

**SIMULATION STUDIES OF EFFICIENCY
ENHANCEMENT OF EPITAXIAL THIN FILM
SILICON SOLAR CELL BY PLASMONIC
NANOSTRUCTURES**

LIM SHYUE PIIN

UNIVERSITI SAINS MALAYSIA

2015

**SIMULATION STUDIES OF EFFICIENCY ENHANCEMENT OF
EPITAXIAL THIN FILM SILICON SOLAR CELL BY PLASMONIC
NANOSTRUCTURES**

by

LIM SHYUE PIIN

**Thesis submitted in fulfillment of the
requirements for the degree
of Master of Science**

February 2015

ACKNOWLEDGEMENTS

First of all, I would like to thank my supervisor, Prof. Md Roslan Hashim for his patience and guidance throughout this work. Without the help from my supervisor, I would not be able to overcome some major problems that I encounter in this work.

I would also like to thank my friend, Mr. Lee Sai Cheong for his helpful discussion regarding curve fitting of Lorentz-Drude model for dielectric function. Thanks to Mr. Lee Sai Cheong for his advice regarding master's study.

I would like to thank Mr Mohammad Zaki for his help in Silvaco Atlas simulation at the beginning of my master's study. Special thanks to all the supporting staffs in N.O.R lab for their assistance.

I would like to acknowledge Ministry of Science, Technology and Innovation (MOSTI) for the scholarship granted. I would also like to acknowledge Universiti Sains Malaysia for the postgraduate research grant (USM-RU-PRGS) granted with account no. 1001/PFIZIK/843035.

Finally, I would like to thank my father and mother for their support and help given throughout my study.

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LIST OF SYMBOLS

r_1	Inner silica core radius
r_2	Total particle radius
α	Polarizability
π	Pi constant
a	Radius of sphere
ε	Dielectric function of sphere
ε_m	Dielectric constant of the surrounding medium
ω	Angular frequency
C_{sca}	Scattering cross section
C_{abs}	Absorption cross section
k	Wave vector
C_{ext}	Extinction cross section
Q_{sca}	Scattering efficiency
Q_{abs}	Absorption efficiency
a_1	Inner radius
a_2	Outer radius
ε_1	Dielectric function of core material

ϵ_2	Dielectric function of shell material
f	The fraction of the total particle volume occupied by the core.
a_n	Scattering coefficient
b_n	Scattering coefficient
ψ_n	Riccati-Bessel function
ξ_n	Riccati-Bessel function
x	Size parameter
m	Relative refractive index
$N_{particle}$	Refractive index of particle
N_{medium}	Refractive index of medium
f_{subs}	Fraction of light scattered into substrate
d_{av}	The ratio of the optical path length in a single pass through a substrate to the thickness of the substrate, averaged over the angular distribution of the scattered light.
ϵ_{∞}	The value of ϵ as ω approaching ∞
ϵ_{inter}	Dielectric function component which describes interband electron transitions from d-band to sp-band (conduction band).
ϵ_{intra}	The dielectric function component that describes intraband electron transitions in sp-band.
$\Delta\epsilon_{Ln}$	The shift in relative permittivity at electron transition

δ_{Ln}	The electron dephasing rate.
ω_D	Plasma frequency
γ	Collision frequency
\hbar	hbar constant
I_{sc}	Short circuit current
V_{oc}	Open circuit voltage
V_m	Maximum output voltage
I_m	Maximum output current
P_m	Maximum Output Power

LIST OF ABBREVIATIONS

Ag	Silver
Ag ₂ O	Silver oxide
AM 1.5	Air mass 1.5 condition
Au	Gold
BSF	Back surface field
BSR	Back surface reflector
CdTe	Cadmium telluride
CIGS	Copper indium gallium diselenide
CIS	Copper indium diselenide
CPV	Concentrated photovoltaic
c-Si	Crystalline silicon
Cu	Copper
CuInGaSe ₂	Copper indium gallium diselenide
CuInSe ₂	Copper indium diselenide
EQE	External quantum efficiency
ESA	Excited state absorption
ETU	Energy transfer up-conversion

FDTD	Finite-difference time-domain
FSE	Forward-scattering efficiency
Ga	Galium
GaN	Galium Nitride
GaAs	Galium Arsenide
GSA	Ground state absorption
HMA	Highly Mismatched Alloys
HWCVD	Hot-wire chemical vapor deposition
IB	Intermediate band
In	Indium
InGaN	Indium Galium Nitride
ITO	Indium Tin Oxide
LTE	Light trapping efficiency
LSPR	Localized Surface Plasmon Resonance
MEG	Multiple exciton generation
MgF ₂	Magnesium Fluoride
NP	Nanoparticle
P3HT	poly(3-hexylthiophene)
PCBM	phenyl-C60-butyric acid methyl ester

PERL	Passivated emitter, rear locally diffused
PML	Perfectly matched layers
PV	Photovoltaic
QW	Quantum well
Se	Selenium
SERS	Surface-enhanced raman scattering
Si	Silicon
Si ₃ N ₄	Silicon nitride
SiO ₂	Silicon dioxide
SiO _x	Silicon Oxide
SOI	Silicon-on-insulator
Te	Tellurium
TFSF	Total-field / scattered-field
TiO ₂	Titanium dioxide
UV	Ultraviolet

**SIMULASI KAJIAN PENINGKATAN KECEKAPAN SEL SOLAR
EPITAKSI FILEM NIPIS SILIKON OLEH NANOSTRUKTUR PLASMONIK**

ABSTRAK

Kajian simulasi tentang kesan nanostruktur teras shell plasmonic ke atas prestasi sel solar filem nipis silikon dilaporkan. Enam nanostruktur teras shell yang dikaji ialah Ag nanoshell, Au nanoshell, Cu nanoshell, Ag-teras SiO₂-shell zarah, Au-teras SiO₂-shell zarah dan Cu-teras SiO₂-shell zarah. Dipolar resonants plasmon permukaan (LSPR) nanostruktur telah diubah ke 850 nm (berhampiran kawasan inframerah) dengan mengubah diameter teras. Untuk Ag nanoshell, diameter teras juga diubah untuk mendapatkan LSPR pada 807 nm dan 927 nm. Diameter teras yang telah ditetapkan sebelum ini digunakan dalam simulasi respons spektrum, kecekapan quantum luar, spektrum refleksi dan transmisi dan ciri-ciri IV sel solar filem nipis silikon dengan kehadiran nanostruktur teras shell. Peningkatan respons sel solar terhadap cahaya berhampiran inframerah dikaitkan dengan penyebaran cahaya yang kuat ke hadapan dan kesan memerangkap cahaya yang diperuntukan oleh LSPR dipol struktur-struktur nano teras shell. Ag, Au dan Cu nanoshells meningkatkan respons spektrum sel solar filem nipis silikon dalam julat sudut tuju cahaya yang besar (30° ke 90°). Selepas pengoptimuman kepadatan permukaan, Ag nanoshell dengan jejari dalaman 35 nm dan jejari luar 45 nm memberikan peningkatan kecekapan penukaran kuasa cahaya terbesar (peningkatan sebanyak 38.1%) di antara nanostruktur yang dikaji. Kecekapan penukaran kuasa cahaya adalah setinggi 9.20% untuk sel solar filem nipis silikon dengan Ag nanoshells.

**SIMULATION STUDIES OF EFFICIENCY ENHANCEMENT OF
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ABSTRACT

Simulation studies of the effects of plasmonic core-shell nanostructures on the performance of thin film silicon solar cell were reported. Six different core-shell nanostructures were studied. They are Ag nanoshell, Au nanoshell, Cu nanoshell, Ag-core SiO₂-shell particle, Au-core SiO₂-shell particle and Cu-core SiO₂-shell particle. The dipole localized surface plasmon resonances (LSPR) of these nanostructures were tuned to 850 nm (near infrared region) by varying their core diameter. For Ag nanoshell, the core diameter is also varied to obtain LSPR at 807 nm and 927 nm. These predetermined core diameters were then used in the simulation of spectral response, external quantum efficiency, reflection and transmission spectra and I-V characteristics of thin film silicon solar cell in the presence of the core-shell nanostructures. The enhanced near infrared light response of the solar cell was associated to the strong forward scattering and light trapping effect provided by dipolar LSPR of core-shell nanostructures. Ag, Au and Cu nanoshells enhance spectral response of thin film silicon solar cells over broad range of incidence angles of light (30° to 90°). After surface coverage optimization, Ag nanoshell with inner radius of 35 nm and outer radius of 45 nm produces the largest enhancement (38.1 % increase) of power conversion efficiency among the nanostructures simulated with power conversion efficiency as high as 9.20% for thin film silicon solar cell with Ag nanoshells.

CHAPTER 1

INTRODUCTION

1.1 Motivation

Silicon is a good photovoltaic material since it has an energy band gap of 1.1eV which is near to the ideal bandgap of 1.4 eV for single-junction solar cell and it is abundant, non-toxic. Silicon is one of the most researched and technologically developed materials. Cadmium telluride (CdTe) thin film solar cells, the strongest competition to silicon solar cell, might have problem in tera-watt scale production due to the scarcity of tellurium (Te). CdTe solar cell is toxic and would need end-of-life disposal plan. Scarcity of indium (In), gallium (Ga) and selenium (Se) might prevent large scale production of certain solar cells such as copper indium diselenide (CuInSe₂ or CIS) and copper indium gallium diselenide (CuInGaSe₂ or CIGS) solar cells.

Epitaxial thin film silicon solar cell is a potential candidate for low cost and high efficiency solar cell. Energy conversion efficiency above 15% can be achieved for silicon solar cell with active layer thickness as low as 0.5 μm by optimizing light trapping (Poortmans, 2006). Branz et al. have demonstrated a fast, scalable, inexpensive epitaxy of high-quality crystalline silicon (c-Si) at substrate temperatures from 620 to 800 °C by hot-wire chemical vapor deposition (HWCVD) (Branz et al., 2011). This technique can be used to produce thin film silicon solar cell

of high material quality at low cost on inexpensive substrates such as display glass and metal foil.

The use of metal nanostructures in enhancing the performance of solar cell is gaining a lot of attention in recent years (Temple et al., 2009; Wang et al., 2010; Schmid et al., 2010; Qu et al., 2011; Temple and Bagnall, 2011; Li et al., 2011; Paris et al., 2012; Fahim et al., 2012). Metal nanostructures placed on the surface of solar cell scatter incident light preferentially into solar cell and thus improving the transmission of light into solar cell (Catchpole and Polman, 2008). The fraction of incident light scattered into solar cell can reach as high as 90% for hemispherical nanoparticles at certain wavelength range (Catchpole and Polman, 2008). Pillai et al. measured the total and diffuse reflectance of plain silicon wafer and silicon wafers with silver (Ag) islands on top. They observed reduced total reflectance in the visible wavelength range for silicon wafers with Ag islands on top which shows that Ag islands act as antireflection coating in that regime (Pillai et al., 2007). They also found that scattering increases when the size of Ag islands increases as evident from diffuse reflectance measurements. Apart of this antireflective behavior of metal nanostructures, metal nanostructures can provide light trapping in thin film solar cell. Metal nanostructures placed on top of thin film solar cell couple incident light into guided modes and increase the optical path length and absorption of light (Spinelli et al., 2012). Metal nanostructures placed on top of solar cell can serve as a better light trapping method since it does not increase surface recombination of solar cell as compared to surface texturing (Pillai, 2007). So far, most of the research of particle plasmon enhanced silicon solar cell focus on simple metal nanoparticles and less attention is given to other types of particles (Derkacs et al., 2006; Pillai et al., 2007; Hägglund et al., 2008; Rockstuhl and Lederer, 2009; Beck et al., 2009; Temple and

Bagnall, 2011; Ouyang et al., 2011; Singh et al., 2013). The use of other types of particles such as metal nanoshells and metal-core dielectric-shell particles provide some advantages over simple metal nanoparticles. The use of nanoshells allows easy tuning of surface plasmon resonance wavelength across the entire visible and infrared regions of the electromagnetic spectrum (Halas, 2005). This tuning is done by adjusting the relative core and shell dimensions (Hirsch et al., 2006). So far, the use of metal nanoshell has been limited to surface-enhanced raman scattering (SERS) substrate, chemical sensing and biomedical application (Halas, 2005; Hirsch et al., 2006). The use of metal nanoshell in solar cell might reduce the use of expensive metal such as gold (Au) since a thin layer of metal shell is coated on a dielectric core as compared to simple metal nanoparticles. Ag nanoparticles placed on top of thin film solar cell provide optical absorption enhancement. However, the oxidation of Ag nanoparticles' surface when they are in contact with air or moisture can reduce the efficiency enhancement of solar cell provided by Ag nanoparticles (Akimov and Koh, 2010). This decrease in enhancement is due to the reduced size of Ag core and increased absorption of light by silver oxide (Ag_2O) shell (Akimov and Koh, 2010). Silicon dioxide (SiO_2) is a stable dielectric material and can be used to isolate metal nanoparticle from air or moisture. Nanoparticles which consist of metal core coated with SiO_2 layer might prevent or at least slow down the oxidation of metal nanoparticles' surface. In this work, the use of metal nanoshells and metal-core SiO_2 -shell particles in thin film silicon solar cell are explored and their effects on the performance of thin film silicon solar cell are investigated.

1.2 Objectives and Scope of work

The main objective of this dissertation is to investigate the effects of metal nanoshells and metal-SiO₂ core-shell nanoparticles on the performance of thin film silicon solar cell. All the works done in this dissertation are theoretical works based on finite-difference time-domain (FDTD) simulation. The objectives of this works are listed below:

- (a) To investigate the effects of three different nanoshells i.e. Ag, Au and Cu nanoshells on the performance of thin film silicon solar cell at different incident angles of light and to optimize the surface coverage of Ag nanoshells.
- (b) To investigate the effects of three different metal-dielectric core-shell nanoparticles i.e. Ag core SiO₂ shell nanoparticles, Au core SiO₂ shell nanoparticles and Cu core SiO₂ shell nanoparticles on the performance of thin film silicon solar cell.

1.3 Originality of the research

1. The use of metal nanoshells and metal-SiO₂ core-shell nanoparticles to improve the performance of thin film silicon solar cell.
2. The effects of metal nanoshells on the performance of thin film silicon solar cell at different light incident angles.
3. The effects of size and surface coverage of Ag nanoshell on the performance of thin film silicon solar cell.

1.4 Thesis outline

After introduction in this chapter, three generations of photovoltaic and research on particle plasmon enhanced solar cell are reviewed in chapter 2. Chapter 3 gives definition of localized surface plasmon and discusses the quasi-static approximation, Mie theory, the enhancement mechanism of particle plasmon enhanced solar cell and the design principles of plasmonic solar cell. Chapter 4 describes the three stages of the simulation work which involve fitting of Drude-Lorentz model to experimental data, tuning of localized surface plasmon resonance of core-shell nanostructures and the simulation of optical and electrical characteristics of thin film silicon solar cell in the presence of core-shell nanostructures. Chapters 5, 6 and 7 illustrate the main results of the research. The spectral response, external quantum efficiency, reflection and transmission spectra and I-V characteristics of thin film silicon solar cell in the presence of Ag nanoshell, Au nanoshell and Cu nanoshell are given in chapter 5 followed by the corresponding simulation results for Ag-core SiO₂-shell particle, Au-core SiO₂-shell particle and Cu-core SiO₂-shell particle in chapter 6. In chapter 7, simulation results for Ag nanoshells of three different sizes and surface coverages are presented. The effects of metal nanoparticles and metal microparticles on the performance of thin film silicon solar cell are compared and studied in chapter 7. Finally, chapter 8 concludes the work in this dissertation and suggests possible future work in the field.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter gives overview of photovoltaic research from first generation to third generation photovoltaic. This chapter also discusses the issues of conventional surface texturing of solar cell for light trapping. Important works on the use of plasmonic nanostructures to enhance the performance of solar cell are reviewed.

2.2 Overview of Photovoltaic Research

Photovoltaic (PV) technology is a potential solution for global warming issue which is mainly caused by greenhouse gases emission during electrical power generation by means of burning fossil fuels i.e. oil, coal and natural gas. Solar energy is abundant and in fact, the amount of energy that the sun radiates upon earth in 1 hour is more than that used in 1 year by humanity. However, the price of solar cell is still too expensive as compared with fossil fuel. In order to compete with fossil fuel, the cost of solar cell has to be reduced by a factor of 2-5 (Atwater and Polman, 2010). Currently, solar cell market is dominated by first generation solar cell i.e. silicon wafer-based solar cell. In 2011, silicon wafer-based PV accounted for about 86% of the global PV market share with monocrystalline silicon wafer make up 40% of the global market share (Fraunhofer ISE, 2012). Researchers from University of New

South Wales set the world-record efficiency of 25% for wafer-based crystalline silicon solar cell (passivated emitter, rear locally diffused - PERL) in 1998 (Zhao et al., 1998; Green, 2009; Green et al., 2012). The thicknesses of silicon wafers are between 180-300 μm . Most of the cost of silicon wafer-based solar cell is from silicon materials and processing. Producing silicon feedstock from silane or trichlorosilane, growing silicon crystals at temperature above 1414°C and sawing ingots into wafers with kerf loss of about 50% are costly steps in manufacturing silicon wafer-based solar cell.

In order to lower the cost of solar cell, second generation solar cell i.e. thin film solar cell was introduced. Thin film solar cell was manufactured by depositing thin layers of photoactive materials on low cost substrate or superstrate instead of growing ingots for wafer production. Thus, the cost per unit area of thin film solar cell is a lot lesser than that of wafer-based solar cell. Photoactive materials used in thin film solar cell include indirect band gap semiconductor such as polycrystalline silicon and direct band gap semiconductors such as amorphous silicon, cadmium telluride (CdTe), copper indium diselenide (CuInSe₂ or CIS), copper indium gallium diselenide (CuInGaSe₂ or CIGS) and gallium arsenide (GaAs). Materials such as poly(3-hexylthiophene) (P3HT) and phenyl-C60-butyric acid methyl ester (PCBM) are used in organic thin film solar cell. There has been a lot of research interest in epitaxial growth of thin film silicon directly on cheap substrate as low cost alternative to wafer-based silicon cell (Thiesena et al., 1999; Rentsch et al., 2003; Ai et al., 2005; Duerinckx et al., 2005; Aberle, 2006; Nieuwenhuysen et al., 2006; Teplin et al., 2006; Andrä et al., 2008; Gordon et al., 2009; Nieuwenhuysen et al., 2009; Gordon et al., 2010; Kuzma-Filipek et al. 2010; Fukuda et al., 2011). Global PV market share of thin film PV in 2011 is 14% with cadmium telluride leads with

global market share of about 8% (Fraunhofer ISE, 2012). Thickness of photoactive layer in thin film solar cell ranges from a few nanometers to tens of micrometers. Reduced thickness of photoactive layers in thin film solar cell as compared to wafer-based solar cell has resulted in lower absorption of light and thus, lower efficiency. Nevertheless, the manufacturing cost per watt of thin film solar cell is lower than that of wafer-based solar cell.

Third generation solar cell is developed to bring down the total cost per watt to below US\$ 0.50/W or better (UNSW, 2004). Third generation PV are based on operating principles that would increase PV efficiency above Shockley-Queisser limit i.e. theoretical efficiency limit for a single junction solar cell (31% for one sun illumination) while having cost per unit area similar to second generation PV (Shockley and Queisser, 1960). One of the approaches to achieve high solar cell efficiency is the development in multi-junction solar cell which can harness solar spectrum more efficiently. Multi-junction solar cell, also called tandem solar cell, is consist of stack of solar cells arranged in the order of decreasing bandgap energy where high energy photons are absorbed in the upper cell while lower energy photons pass to the lower cells (Green, 2002). In June 19, 2013, National Renewable Energy Laboratory (NREL) announced a world record of 31.1% conversion efficiency for a two-junction solar cell under one sun illumination (NREL, 2013). Sharp Corporation holds the world records of 37.9% conversion efficiency for a triple-junction solar cell under one sun illumination in February 2013 and 44.4% conversion efficiency for a concentrator triple-junction solar cell at 302 times concentrated sunlight in April 2013 (Sharp, 2013). The applications of multi-junction solar cells are limited due to their high cost. Multi-junction solar cells are used in aerospace due to their high power to weight ratio and in concentrated photovoltaic

(CPV) systems of utility-scale power plant. Active research has been going on to lower the cost and increasing the efficiency of multi-junction solar cell.

Another way to achieve high solar cell efficiency is by developing intermediate-band (IB) solar cell. IB solar cells are based on the concept of having narrow density of states within the bandgap of a semiconductor to allow sub-bandgap photon absorption while maintaining the same open circuit voltage (Brown and Wu, 2009). Quantum dots, quantum wells and Highly Mismatched Alloys (HMA) can be used to make IB solar cell.

It was suggested that the efficiency of single-junction solar cell can be improved by utilizing hot carriers (Ross and Nozik, 1982). When photons with energy greater than the bandgap are being absorbed, electrons are excited and occupy states with higher energy than the conduction band minimum. These energies in excess of the bandgap will be lost through thermalization in less than 0.5 picosecond in most bulk semiconductors (Shank et al., 1979). However, thermalization time in quantum systems such as quantum wells and quantum dots can be much larger than 0.5 picosecond (Benisty et al., 1991). There are two ways to realize hot carrier cells. They are hot-carrier extraction or multiple exciton generation (MEG). For hot-carrier extraction, the carriers are collected by energy selective contacts which collect carriers of certain energy only before thermalization occur. Theoretical calculation shows that hot carrier extraction can increase the efficiency of solar cell to more than 80% under fully concentrated sunlight (Ross and Nozik, 1982). For MEG, the excess energy of electrons are used to generate more excitons. These electrons have to have energy of at least two times the bandgap energy. Theoretically, MEG can enhance the efficiency of solar cell to over 44% under 1 sun AM 1.5 spectrum and

approaching that of hot carrier cells under maximum concentrated sunlight condition (Green, 2003; Hanna and Nozik, 2006).

Spectrum conversion is another way to achieve higher efficiency in solar cell. Through spectrum conversion, solar spectrum is converted to a spectrum more suitable for solar cell. Up-conversion process converts sub-bandgap photons to above-bandgap photons while down-conversion process converts above-bandgap photons to multiple lower energy photons. Two types of up-conversion process that are most frequently discussed are ground state absorption/excited state absorption (GSA/ESA) and energy transfer up-conversion (ETU) (Brown and Wu, 2009). For GSA/ESA, two sub-bandgap photons are subsequently absorbed and converted to a higher energy photon. For ETU, sub-bandgap photons are absorbed by separate ions and one ion transfer energy non-radiatively to its neighboring ion. Spectrum conversion is implemented by adding a conversion layer above or at the back of solar cell and is compatible with many solar cell technologies (Trupke et al., 2002).

In this work, we will focus on improvement of efficiency of second generation solar cell i.e. thin film silicon solar cell by depositing metal nanoparticles on top of solar cell. This will be discussed in more details in next section.

2.3 Plasmonic Enhancement of Efficiency of Thin Film Solar Cell

The thickness of photoactive layer in thin film solar cell is a very small fraction of that in wafer-based solar cell. This has caused lower light absorption and lower efficiency. Therefore, light trapping is very important in thin film solar cell to increase its effective thickness and allow sufficient near-bandgap light absorption. The conventional light trapping technique used in wafer-based solar cell is based on

pyramidal surface texture that scatters light into solar cell at large angular range such as that used in PERL (passivated emitter rear locally-diffused) solar cell fabricated by researchers of University of New South Wales (Zhao et al., 1999). This conventional technique is not suitable for thin film solar cell since the feature size of surface texture which is typically about ten microns is comparable or larger than the thickness of thin film solar cell. Sub-micron texturing of substrate or transparent conductive oxide on which the solar cell is fabricated provides light trapping but also increases minority carrier recombination losses in the surface and junction region due to larger surface area. Sub-micron texturing of the surface of solar cell by plasma etching also increases surface recombination losses. These increases in recombination losses partially offset the gain provided by light trapping. In order to further improve the efficiency of thin film solar cell, a better light trapping method that does not increase recombination losses is needed.

Light scattering by using localized surface plasmon can serve as a better way of light trapping which does not increase recombination loss. A metal nanostructure placed in a homogeneous medium will scatter light almost symmetrically in the forward and backward direction when light is incident on it (Bohren and Huffman, 1998). However, when metal nanostructure is placed on the surface of solar cell, most of the light will be scattered in the forward direction into solar cell as solar cell has higher permittivity than air. The fraction of light scattered into solar cell can reach between 80% and 90% at wavelength range of 500-800 nm for the case of cylindrical silver nanoparticle with diameter of 100 nm and height of 50 nm placed on top of 10 nm thick silicon dioxide underlayer on silicon (Catchpole and Polman, 2008). Furthermore, metal nanostructure also couples large fraction of incident light into solar cell at an angle larger than critical angle of reflection and causes the light

to be trapped in the solar cell. Light that is reflected to the surface of solar cell is mostly radiated back into solar cell by metal nanostructure on the surface. Thus, light passes through the solar cell several times and optical path length and absorption of light are increased. Stuart and Hall pioneer the research on using metal nanostructures to enhance the absorption of a thin semiconductor layer. Metal island film was deposited on a spacer layer on silicon-on-insulator (SOI) photodetector with 160 nm-thick active layer and photocurrent enhancement was observed for most of the wavelengths between 400 and 1060 nm (Stuart and Hall, 1996). The enhancement was associated with the coupling of light into waveguide modes of the SOI structure. In another study by Stuart and Hall, the size of the silver islands on top of the SOI photodetector was varied and photocurrent enhancement by 18 times at 800 nm wavelength was observed for the case of 108 nm mean particle diameter (Stuart and Hall, 1998). Schaadt et al. fabricated silicon pn junction diodes with gold nanoparticles deposited on top. Enhanced photocurrent response was observed for the diodes with gold nanoparticles at wavelength shorter than ~900 nm (Schaadt et al., 2005). The enhancement was attributed to the near field of localized surface plasmon in silicon which is of much greater amplitude than the incident field and increased interaction time between the field and the semiconductor. Derkacs et al. fabricated amorphous silicon p-i-n thin film solar cell with 100 nm diameter gold nanoparticles deposited on the surface at concentration of $3.7 \times 10^8 \text{ cm}^{-2}$ (Derkacs et al., 2006). They reported 8.1% increase in short-circuit current density and 8.3% increase in energy conversion efficiency for amorphous silicon solar cell with gold nanoparticles compared with that without gold nanoparticles. Finite-element electromagnetic simulations by Derkacs et al. show that Au nanoparticles causes increased transmission of light into solar cell and increased concentration of

electromagnetic fields in the amorphous silicon layer, and suggest that larger increase can be achieved by higher particle densities. Pillai et al. deposited silver nanoparticles on SOI solar cell with 1.25 μm active layer and on 300 μm thick wafer-based silicon solar cell. They found that localized surface plasmons on silver nanoparticles increase the spectral response of thin film solar cell over almost the entire solar spectrum (Pillai et al., 2007). They also observed photocurrent enhancement for wavelength larger than 500 nm for the case of silver nanoparticles (sizes correspond to 12 nm and 14 nm mass thickness of silver) on top of wafer-based silicon solar cell. They measured reduced total reflectance for silver nanoparticles on top of silicon wafer as compared with plain silicon wafer for most of the wavelengths in wavelength range from 300 nm to 1200 nm. This shows that silver nanoparticles acts as an antireflection coating over that wavelength range. Diffuse reflectance measurement shows increased scattering for larger particles as compared to smaller particles. They reported 16 fold enhancement at 1050 nm wavelength for SOI solar cells and 7 fold enhancement for wafer-based silicon solar cells at 1200 nm wavelength. Lim et al. performed spectral response measurements on silicon pn junction photodiodes with and without gold nanoparticles deposited on top. They found that gold nanoparticles at density of $\sim 3 \times 10^8 \text{ cm}^{-2}$ increased photocurrent of the photodiode at wavelengths of 600 nm to over 1000 nm, but decreased photocurrent at wavelengths below 600 nm (Lim et al., 2007). Finite-element numerical simulations by Lim et al. agree well with the above observations and show that the phase relationship between the electromagnetic field component transmitted across the silicon surface and that scattered by Au nanoparticle is wavelength dependent. They found that at wavelengths below surface plasmon resonance wavelength, destructive interference occur between the transmitted and

scattered field components which results in reduced photocurrent while at wavelengths above resonance wavelength, constructive interference occur between the transmitted and scattered field components which results in enhanced photocurrent (Lim et al., 2007). Xu et al. fabricated silver nanoparticles on top of silicon dioxide (SiO_2) layer which is on the surface of wafer-based silicon solar cell. They studied the effect of SiO_2 layer thickness on the performance of the plasmonic solar cell. As the thickness of SiO_2 layer increases from 0 nm to 35 nm, the efficiency of the plasmonic solar cell increases from 4.3% to 6.1% and as the thickness of SiO_2 layer increases further to 100 nm, the efficiency decreases to 4.9% (Xu et al., 2012). They also observed that external quantum efficiency (EQE) spectra become narrower as the thickness of SiO_2 layer increases from 9 nm to 100 nm. Significant overall EQE enhancement at 400-1100 nm wavelength range was observed by them when SiO_2 layer thickness is 9-35 nm. They concluded that 9-35 nm were the appropriate SiO_2 thicknesses for broadening of plasmon resonance and narrowing of photocurrent suppression range. Sardana et al. deposited silver nanoparticles on textured silicon substrates by using RF magnetron sputtering for different deposition time (15 s, 30 s, 60 s, 120 s, and 180 s), followed by annealing at three different temperatures 200°C, 300°C, and 400 °C in nitrogen environment for 1 hour. They reported that sample with deposition time of 120 s and annealed at 300°C gave the highest average reflectance reduction of 8.05 % in wavelength range from 300 nm to 1100 nm (Sardana et al., 2014). They observed efficiency increase of the sample from 4.49% to 6.42% along with improvement in series resistance, fill factor, and open-circuit voltage. Derkacs et al. demonstrated improved power conversion efficiency of InP/ InGaAsP multiple-quantum-well p-i-n solar cell with 100-nm-diameter gold nanoparticles deposited on top. They reported reduced photocurrent

response of the solar cell with Au nanoparticles at wavelengths of ~570 nm and below and associated it with phase shift in the scattered wave which causes partial destructive interference between the scattered and the directly transmitted waves (Derkacs et al., 2008). They attribute photocurrent increase (from ~570 nm to over 900 nm) to strong forward scattering of light by Au nanoparticles. They observed increase in photocurrent response at wavelengths between 960 nm and cutoff at 1200 nm. They attributed this to the coupling of incident radiation into lateral optical propagation mode supported by the quantum wells. Nakayama et.al fabricated thin film gallium arsenide solar cell on gallium arsenide substrate with silver nanoparticles deposited on top surface by masked deposition through anodic aluminum oxide templates. 4 different Ag nanoparticle arrays were studied and they are densely formed low (DL) nanoparticles, sparsely formed low (SL) nanoparticles, densely formed high (DH) nanoparticles, and sparsely formed high (SH) nanoparticles. They found that all the nanoparticle-deposited cells have decreased photocurrent responses at wavelengths shorter than ~600 nm but enhanced photocurrent responses at longer wavelengths (Nakayama et.al, 2008). Solar cell with DH nanoparticles show largest photocurrent enhancement with an 8% increase in the short circuit current density and it is attributed to the strong scattering by the interacting surface plasmons. Pryce et.al demonstrated enhanced external quantum efficiency (EQE) of 2.5 nm thick indium gallium nitride (InGaN) single quantum well (QW) based photovoltaic devices due to the presence of 100-nm-diameter silver nanoparticles on the surface. Ag nanoparticles were deposited by using porous anodic aluminum oxide masking technique. The presence of Ag nanoparticles enhanced the photocurrent of QW solar cell (50 nm emitter layer thickness) by 6% with the increase occurring mainly in the InGaN QW layer (Pryce et.al, 2010).

Photocurrent of QW solar cell (200 nm emitter layer thickness) was enhanced by 54% by the presence of Ag nanoparticles with the enhancement due primarily to the increased light absorption and photogenerated carrier collection in the p-GaN emitter layer. Pryce et al. suggested the observed photocurrent enhancement may be caused by a combination of scattering, local field enhancement, and antireflection coating effects. Wan et al. perform simulation on transmission and reflection spectra of Si substrate with a monolayer of gold nanoparticle (Au NP) array deposited on top at different surface coverages in the near field regime by using three dimensional finite-difference time-domain (FDTD) method. They found that the enhancement in transmission power occur at longer wavelengths when the Au NP surface coverage increases, while transmission power decreased dramatically at wavelengths smaller than 550 nm (Wan et al., 2010). They attribute the increases in transmission power to the forward scattering of the Au NPs while the dip in the transmission power curves at wavelength range smaller than 550 nm was due to the intrinsic absorption of Au NPs. They performed FDTD simulations of the transmission spectra of silicon substrates with ultralow reflection surfaces (a layer of Si_3N_4 antireflection coating or a pyramidal textured structure) and found that Au NPs array deposited on the surface reduces the total transmission power into silicon substrate. They also experimentally demonstrated Au NPs array suppress photocurrents of a commercial textured cell with Si_3N_4 antireflection coating and a planar cell (under no-reflection condition i.e. illuminated by transverse magnetic polarized light at Brewster's angle). The above findings show that Au NPs array cannot improve but lower the spectral response of wafer-based silicon solar cells if the solar cell already have ultralow reflection surface. This proves that Au NPs array acts as deficient antireflection coating for wafer-based silicon solar cell which can reduce the amount of reflected light but

strongly absorbs the incident light at surface plasmon resonance wavelengths. Yang et al. suggested that resonant localized surface plasmon (LSP) modes of nanoparticle and nanoparticle-induced local Fabry-Perot (FP) modes were the mechanisms of absorption enhancement of thin film silicon solar cell with a silver nanoparticle on top. For thin film silicon solar cell with a silver nanosphere on top, the spectral position of LSP resonance changes as the incident angle of light changes (Yang et al., 2011). However, the change in incident angle of light has very little effect on local FP modes. The average absorption enhancement is affected by the incident angle of light. They suggested that incident angle of light should be kept close to normal for thin film silicon solar cell and incident angles over 35° should be avoided. Yang et al. studied transmission of light into silicon substrate through silver nanoparticles which were embedded in a silica layer atop the silicon substrate. They found that maximum transmission of light occur at longer wavelengths as the silica layer thickness increases (Yang et al., 2013). They also found that period of nanoparticles did not have much effect on number of photons transmitted into silicon substrate for the case of small Ag nanoparticles i.e. radii of 10 and 25 nm. For the case of larger Ag nanoparticles i.e. 50 and 70 nm radii, number of photons transmitted into silicon substrate was sensitive to period of the Ag nanoparticles. By optimizing nanoparticles' size and period, the optical transmissions of the structures consist of Ag nanoparticles embedded in silica layer were higher than that of Ag nanoparticles alone or silica layer alone. The transmission of unpolarized light into silicon substrate is good for incidence angle range from 0° to 45° .

Beck et al. fabricated Ag nanoparticle arrays on different sets of silicon wafers where each set has different dielectric layer on top. They show that tuning of localized surface plasmon resonance (LSPR) wavelength of Ag nanoparticles to

longer wavelengths can enhance light absorption of silicon solar cell at long wavelengths, the wavelength region where transmission losses are most significant (Beck et al., 2009). The LSPR wavelength tuning was done by modifying local dielectric environment of Ag nanoparticles i.e. by using different dielectric layers under Ag nanoparticle array. They showed that depositing nanoparticles on the rear surface of solar cell can avoid absorption losses due to partial destructive interference effects at wavelengths smaller than the resonance wavelength while still allow long wavelength light to be coupled into the cell. When nanoparticles are deposited on the rear surface of solar cell, short wavelength light that transmitted through the front surface get fully absorbed in a single pass through the cell while poorly absorbed light (long wavelength or near infrared) reach the rear surface and being scattered back to the cell by rear located nanoparticles. Numerical simulations by Beck et al. show that fraction of light backscattered into the cell by rear located nanoparticles is comparable to the forward scattering effect of front located nanoparticles. Beck et al. experimentally show that there is asymmetry in photocurrent enhancement by Ag nanoparticle arrays located on the front surface and on the rear surface of solar cells. This asymmetry is due to the additional antireflection effect provided by front surface nanoparticles and to the difference in scattering cross sections of front and rear located nanoparticles (Beck et al., 2010). However, there is no significant difference in coupling efficiency between front and rear located nanoparticles. Beck et al. attributed the difference in scattering cross sections to the difference in the electric field strength that excites localized surface plasmons (LSP) of front and rear located nanoparticles. The driving field of LSP increases with the thickness of dielectric spacer layer for both front and rear surface of solar cell. Nevertheless, for very thin spacer layers (<10 nm), the scattering cross

section of rear-located particles increases with the decrease of spacer layer thickness. Ouyang et al. studied the effects of front-located and rear-located Ag nanoparticles on 2- μm -thick poly-Si solar cell (with no spacer layer under Ag nanoparticles). They found that both the front-located and rear-located nanoparticles enhance external quantum efficiency (EQE) of poly-Si solar cell at wavelengths longer than 600 nm due to the effect of surface plasmon. They associated the higher EQE enhancement for rear-located nanoparticles to the larger scattering cross section of rear-located nanoparticles as shown by Beck et al. for the case of no spacer layer (Beck et al., 2010; Ouyang et al., 2011). For solar cells with front-located Ag nanoparticles, Ouyang et al. attributed the suppression of EQE at wavelengths shorter than 450 nm to the parasitic absorption of Ag nanoparticles at UV wavelengths and the destructive interference between the scattered and directly transmitted light at wavelengths shorter than LSPR wavelength. They suggested that Ag nanoparticles directly deposited on Si with no spacer layer provide the best plasmonic light trapping as compared to those with spacer layer (Ouyang et al., 2011). Ag nanoparticles directly fabricated on the rear surface of the cell can enhance short-circuit current density by 27%. They found that among the structures studied, rear-located Ag nanoparticles combined with a magnesium fluoride (MgF_2) overcoating and white paint are the closest to an ideal back surface reflector (BSR) in terms of high reflectivity and large-angle scattering and can provide short-circuit current density enhancement of 44%. Yang et al. fabricated 6 types of rear structures with silver nanoparticles (Ag NPs) on the rear surfaces of planar Passivated Emitter and Rear Totally Diffused (PERT) silicon wafer cells. They used standard PERT cell, with 800 nm evaporated aluminum (Al) film on the 40 nm rear silicon dioxide (SiO_2) layer as reference cell. All 6 types of rear structures with Ag NPs showed external

quantum efficiency (EQE) improvement over the reference structure in the wavelength range 1060 – 1200 nm (Yang et al., 2012). The combination of Ag NPs, Zinc Sulfide (ZnS) layer and Detached Al layer gives the largest overall EQE enhancement with 2.6-fold enhancement at 1160 nm wavelength. They evaporated 5 different thicknesses of Ag films (from 12 nm to 28 nm with 4 nm steps) on the rear of 5 planar PERT cells followed by annealing to form Ag nanoparticles and they observed that 28 nm Ag film gives the largest overall EQE enhancement. There is a tradeoff between silicon rear surface passivation and optical coupling of Ag NPs when optimizing the thickness of rear SiO₂ layer. They noticed that the optimized SiO₂ thickness is around 20-30 nm. After optimization of Ag mass thickness and SiO₂ layer thickness, silicon wafer cell with rear structure consisted of SiO₂ layer, Ag NPs and detached Ag layer achieved maximum 4.0-fold EQE enhancement at 1160 nm and 16% photocurrent enhancement for 900 nm to 1200 nm wavelength range (Yang et al., 2012). Shi et al. theoretically studied the effect of incorporating multilayer of silver nanoparticles (Ag NPs) on the front surface and rear surface of thin film crystalline silicon solar cell. They found that when Ag NPs are on the front surface of solar cell, single layer of NPs perform better than double layer of NPs (Shi et al., 2013). For the case of double layers NPs on the front surface, surface reflectivity and parasitic absorption of Ag NPs increases. They showed that when Ag NPs are located on the rear surface of solar cell, multilayer Ag NPs provide better light trapping than single layer Ag NPs. Double layers Ag NPs on the rear surface give the best light absorption enhancement for solar cell with 6.65% increase in intergraded quantum efficiency across the solar spectrum compared with single layer Ag NPs on the rear surface. Yang et al. fabricated single and double layer light trapping structure on the rear surface of 400 μm thick silicon Passivated Emitter Rear

Totally diffused (PERT) cells. For single layer light trapping structure, Ag NPs, which act as scattering reflectors, perform better than all other single layer reflectors and provide maximum photocurrent enhancement of 11% (900 nm – 1200 nm wavelength range) compared to metal back reflectors (Yang et al., 2013). However, scattering properties of Ag NPs degrade over time when exposed to air or moisture. In order to overcome this problem, double layer light trapping structure which includes Ag NPs as the first reflective layer and evaporated Ag as the second reflective layer with both layers separated by magnesium fluoride (MgF_2) was introduced. They found that this double layer structure did not show external quantum efficiency (EQE) or photocurrent degradation over time. After optimizing MgF_2 thickness, the double layer structure enhanced EQE by 4.5-fold at 1160 nm and enhanced photocurrent by 25.6% (900nm - 1200nm wavelength range) compared to cells with metal back reflectors. Optimum thickness of MgF_2 depends on angular distribution of light scattered into MgF_2 layer and type of metal reflector since both of these affect phase shift of light which then affect the interference of light. The double layer structure performs best when constructive interference of light occur at the rear silicon interface. Park et al. deposited Ag NPs on the rear surface of thin film polycrystalline silicon (poly-Si) solar cell and investigated the effects of three different dielectric environments under the nanoparticles i.e. 45 nm-thick thermal silicon dioxide (SiO_2), 3 nm-thick native SiO_2 , and oxide-free silicon surface. They found that the presence of thermal SiO_2 layer between Si and nanoparticles blue-shifted the LSPR wavelength of Ag NPs to near 675 nm as compared to Ag NPs on native SiO_2 and Ag NPs directly on Si sample where their LSPR wavelengths are near 1200 nm (Park et al., 2014). They also found that the external quantum efficiency (EQE) of native SiO_2 and Si film sample are higher than

the thermal SiO₂ sample for wavelengths longer than 650 nm. They discovered that the solar cell with nanoparticles on native SiO₂ layer give the highest potential short circuit current density (J_{sc}) enhancement (62.5%) and highest absolute J_{sc} enhancement (32.3%). They concluded that native SiO₂ layer is the optimum surface for Ag NPs on the rear surface of poly-Si thin-film solar cells.

Yi-Ming et al. calculated forward-scattering efficiency (FSE) and light trapping efficiency (LTE) of two SiO₂/Au nanoshells of different dimensions based on Mie theory to analyze the contributions of dipolar and quadrupolar modes to light trapping. They found that for dipolar modes of (31 nm, 69 nm) and (53 nm, 141 nm) SiO₂/Au nanoshells, the amount of forward scattered light almost equals to the amount of back scattered light for both perpendicular and parallel polarization modes (Yi-Ming et al., 2011). They also found that for quadrupolar mode of (53 nm, 141 nm) SiO₂/Au nanoshells, the forward scattered light intensity is higher than that of back scattered light for both perpendicular and parallel polarizations. For surface coverage of 5%, the LTEs for SiO₂/Au nanoshells with sizes of (31 nm, 69 nm) and (53 nm, 141 nm) are 21.7% and 46.9% respectively. They suggested that quadrupolar mode is more favorable for light trapping in thin film solar cells. However, all the calculations done by Yi-Ming et al. were based on Mie theory which describe light scattering by an isotropic sphere embedded in a homogeneous medium. It is unclear how light will be scattered by nanoshells in dipolar and quadrupolar mode when the nanoshells are placed on top of solar cell (nanoshells in inhomogeneous medium). Sundararajan et al. deposited Au-silica nanoshells on the light-collecting surface of silicon photodiodes and measured local photocurrent enhancement due to individual nanoparticle. All studied Au nanoshells (of sizes $[r_1, r_2] = [38, 62]$ nm, $[r_1, r_2] = [62, 81]$ nm, $[r_1, r_2] = [96, 116]$ nm, where r_1 is the inner

silica core radius and r_2 is the total particle radius) suppress the photocurrent at wavelengths of 532 nm and 633 nm and enhance the photocurrent at wavelengths of 785 nm and 980 nm (Sundararajan et al., 2008). They observed that most of the Au nanoshell dimers which constitute of [62, 81] nm Au nanoshells suppress the photocurrent at all four wavelengths studied (532 nm, 633 nm, 785 nm, 980 nm). They found that at 633 nm wavelength, change in photocurrent due to the presence of [38, 61] nm Au nanoshell vary widely from +5% to -20% while at 980 nm wavelength, the changes are quite consistent. They carry out finite element simulations for [38, 61] nm Au nanoshells on a silicon slab and they observed vortex-like behavior of forward scattered field at incident wavelength of 633 nm. At wavelength of 633 nm, energy flow is directed toward the surface and the nanoshell with energy concentrated near the nanoshell-silicon interface while at wavelength of 980 nm, the energy flow is directed toward the bottom surface of silicon slab and energy is distributed uniformly throughout the entire simulation region.

Experimental study by Sundararajan et al. only focused on one type of nanoshell, that is, Au nanoshell of three different sizes on top of silicon photodiodes (Sundararajan et al., 2008). Simulation study of Guilatt et al. was limited to Ag nanoshells embedded in thin film silicon (Guilatt, Apter and Efron, 2010). Theoretical study by Yi-Ming et al. on the scattering properties of Au nanoshell was limited to homogeneous medium only and did not provide information about optical properties of Au nanoshell when it is deposited on thin film silicon solar cell (Yi-Ming et al., 2011). Qu et al. conducted experimental and simulation studies on a special kind of metal-dielectric core-shell nanoparticle, that is, Au-citrate core-shell nanoparticles deposited on the surface of wafer-based silicon photovoltaic devices (Qu et al., 2011). Despite the reported works, there is still

lacking of systematic study on optical and electrical effects of metal nanoshells and metal-dielectric core-shell nanoparticles deposited on top of thin film silicon solar cell. Thin film silicon solar cell has the potential to reduce total cost per watt of solar cell as new fabrication techniques emerge (Branz et al., 2011; Teplin et al., 2011; Wee et al., 2012; Teplin et al., 2014). Depositing nanoshell on top of thin film silicon solar cell allows easy tuning of surface plasmon resonance wavelength to near infrared regions to improve near infrared light absorption of the solar cell (Halas, 2005). SiO₂ shell of metal-dielectric core-shell nanoparticle protects metal core from oxidation that might decrease light absorption enhancement of solar cell (Akimov and Koh, 2010). In this work, the effects of metal nanoshells and metal-dielectric core-shell nanoparticles on the spectral response, external quantum efficiency, transmittivity and reflectivity spectra and I-V characteristics of thin film silicon solar cell were studied by using commercial software called SILVACO ATLAS. In this study, silver nanoparticles show superior performance as compared to gold and copper nanoparticles. Since synthesis of Ag nanoshell uses very little of silver compared with Ag nanosphere, depositing Ag nanoshells on top of thin film silicon solar cell might serve as a potential low cost method of improving the performance of solar cell. Therefore, Ag nanoshell was studied in detail by optimizing its size and surface coverage to obtain optimum enhancement of efficiency of thin film silicon solar cell. The effects of metal nanoparticle and metal microparticle on the performance of solar cell were also studied and compared to confirm the necessity of using nano size particle.