrays				
NW arrays	Regularly arranged	48% position random	Random NW in a regular unit cell	30% position random
Ultimate Efficiency	26.12%	29.61%	27.39%	24.53%
Enhancement		13.4%	4.8%	-6.1%

The ultimate efficiencies [9] for all cases were calculated under Air Mass 1.5 (AM1.5) [7] irradiation and are shown in Table 6-1. The efficiency of regularly arranged, random NW contained in regular unit cell, 48% position random, 30% position random NW arrays are 26.12%, 27.39%, 29.61%, and 24.53% respectively. It additionally verifies that the absorptance of random NW contained in regular unit cell NW array is only slightly better than the regularly arranged one. The ultimate efficiency of the 30% position random NW array is only slightly

lower than that of the regularly arranged one. The ultimate efficiencies of other filling ratios were also calculated. Our results show that the ultimate efficiency is always larger than that of the regularly arranged one for position random structures with a filling ratio larger than 36%. The ultimate efficiency of 48% position random NW array is 15% improved compared to the regularly arranged one. Thus the efficiency of general case position random NW arrays has better performance compared to others.

6.4 Conclusion

In conclusion, optical properties of various random NW arrays are studied in detail. Better absorption performance of random structure is owing to better anti-reflective performance, additional resonances introduced by the structural disorder and existing resonances broadening. With comparable filling ratio, more randomness leads to larger absorption enhancement. Our results here indicate that high performance silicon NW solar cells can be obtained by low-cost bottom-up approaches.

Chapter 7 Conclusion and future work

7.1 Conclusion

In this thesis, light management in nanostructures is studied in detail. Here, nanostructures are applied as anti-reflective coatings (ARCs), transparent electrodes and active layers in solar cells.

In the study of ARCs, ZnO NW and NH structures were designed and investigated. The ZnO NW and NH nanostructures can be used as perfect ARCs in the visible range with effective UV blocking. Both NW and NH structures showed better anti-reflective performance in the visible range and better absorption in the UV range compared to the ZnO thin film with the same thickness. The absorption of both of the nanostructures was similar to each other while the reflectance of NW structure in the visible range was slightly better than that of the NH structure. Thus, this work showed that the NW structure is a better candidate for ARC as compared to NH structure.. On the other hand, the absorption in the UV range and the reflectance in the visible range of the nanostructures showed slightly dependence on the incident angle of light, which enabled them to be used as a wide angle ARCs with UV blocking.

Nanopatterned metallic electrodes were also demonstrated in this work as high transparent electrodes to replace ITO. Underlying physics of the high transmittance in broad spectra from 300 nm - 1000 nm are analyzed in detail.

When the resistance is fixed as a constant, thicker films with a larger filling ratio lead to better transmittance in the visible range. The influence of the hole filling materials and angular response were also presented. The films still maintain high transmittance in the broad wavelength range from 300 nm - 1000 nm even with hole filling materials and substrates. The optical properties of several commonly used metals are also investigated. Through the comparison, Al showed the best transmittance in the visible range which makes it to be a better potential candidate replacing ITO.

Texturing the active layer into nano-cone-hole (NCH) structure was firstly reported here. With the NCH textured silicon active layer, the absorption has been largely enhanced compared to a silicon thin film with the same thickness and even better than the optimized NH array. A 32.65% ultimate efficiency was achieved with the optimized NCH array which had been enhanced by 23.11% as compared to the optimized NH array. The absorption enhancement was mainly due to the lower surface reflectance, more supported resonant modes and enhanced modes interaction. Both TE and TM polarizations of NCH array have better angular response compared to NH array.

The influence of introducing random in to nanostructured active layer was studied here as well. The random NW array showed better absorptance compared to the regularly arranged one. Electric field distribution was used to explain the absorption enhancement. The ultimate efficiency of the optimized

random NW array is improved by 15% as compared to the regularly arranged one. Better absorption performance of random structures originated from the better anti-reflective performance, additional resonances introduced by the structural disorder and existing resonances broadening.

7.2 *Future work*

ZnO nanostructures have great potential application as ARCs for solar cells. With the optimized parameters designed for the ZnO NW structure, the real structure will be achieved by experiments. ZnO NW can easily be fabricated by many methods such as hydrothermal method, CVD method and so on. The challenge is to control the growth with the optimized parameters. Different methods will be tested and compared to realize designed nanostructures.

Efforts will be devoted to fabricate the Al nanostructure electrodes with various methods such as the electron beam lithography (EBL), polystyrene (PS) sphere lithography and anodization. A better way should be developed in order to produce low cost, large area, high transmittance and low sheet resistant nanopatterned Al electrodes. Numerical study of the solar cell performance with integrated nanopatterned Al electrodes should also be carried out. Some work has been done which showed the improved absorptance in the active layer of organic solar cell with integrated nanopatterned Al electrodes. Further work

need to be done to understand the underlying physics and the mechanism of the absorption enhancement.

Numerical results have shown that the designed NCH array and the random NW array can be both used to enhance the light absorption in the active layer and further increase the solar cell efficiency. With the understanding of the physics in the absorption enhancement, new types of nanostructures will be designed to improve the absorption for the application of next generation solar cells. For the NCH structure, with the optimized structure parameter, it could be achieved by nanoimprinting technique. This designed structure can be used not only in silicon solar cells, but also for other kind of solar cells such as organic, dye-sensitized and quantum dot solar cells. The analysis of the random NW array may probably provide a cheaper way to achieve high performance nanostructure solar cells.

In conclusion, this thesis presents some novel designs of ARCs with dielectric ZnO material. Optimized structure parameters were obtained through numerical calculation. The photon behavior in the nanostructure was clearly explained. On top of the ARCs, similar work was done on nanopatterned metallic electrodes and nanostructured active layer analysis. High transmittance nanopatterned metallic electrodes are achieved and the detail investigation of the absorption enhancement in the active layer was illustrated. Last but not least, some interesting topics and possible methods for nanostructure fabrication were

proposed in the thesis. According to the design rules, it is possible to design some new types of nanostructures which can be used for nanostructure active layer.

Author's Publications

1. **Q. G. Du**, G. Alagappan, H. T. Dai, H. V. Demir, H. Y. Yu, X. W. Sun and C. H. Kam, , “UV-blocking ZnO nanostructure anti-reflective coatings” Opt. Commun., **285**, 3238-3241, (2012).
2. **Q. G. Du**, C. H. Kam, H. V. Demir, H. Y. Yu and X. W. Sun, “ Broadband absorption enhancement in randomly positioned silicon nanowire arrays for solar cell applications”, Opt. Lett., **36**, 1884-1886, (2011).
3. **Q. G. Du**, C. H. Kam, H. V. Demir, H. Y. Yu and X. W. Sun, “Enhanced optical absorption in nanopatterned silicon thin films with a nano-cone-hole structure for photovoltaic applications”, Opt. Lett., **35**, 1713-1715, (2011)
4. **Q. G. Du**, G. Alagappan, H. V. Demir, C. H. Kam, X. W. Sun, and P. Wu, “Geometrically distributed aperiodic circular photonic crystals with broad and isotropic photonic band gaps,” Opt. Commun. **284**, 2239-2241 (2011).
5. **Q. G. Du**, F. F. Ren, C. H. Kam, and X. W. Sun, "Second-harmonic generation in photonic crystals with a pair of epsilon-negative and mu-negative defects", Optics Express **17**, 6682-6687 (2009).
6. F. F. Ren, J. Chen, **Q. G. Du**, N. H. Shen, B. K. Tan and H. T. Wang,, “Electromagnetic Transmission through One-dimensional Gratings with Left-Handed Materials,” Phys. Rev. B , **75**, 045127 (2007).
7. **Q. G. Du**, K. Sathiyamoorthy, L. P. Zhang, H. V. Demir, X. W. Sun and C. H. Kam, “A two-dimensional nanopatterned thin metallic transparent conductor with high transparency from the ultraviolet to the infrared”, Applied Physics Letters, under review.
8. **Q. G. Du**, L. P. Zhang, H. V. Demir, X. W. Sun and C. H. Kam, “Enhancing the light absorption in organic solar cells with a transparent nanopatterned aluminum electrode assisted by co-existing surface plasmon and wave guided modes”, under preparation.

Conference presentation

1. **Q. G. Du**, C. H. Kam and X. W. Sun, Enhanced optical absorption in nanopatterned silicon thin films with a nano-cone-hole structure for photovoltaic applications, Poster, Material Research Society (MRS) Fall Meeting, Boston, United States, 2011.

Bibliography

1. Organizing Committee for the Workshop on Energy and Transportation, *Energy and Transportation: Challenges for the Chemical Sciences in the 21st Century*. (The National Academies Press, 2003).
2. E. Yablonovitch and G. D. Cody, "Intensity enhancement in textured optical sheets for solar cells," *IEEE Trans. Electron Devices* **29**, 300-305, (1982).
3. E. Yablonovitch, "STATISTICAL RAY OPTICS," *J. Opt. Soc. Am.* **72**, 899-907, (1982).
4. J. Nelson, *The Physics of Solar Cells*. (Imperial College Press, 2003).
5. P. Würfel, *Physics of Solar Cells: From Principles to New Concepts*. (John Wiley & Sons, 2008).
6. P. Bermel, C. Luo, L. Zeng, L. C. Kimerling and J. D. Joannopoulos, "Improving thin-film crystalline silicon solar cell efficiencies with photonic crystals," *Opt. Express* **15**, 16986-17000, (2007).
7. "Air Mass 1.5 Spectra, American Society for Testing and Materials, " retrieved <http://rredc.nrel.gov/solar/spectra/am1.5/>.
8. S. M. Wu, W. Wang, K. Reinhardt, Y. L. Lu and S. C. Chen, "Absorption enhancement in thin-film silicon solar cells by two-dimensional periodic nanopatterns," *J. Nanophotonics* **4**, 043515, (2010).
9. W. Shockley and H. J. Queisser, "Detailed balance limit of efficiency of p-n junction solar cells," *J. Appl. Phys.* **32**, 510-513, (1961).
10. K. S. Yee, "NUMERICAL SOLUTION OF INITIAL BOUNDARY VALUE PROBLEMS INVOLVING MAXWELLS EQUATIONS IN ISOTROPIC MEDIA," *IEEE Trans. Antenn. Propag.* **AP14**, 302-307, (1966).
11. A. Mekis, S. H. Fan and J. D. Joannopoulos, "Absorbing boundary conditions for FDTD simulations of photonic crystal waveguides," *IEEE Microw. Guided Wave Lett.* **9**, 502-504, (1999).
12. E. P. Kosmidou and T. D. Tsiboukis, "An FDTD analysis of photonic crystal waveguides comprising third-order nonlinear materials," *Optical and Quantum Electronics* **35**, 931-946, (2003).
13. A. C. Cangellaris, "Numerical stability and numerical dispersion of a compact 2-D/FDTD method used for the dispersion analysis of waveguides," *IEEE Microw. Guided Wave Lett.* **3**, 3-5, (1993).
14. E. Hecht, *Optics*. (Pearson Education, 2008).
15. L. B. Lockhart and P. King, "3-LAYERED REFLECTION-REDUCING COATINGS," *J. Opt. Soc. Am.* **37**, 689-694, (1947).
16. C. L. Nagendra and G. K. M. Thutupalli, "DESIGN OF 3-LAYER ANTIREFLECTION COATINGS - A GENERALIZED-APPROACH,"

- Appl. Opt. **27**, 2320-2333, (1988).
17. H. G. Shanbhogue, C. L. Nagendra, M. N. Annapurna, S. A. Kumar and G. K. M. Thutupalli, "Multilayer antireflection coatings for the visible and near-infrared regions," Appl. Opt. **36**, 6339-6351, (1997).
18. D. Bouhafs, A. Moussi, A. Chikouche and J. M. Ruiz, "Design and simulation of antireflection coating systems for optoelectronic devices: Application to silicon solar cells," Sol. Energy Mater. Sol. Cells **52**, 79-93, (1998).
19. B. C. Chakravarty, P. N. Vinod, S. N. Singh and B. R. Chakraborty, "Design and simulation of antireflection coating for application to silicon solar cells," Sol. Energy Mater. Sol. Cells **73**, 59-66, (2002).
20. M. Ghebrebrhan, P. Bermel, Y. Avniel, J. D. Joannopoulos and S. G. Johnson, "Global optimization of silicon photovoltaic cell front coatings," Opt. Express **17**, 7505-7518, (2009).
21. M. J. Minot, "Single-layer, gradient refractive index antireflection films effective from 0.35 to 2.5 μ m," J. Opt. Soc. Am. **66**, 515-519, (1976).
22. S. J. Jang, Y. M. Song, C. I. Yeo, C. Y. Park, J. S. Yu and Y. T. Lee, "Antireflective property of thin film a-Si solar cell structures with graded refractive index structure," Opt. Express **19**, A108-A117, (2011).
23. M. L. Kuo, D. J. Poxson, Y. S. Kim, F. W. Mont, L. K. Kim, E. F. Schubert and S. Y. Lin, "Realization of a near-perfect antireflection coating for silicon solar energy utilization," Opt. Lett. **33**, 2527-2529, (2008).
24. J. Q. Xi, M. F. Schubert, J. K. Kim, E. F. Schubert, M. F. Chen, S. Y. Lin, W. Liu and J. A. Smart, "Optical thin-film materials with low refractive index for broadband elimination of Fresnel reflection," Nat. Photonics **1**, 176-179, (2007).
25. S. A. Mann, R. R. Grote, R. M. Osgood and J. A. Schuller, "Dielectric particle and void resonators for thin film solar cell textures," Opt. Express **19**, 25729-25740, (2011).
26. Y. C. Lee, C. F. Huang, J. Y. Chang and M. L. Wu, "Enhanced light trapping based on guided mode resonance effect for thin-film silicon solar cells with two filling-factor gratings," Opt. Express **16**, 7969-7975, (2008).
27. J. S. Li, H. Y. Yu, Y. L. Li, F. Wang, M. F. Yang and S. M. Wong, "Low aspect-ratio hemispherical nanopit surface texturing for enhancing light absorption in crystalline Si thin film-based solar cells," Appl. Phys. Lett. **98**, 021905-021908, (2011).
28. A. P. Vasudev, J. A. Schuller and M. L. Brongersma, "Nanophotonic light trapping with patterned transparent conductive oxides," Opt. Express **20**, A385-A394, (2012).
29. D. Shir, J. Yoon, D. Chanda, J.-H. Ryu and J. A. Rogers, "Performance of Ultrathin Silicon Solar Microcells with Nanostructures of Relief Formed

- by Soft Imprint Lithography for Broad Band Absorption Enhancement," *Nano Lett.* **10**, 3041-3046, (2010).
30. A. Bozzola, M. Liscidini and L. C. Andreani, "Photonic light-trapping versus Lambertian limits in thin film silicon solar cells with 1D and 2D periodic patterns," *Opt. Express* **20**, A224-A244, (2012).
31. R. Y. Zhang, B. Shao, J. R. Dong, J. C. Zhang and H. Yang, "Absorption enhancement analysis of crystalline Si thin film solar cells based on broadband antireflection nanocone grating," *J. Appl. Phys.* **110**, 113105, (2011).
32. Y. C. Chao, C. Y. Chen, C. A. Lin, Y. A. Dai and J. H. He, "Antireflection effect of ZnO nanorod arrays," *J. Mater. Chem.* **20**, 8134-8138, (2010).
33. Y. M. Song, J. S. Yu and Y. T. Lee, "Antireflective submicrometer gratings on thin-film silicon solar cells for light-absorption enhancement," *Opt. Lett.* **35**, 276-278, (2010).
34. Y. D. Wang, N. Lu, H. B. Xu, G. Shi, M. J. Xu, X. W. Lin, H. B. Li, W. T. Wang, D. P. Qi, Y. Q. Lu and L. F. Chi, "Biomimetic corrugated silicon nanocone arrays for self-cleaning antireflection coatings," *Nano Res.* **3**, 520-527, (2010).
35. S. L. Diedenhofen, G. Vecchi, R. E. Algra, A. Hartsuiker, O. L. Muskens, G. Immink, E. Bakkers, W. L. Vos and J. G. Rivas, "Broad-band and Omnidirectional Antireflection Coatings Based on Semiconductor Nanorods," *Adv. Mater.* **21**, 973-978, (2009).
36. S. S. Lo, C. C. Chen, F. Garwe and T. Pertch, "Broad-band anti-reflection coupler for a : Si thin-film solar cell," *J. Phys. D: Appl. Phys.* **40**, 754-758, (2007).
37. C.-H. Sun, P. Jiang and B. Jiang, "Broadband moth-eye antireflection coatings on silicon," *Appl. Phys. Lett.* **92**, 061112-061113, (2008).
38. C. H. Chang, P. C. Yu, M. H. Hsu, P. C. Tseng, W. L. Chang, W. C. Sun, W. C. Hsu, S. H. Hsu and Y. C. Chang, "Combined micro- and nano-scale surface textures for enhanced near-infrared light harvesting in silicon photovoltaics," *Nanotechnology* **22**, 095201, (2011).
39. O. L. Muskens, J. G. Rivas, R. E. Algra, E. Bakkers and A. Lagendijk, "Design of light scattering in nanowire materials for photovoltaic applications," *Nano Lett.* **8**, 2638-2642, (2008).
40. P. C. Yu, C. H. Chang, C. H. Chiu, C. S. Yang, J. C. Yu, H. C. Kuo, S. H. Hsu and Y. C. Chang, "Efficiency Enhancement of GaAs Photovoltaics Employing Antireflective Indium Tin Oxide Nanocolumns," *Adv. Mater.* **21**, 1618-1621, (2009).
41. M. Kroll, S. Fahr, C. Helgert, C. Rockstuhl, F. Lederer and T. Pertsch, "Employing dielectric diffractive structures in solar cells - a numerical study," *Phys. Status Solidi a* **205**, 2777-2795, (2008).
42. R. Bouffaron, L. Escoubas, J. J. Simon, P. Torchio, F. Flory, G. Berginc and P. Masclet, "Enhanced antireflecting properties of micro-structured

- top-flat pyramids," *Opt. Express* **16**, 19304-19309, (2008).
43. J. Y. Chen and K. W. Sun, "Enhancement of the light conversion efficiency of silicon solar cells by using nanoimprint anti-reflection layer," *Sol. Energy Mater. Sol. Cells* **94**, 629-633, (2010).
44. Y. F. Huang, S. Chattopadhyay, Y. J. Jen, C. Y. Peng, T. A. Liu, Y. K. Hsu, C. L. Pan, H. C. Lo, C. H. Hsu, Y. H. Chang, C. S. Lee, K. H. Chen and L. C. Chen, "Improved broadband and quasi-omnidirectional anti-reflection properties with biomimetic silicon nanostructures," *Nat. Nanotechnol.* **2**, 770-774, (2007).
45. X. D. Wang, C. J. Summers and Z. L. Wang, "Large-Scale Hexagonal-Patterned Growth of Aligned ZnO Nanorods for Nano-optoelectronics and Nanosensor Arrays," *Nano Lett.* **4**, 423-426, (2004).
46. J. Grandidier, D. M. Callahan, J. N. Munday and H. A. Atwater, "Light Absorption Enhancement in Thin-Film Solar Cells Using Whispering Gallery Modes in Dielectric Nanospheres," *Adv. Mater.* **23**, 1272-1276, (2011).
47. S. H. Lee, G. E. Jellison, C. E. Duty and J. Xu, "Light confinement-induced antireflection of ZnO nanocones," *Appl. Phys. Lett.* **99**, 153113-153116, (2011).
48. O. Isabella, F. Moll, J. Krc and M. Zeman, "Modulated surface textures using zinc-oxide films for solar cells applications," *Phys. Status Solidi a* **207**, 642-646, (2010).
49. C. Battaglia, J. Escarre, K. Soderstrom, M. Charriere, M. Despeisse, F. J. Haug and C. Ballif, "Nanomoulding of transparent zinc oxide electrodes for efficient light trapping in solar cells," *Nat. Photonics* **5**, 535-538, (2011).
50. L. Sainiemi, V. Jokinen, A. Shah, M. Shpak, S. Aura, P. Suvanto and S. Franssila, "Non-Reflecting Silicon and Polymer Surfaces by Plasma Etching and Replication," *Adv. Mater.* **23**, 122-126, (2011).
51. V. V. Iyengar, B. K. Nayak and M. C. Gupta, "Optical properties of silicon light trapping structures for photovoltaics," *Sol. Energy Mater. Sol. Cells* **94**, 2251-2257, (2010).
52. S. A. Boden and D. M. Bagnall, "Optimization of moth-eye antireflection schemes for silicon solar cells," *Prog. Photovoltaics* **18**, 195-203, (2010).
53. M. J. Sher, M. T. Winkler and E. Mazur, "Pulsed-laser hyperdoping and surface texturing for photovoltaics," *MRS Bull.* **36**, 439-445, (2011).
54. V. G. Kravets and A. N. Grigorenko, "Retinal light trapping in textured photovoltaic cells," *Appl. Phys. Lett.* **97**, 143701-143703, (2010).
55. J. Li, H. Yu, S. M. Wong, G. Zhang, G.-Q. Lo and D.-L. Kwong, "Si nanocone array optimization on crystalline Si thin films for solar energy harvesting," *J. Phys. D: Appl. Phys.* **43**, 255101, (2010).
56. G. J. Lin, K. Y. Lai, C. A. Lin and J. H. He, "Solar energy harvesting

- scheme using syringe-like ZnO nanorod arrays for InGaN/GaN multiple quantum well solar cells," *Opt. Lett.* **37**, 61-63, (2012).
57. F. Llopis and I. Tobias, "Texture profile and aspect ratio influence on the front reflectance of solar cells," *J. Appl. Phys.* **100**, 124504 (2006).
58. L. Ae, D. Kieven, J. Chen, R. Klenk, T. Rissom, Y. Tang and M. C. Lux-Steiner, "ZnO nanorod arrays as an antireflective coating for Cu(In,Ga)Se-2 thin film solar cells," *Prog. Photovoltaics* **18**, 209-213, (2010).
59. Y. J. Lee, D. S. Ruby, D. W. Peters, B. B. McKenzie and J. W. P. Hsu, "ZnO nanostructures as efficient antireflection layers in solar cells," *Nano Lett.* **8**, 1501-1505, (2008).
60. Y. S. Tian, C. G. Hu, Y. F. Xiong, B. Y. Wan, C. H. Xia, X. S. He and H. Liu, "ZnO Pyramidal Arrays: Novel Functionality in Antireflection," *J. Phys. Chem. C* **114**, 10265-10269, (2010).
61. S. Fahr, T. Kirchartz, C. Rockstuhl and F. Lederer, "Approaching the Lambertian limit in randomly textured thin-film solar cells," *Opt. Express* **19**, A865-A874, (2011).
62. C. Rockstuhl, S. Fahr, K. Bittkau, T. Beckers, R. Carius, F. J. Haug, T. Söderström, C. Ballif and F. Lederer, "Comparison and optimization of randomly textured surfaces in thin-film solar cells," *Opt. Express* **18**, A335-A341, (2010).
63. C. Battaglia, K. Soderstrom, J. Escarre, F. J. Haug, D. Domine, P. Cuony, M. Boccard, G. Bugnon, C. Denizot, M. Despeisse, A. Feltrin and C. Ballif, "Efficient light management scheme for thin film silicon solar cells via transparent random nanostructures fabricated by nanoimprinting," *Appl. Phys. Lett.* **96**, 213504-213506 (2010).
64. D. Domine, F. J. Haug, C. Battaglia and C. Ballif, "Modeling of light scattering from micro- and nanotextured surfaces," *J. Appl. Phys.* **107**, 044504, (2010).
65. K. Bittkau, T. Beckers, S. Fahr, C. Rockstuhl, F. Lederer and R. Carius, "Nanoscale investigation of light-trapping in a-Si:H solar cell structures with randomly textured interfaces," *Phys. Status Solidi a* **205**, 2766-2776, (2008).
66. Z. Chen, B. Cotterell, W. Wang, E. Guenther and S. J. Chua, "A mechanical assessment of flexible optoelectronic devices," *Thin Solid Films* **394**, 202-206, (2001).
67. M. G. Kang, M. S. Kim, J. S. Kim and L. J. Guo, "Organic Solar Cells Using Nanoimprinted Transparent Metal Electrodes," *Adv. Mater.* **20**, 4408-4413, (2008).
68. J.-Y. Lee, S. T. Connor, Y. Cui and P. Peumans, "Solution-Processed Metal Nanowire Mesh Transparent Electrodes," *Nano Lett.* **8**, 689-692, (2008).
69. L. B. Hu, H. S. Kim, J. Y. Lee, P. Peumans and Y. Cui, "Scalable Coating and Properties of Transparent, Flexible, Silver Nanowire Electrodes," *Acs*

- Nano **4**, 2955-2963, (2010).
70. P. B. Catrysse and S. Fan, "Nanopatterned Metallic Films for Use As Transparent Conductive Electrodes in Optoelectronic Devices," Nano Lett. **10**, 2944-2949, (2010).
71. P. Kuang, J.-M. Park, W. Leung, R. C. Mahadevapuram, K. S. Nalwa, T.-G. Kim, S. Chaudhary, K.-M. Ho and K. Constant, "A New Architecture for Transparent Electrodes: Relieving the Trade-Off Between Electrical Conductivity and Optical Transmittance," Adv. Mater. **23**, 2469-2473, (2011).
72. J. van de Groep, P. Spinelli and A. Polman, "Transparent Conducting Silver Nanowire Networks," Nano Lett. **12**, 3138-3144, (2012).
73. M. Green and F. T. Yi, "Light transmission through perforated metal thin films made by island lithography," Thin Solid Films **467**, 308-312, (2004).
74. T. H. Reilly, R. C. Tenent, T. M. Barnes, K. L. Rowlen and J. van de Lagemaat, "Controlling the Optical Properties of Plasmonic Disordered Nanohole Silver Films," Acs Nano **4**, 615-624, (2010).
75. Y. Park, E. Drouard, O. El Daif, X. Letartre, P. Viktorovitch, A. Fave, A. Kaminski, M. Lemiti and C. Seassal, "Absorption enhancement using photonic crystals for silicon thin film solar cells," Opt. Express **17**, 14312-14321, (2009).
76. S. Zanotto, M. Liscidini and L. C. Andreani, "Light trapping regimes in thin-film silicon solar cells with a photonic pattern," Opt. Express **18**, 4260-4274, (2010).
77. O. El Daif, E. Drouard, G. Gomard, A. Kaminski, A. Fave, M. Lemiti, S. Ahn, S. Kim, P. Roca i Cabarrocas, H. Jeon and C. Seassal, "Absorbing one-dimensional planar photonic crystal for amorphous silicon solar cell," Opt. Express **18**, A293-A299, (2010).
78. L. Hu and G. Chen, "Analysis of Optical Absorption in Silicon Nanowire Arrays for Photovoltaic Applications," Nano Lett. **7**, 3249-3252, (2007).
79. C. X. Lin and M. L. Povinelli, "Optical absorption enhancement in silicon nanowire arrays with a large lattice constant for photovoltaic applications," Opt. Express **17**, 19371-19381, (2009).
80. J. S. Li, H. Y. Yu, S. M. Wong, G. Zhang, X. W. Sun, P. G. Q. Lo and D. L. Kwong, "Si nanopillar array optimization on Si thin films for solar energy harvesting," Appl. Phys. Lett. **95**, 033102-033104 (2009).
81. J. S. Li, H. Y. Yu, S. M. Wong, X. C. Li, G. Zhang, P. G. Q. Lo and D. L. Kwong, "Design guidelines of periodic Si nanowire arrays for solar cell application," Appl. Phys. Lett. **95**, 243113-243115 (2009).
82. L. Tsakalakos, J. Balch, J. Fronheiser, B. A. Korevaar, O. Sulima and J. Rand, "Silicon nanowire solar cells," Appl. Phys. Lett. **91**, 233117-233119 (2007).
83. T. Stelzner, M. Pietsch, G. Andra, F. Falk, E. Ose and S. Christiansen, "Silicon nanowire-based solar cells," Nanotechnology **19**, 295203 (2008).

84. E. C. Garnett and P. Yang, "Silicon Nanowire Radial p-n Junction Solar Cells," *J. Am. Chem. Soc.* **130**, 9224-9225, (2008).
85. J. A. Czaban, D. A. Thompson and R. R. LaPierre, "GaAs Core-Shell Nanowires for Photovoltaic Applications," *Nano Lett.* **9**, 148-154, (2008).
86. V. Sivakov, G. Andra, A. Gawlik, A. Berger, J. Plentz, F. Falk and S. H. Christiansen, "Silicon Nanowire-Based Solar Cells on Glass: Synthesis, Optical Properties, and Cell Parameters," *Nano Lett.* **9**, 1549-1554, (2009).
87. K. E. Plass, M. A. Filler, J. M. Spurgeon, B. M. Kayes, S. Maldonado, B. S. Brunschwig, H. A. Atwater and N. S. Lewis, "Flexible Polymer-Embedded Si Wire Arrays," *Adv. Mater.* **21**, 325-328, (2009).
88. Z. Y. Fan, D. J. Ruebusch, A. A. Rathore, R. Kapadia, O. Ergen, P. W. Leu and A. Javey, "Challenges and Prospects of Nanopillar-Based Solar Cells," *Nano Res.* **2**, 829-843, (2009).
89. M. D. Kelzenberg, S. W. Boettcher, J. A. Petykiewicz, D. B. Turner-Evans, M. C. Putnam, E. L. Warren, J. M. Spurgeon, R. M. Briggs, N. S. Lewis and H. A. Atwater, "Enhanced absorption and carrier collection in Si wire arrays for photovoltaic applications," *Nat. Mat.* **9**, 239-244, (2010).
90. E. Garnett and P. D. Yang, "Light Trapping in Silicon Nanowire Solar Cells," *Nano Lett.* **10**, 1082-1087, (2010).
91. H. C. Chang, K. Y. Lai, Y. A. Dai, H. H. Wang, C. A. Lin and J. H. He, "Nanowire arrays with controlled structure profiles for maximizing optical collection efficiency," *Energy Environ. Sci.* **4**, 2863-2869, (2011).
92. H. Bao and X. Ruan, "Optical absorption enhancement in disordered vertical silicon nanowire arrays for photovoltaic applications," *Opt. Lett.* **35**, 3378-3380, (2010).
93. C. X. Lin and M. L. Povinelli, "Optimal design of aperiodic, vertical silicon nanowire structures for photovoltaics," *Opt. Express* **19**, A1148-A1154, (2011).
94. S. E. Han and G. Chen, "Optical Absorption Enhancement in Silicon Nanohole Arrays for Solar Photovoltaics," *Nano Lett.* **10**, 1012-1015, (2010).
95. F. Wang, H. Yu, J. Li, X. Sun, X. Wang and H. Zheng, "Optical absorption enhancement in nanopore textured-silicon thin film for photovoltaic application," *Opt. Lett.* **35**, 40-42, (2010).
96. S. B. Mallick, M. Agrawal and P. Peumans, "Optimal light trapping in ultra-thin photonic crystal crystalline silicon solar cells," *Opt. Express* **18**, 5691-5706, (2010).
97. K.-Q. Peng, X. Wang, L. Li, X.-L. Wu and S.-T. Lee, "High-Performance Silicon Nanohole Solar Cells," *J. Am. Chem. Soc.* **132**, 6872-6873, (2010).
98. Y. Lu and A. Lal, "High-Efficiency Ordered Silicon Nano-Conical-Frustum Array Solar Cells by Self-Powered Parallel

- Electron Lithography," *Nano Lett.* **10**, 4651-4656, (2010).
99. J. Kim, A. J. Hong, J. W. Nah, B. Shin, F. M. Ross and D. K. Sadana, "Three-Dimensional a-Si:H Solar Cells on Glass Nanocone Arrays Patterned by Self-Assembled Sn Nanospheres," *Acs Nano* **6**, 265-271, (2012).
 100. S. Jeong, E. C. Garnett, S. Wang, Z. Yu, S. Fan, M. L. Brongersma, M. D. McGehee and Y. Cui, "Hybrid Silicon Nanocone-Polymer Solar Cells," *Nano Lett.* **12**, 2971-2976, (2012).
 101. K. X. Z. Wang, Z. F. Yu, V. Liu, Y. Cui and S. H. Fan, "Absorption Enhancement in Ultrathin Crystalline Silicon Solar Cells with Antireflection and Light-Trapping Nanocone Gratings," *Nano Lett.* **12**, 1616-1619, (2012).
 102. J. Zhu, Z. F. Yu, S. H. Fan and Y. Cui, "Nanostructured photon management for high performance solar cells," *Mat. Sci. Eng. R* **70**, 330-340, (2010).
 103. C. Heine and R. H. Morf, "SUBMICROMETER GRATINGS FOR SOLAR-ENERGY APPLICATIONS," *Appl. Opt.* **34**, 2476-2482, (1995).
 104. S. H. Zaidi, J. M. Gee, D. S. Ruby and Ieee, in *Conference Record of the Twenty-Eighth Ieee Photovoltaic Specialists Conference - 2000* (2000), pp. 395-398.
 105. F. Llopis and I. Tobias, "The role of rear surface in thin silicon solar cells," *Sol. Energy Mater. Sol. Cells* **87**, 481-492, (2005).
 106. A. Lin and J. Phillips, "Optimization of random diffraction gratings in thin-film solar cells using genetic algorithms," *Sol. Energy Mater. Sol. Cells* **92**, 1689-1696, (2008).
 107. R. Dewan and D. Knipp, "Light trapping in thin-film silicon solar cells with integrated diffraction grating," *J. Appl. Phys.* **106**, 074901, (2009).
 108. R. Dewan, M. Marinkovic, R. Noriega, S. Phadke, A. Salleo and D. Knipp, "Light trapping in thin-film silicon solar cells with submicron surface texture," *Opt. Express* **17**, 23058-23065, (2009).
 109. Y. P. Chiou, S. Y. Wu, C. Y. Chen, in *35th Ieee Photovoltaic Specialists Conference* (2010), pp. 1589-1591.
 110. D. Madzharov, R. Dewan and D. Knipp, "Influence of front and back grating on light trapping in microcrystalline thin-film silicon solar cells," *Opt. Express* **19**, A95-A107, (2011).
 111. J. M. Gee, *Optically enhanced absorption in thin silicon layers using photonic crystals*, *Conference Record of the Twenty-Ninth IEEE Photovoltaic Specialists Conference*, pp. 150-153, (2002).
 112. K. H. Yang and J. Y. Yang, "The analysis of light trapping and internal quantum efficiency of a solar cell with DBR back reflector," *Sol. Energy* **83**, 2050-2058, (2009).
 113. L. Zeng, Y. Yi, C. Hong, J. Liu, N. Feng, X. Duan, L. C. Kimerling and B. A. Alamariu, "Efficiency enhancement in Si solar cells by textured

- photonic crystal back reflector," *Appl. Phys. Lett.* **89**, 111111-111113 (2006).
114. N. N. Feng, J. Michel, L. Zeng, J. Liu, C. Y. Hong, L. C. Kimerling and X. Duan, "Design of highly efficient light-trapping structures for thin-film crystalline silicon solar cells," *IEEE Trans. Electron Devices* **54**, 1926-1933, (2007).
115. J. G. Mutitu, S. Y. Shi, C. H. Chen, T. Creazzo, A. Barnett, C. Honsberg and D. W. Prather, "Thin film silicon solar cell design based on photonic crystal and diffractive grating structures," *Opt. Express* **16**, 15238-15248, (2008).
116. L. Zeng, P. Bermel, Y. Yi, B. A. Alamariu, K. A. Broderick, J. Liu, C. Hong, X. Duan, J. Joannopoulos and L. C. Kimerling, "Demonstration of enhanced absorption in thin film Si solar cells with textured photonic crystal back reflector," *Appl. Phys. Lett.* **93**, 221105-221107 (2008).
117. P. G. O'Brien, N. P. Kherani, A. Chutinan, G. A. Ozin, S. John and S. Zukotynski, "Silicon photovoltaics using conducting photonic crystal back-reflectors," *Adv. Mater.* **20**, 1577-1582, (2008).
118. J. R. Tumbleston, D. H. Ko, E. T. Samulski and R. Lopez, "Electrophotonic enhancement of bulk heterojunction organic solar cells through photonic crystal photoactive layer," *Appl. Phys. Lett.* **94**, 043305, (2009).
119. D. H. Ko, J. R. Tumbleston, L. Zhang, S. Williams, J. M. DeSimone, R. Lopez and E. T. Samulski, "Photonic Crystal Geometry for Organic Solar Cells," *Nano Lett.* **9**, 2742-2746, (2009).
120. B. Curtin, R. Biswas and V. Dalal, "Photonic crystal based back reflectors for light management and enhanced absorption in amorphous silicon solar cells," *Appl. Phys. Lett.* **95**, 231102-231104, (2009).
121. S. Guldin, S. Huttner, M. Kolle, M. E. Welland, P. Muller-Buschbaum, R. H. Friend, U. Steiner and N. Tetreault, "Dye-Sensitized Solar Cell Based on a Three-Dimensional Photonic Crystal," *Nano Lett.* **10**, 2303-2309, (2010).
122. X. Sheng, J. F. Liu, I. Kozinsky, A. M. Agarwal, J. Michel and L. C. Kimerling, "Design and Non-Lithographic Fabrication of Light Trapping Structures for Thin Film Silicon Solar Cells," *Adv. Mater.* **23**, 843-847, (2011).
123. J. Upping, A. Bielawny, R. B. Wehrspohn, T. Beckers, R. Carius, U. Rau, S. Fahr, C. Rockstuhl, F. Lederer, M. Kroll, T. Pertsch, L. Steidl and R. Zentel, "Three-Dimensional Photonic Crystal Intermediate Reflectors for Enhanced Light-Trapping in Tandem Solar Cells," *Adv. Mater.* **23**, 3896-3900, (2011).
124. B. G. Lee, P. Stradins, D. L. Young, K. Alberi, T. K. Chuang, J. G. Couillard and H. M. Branz, "Light trapping by a dielectric nanoparticle back reflector in film silicon solar cells," *Appl. Phys. Lett.* **99**,

- 064101-064103, (2011).
125. H. Anma, Y. Yoshimoto, M. Tanaka, H. Takatsuka and Y. Hatanaka, "Preparation of ZnO thin films deposited by plasma chemical vapor deposition for application to ultraviolet-cut coating," *Jpn. J. Appl. Phys.*, Part 1 **40**, 6099-6103, (2001).
 126. R. X. Li, S. Yabe, M. Yamashita, S. Momose, S. Yoshida, S. Yin and T. Sato, "UV-shielding properties of zinc oxide-doped ceria fine powders derived via soft solution chemical routes," *Mater. Chem. Phys.* **75**, 39-44, (2002).
 127. S. Fay, J. Steinhäuser, N. Oliveira, E. Vallat-Sauvain and C. Ballif, "Opto-electronic properties of rough LP-CVD ZnO : B for use as TCO in thin-film silicon solar cells," *Thin Solid Films* **515**, 8558-8561, (2007).
 128. A. Taflove and S. Hagness, *Computational Electrodynamics: The Finite-Difference Time-Domain Method, Third Edition*. (Artech House Publishers, 2005).
 129. A. R. Forouhi and I. Bloomer, "OPTICAL DISPERSION-RELATIONS FOR AMORPHOUS-SEMICONDUCTORS AND AMORPHOUS DIELECTRICS," *Phy. Rev. B* **34**, 7018-7026, (1986).
 130. A. R. Forouhi and I. Bloomer, "OPTICAL-PROPERTIES OF CRYSTALLINE SEMICONDUCTORS AND DIELECTRICS," *Phys. Rev. B* **38**, 1865-1874, (1988).
 131. X. W. Sun and H. S. Kwok, "Optical properties of epitaxially grown zinc oxide films on sapphire by pulsed laser deposition," *J. Appl. Phys.* **86**, 408-411, (1999).
 132. M. G. Kang and L. J. Guo, "Nanoimprinted semitransparent metal electrodes and their application in organic light-emitting diodes," *Adv. Mater.* **19**, 1391-1396, (2007).
 133. M. G. Kang, T. Xu, H. J. Park, X. G. Luo and L. J. Guo, "Efficiency Enhancement of Organic Solar Cells Using Transparent Plasmonic Ag Nanowire Electrodes," *Adv. Mater.* **22**, 4378-4383, (2010).
 134. H. Wu, L. Hu, M. W. Rowell, D. Kong, J. J. Cha, J. R. McDonough, J. Zhu, Y. Yang, M. D. McGehee and Y. Cui, "Electrospun Metal Nanofiber Webs as High-Performance Transparent Electrode," *Nano Lett.* **10**, 4242-4248, (2010).
 135. B. O'Connor, C. Haughn, K. H. An, K. P. Pipe and M. Shtein, "Transparent and conductive electrodes based on unpatterned, thin metal films," *Appl. Phys. Lett.* **93**, 223304-223306, (2008).
 136. D. S. Ghosh, L. Martinez, S. Giurgola, P. Vergani and V. Pruneri, "Widely transparent electrodes based on ultrathin metals," *Opt. Lett.* **34**, 325-327, (2009).
 137. Z. C. Wu, Z. H. Chen, X. Du, J. M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J. R. Reynolds, D. B. Tanner, A. F. Hebard and A. G. Rinzler, "Transparent, conductive carbon nanotube films," *Science* **305**, 1273-1276,

- (2004).
138. M. Zhang, S. L. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, C. D. Williams, K. R. Atkinson and R. H. Baughman, "Strong, transparent, multifunctional, carbon nanotube sheets," *Science* **309**, 1215-1219, (2005).
 139. J. B. Wu, H. A. Becerril, Z. N. Bao, Z. F. Liu, Y. S. Chen and P. Peumans, "Organic solar cells with solution-processed graphene transparent electrodes," *Appl. Phys. Lett.* **92**, 263302-263304, (2008).
 140. J. B. Wu, M. Agrawal, H. A. Becerril, Z. N. Bao, Z. F. Liu, Y. S. Chen and P. Peumans, "Organic Light-Emitting Diodes on Solution-Processed Graphene Transparent Electrodes," *Acs Nano* **4**, 43-48, (2010).
 141. M. Cox, A. Gorodetsky, B. Kim, K. S. Kim, Z. Jia, P. Kim, C. Nuckolls and I. Kymissis, "Single-layer graphene cathodes for organic photovoltaics," *Appl. Phys. Lett.* **98**, 123303-123305, (2011).
 142. T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio and P. A. Wolff, "Extraordinary optical transmission through sub-wavelength hole arrays," *Nature* **391**, 667-669, (1998).
 143. P. B. Catrysse, W. J. Suh, S. H. Fan and M. Peeters, "One-mode model for patterned metal layers inside integrated color pixels," *Opt. Lett.* **29**, 974-976, (2004).
 144. J. Braun, B. Gompf, G. Kobiela and M. Dressel, "How Holes Can Obscure the View: Suppressed Transmission through an Ultrathin Metal Film by a Subwavelength Hole Array," *Phys. Rev. Lett.* **103**, 203901-203904, (2009).
 145. S. S. Xiao, J. J. Zhang, L. A. Peng, C. Jeppesen, R. Malureanu, A. Kristensen and N. A. Mortensen, "Nearly zero transmission through periodically modulated ultrathin metal films," *Appl. Phys. Lett.* **97**, 071116-071118, (2011).
 146. S. S. Xiao and N. A. Mortensen, "Surface-plasmon-polariton-induced suppressed transmission through ultrathin metal disk arrays," *Opt. Lett.* **36**, 37-39, (2011).
 147. T. Nakanishi, E. Tsutsumi, K. Masunaga, A. Fujimoto and K. Asakawa, "Transparent Aluminum Nanomesh Electrode Fabricated by Nanopatterning Using Self-Assembled Nanoparticles," *Applied Physics Express* **4**, 025201, (2011).
 148. T. Thio, H. F. Ghaemi, H. J. Lezec, P. A. Wolff and T. W. Ebbesen, "Surface-plasmon-enhanced transmission through hole arrays in Cr films," *J. Opt. Soc. Am. B* **16**, 1743-1748, (1999).
 149. Y. H. Ye and J. Y. Zhang, "Enhanced light transmission through cascaded metal films perforated with periodic hole arrays," *Opt. Lett.* **30**, 1521-1523, (2005).
 150. K. R. Catchpole and A. Polman, "Plasmonic solar cells," *Opt. Express* **16**, 21793-21800, (2008).

151. Z. Yu, A. Raman and S. Fan, "Fundamental limit of nanophotonic light trapping in solar cells," *P. Natl. Acad. Sci. USA* **107**, 17491-17496, (2010).
152. Z. Yu, A. Raman and S. Fan, "Fundamental limit of light trapping in grating structures," *Opt. Express* **18**, A366-A380, (2010).
153. V. E. Ferry, L. A. Sweatlock, D. Pacifici and H. A. Atwater, "Plasmonic Nanostructure Design for Efficient Light Coupling into Solar Cells," *Nano Lett.* **8**, 4391-4397, (2008).
154. H. A. Atwater and A. Polman, "Plasmonics for improved photovoltaic devices," *Nat. Mater.* **9**, 205-213, (2010).
155. N. S. Lewis, "Toward cost-effective solar energy use," *Science* **315**, 798-801, (2007).
156. B. Tian, X. Zheng, T. J. Kempa, Y. Fang, N. Yu, G. Yu, J. Huang and C. M. Lieber, "Coaxial silicon nanowires as solar cells and nanoelectronic power sources," *Nature* **449**, 885-889, (2007).
157. M. D. Kelzenberg, D. B. Turner-Evans, B. M. Kayes, M. A. Filler, M. C. Putnam, N. S. Lewis and H. A. Atwater, "Photovoltaic measurements in single-nanowire silicon solar cells," *Nano Lett.* **8**, 710-714, (2008).
158. J. Zhu, Z. F. Yu, G. F. Burkhard, C. M. Hsu, S. T. Connor, Y. Q. Xu, Q. Wang, M. McGehee, S. H. Fan and Y. Cui, "Optical Absorption Enhancement in Amorphous Silicon Nanowire and Nanocone Arrays," *Nano Lett.* **9**, 279-282, (2009).
159. B. M. Kayes, H. A. Atwater and N. S. Lewis, "Comparison of the device physics principles of planar and radial p-n junction nanorod solar cells," *J. Appl. Phys.* **97**, 114302-114311, (2005).
160. E. D. Palik, *Handbook of Optical Constants of Solids*,. (Academic Press, San Diego, CA, 1998).
161. Q. G. Du, C. H. Kam, H. V. Demir, H. Y. Yu and X. W. Sun, "Enhanced optical absorption in silicon nano-cone-hole array for photovoltaic applications," *Opt. Lett.* **36**, 1713-1715, (2011).
162. R. A. Street, W. S. Wong and C. Paulson, "Analytic Model for Diffuse Reflectivity of Silicon Nanowire Mats," *Nano Lett.* **9**, 3494-3497, (2009).
163. A. Chutinan and S. John, "Light trapping and absorption optimization in certain thin-film photonic crystal architectures," *Phys. Rev. A* **78**, 15, (2008).