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Design and Fabrication of Si Nanohole Structures for Photovoltaic Applications

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ABSTRACT

In this thesis, systematic study on silicon based solar cell with nanohole texturing is performed via both software simulation and device fabrication.

To investigate the optical property of Si nanohole texture for PV applications, Si thin film with nanohole textured surface is systematically studied via software simulation. It is found that the optical characteristics are closely correlated to the nanohole structural parameters, such as nanohole depth, diameter and array periodicity. The light trapping of the structure could be optimized when the nanohole array dimensions are set as follows: periodicity of 600 nm, depth of 2000 nm, and nanohole diameter/periodicity ratio of 87.5%. The result provides a guideline for the nanohole surface texturing-process design for photovoltaic applications.

The electrical properties of nanohole textured Si thin film solar cell are also systemically studied via software simulation. The requirement for efficient cells at the optically optimized nanohole geometries are studied in terms of minority carrier diffusion length, emitter doping level, and the emitter junction depth. The impact of surface recombination velocity is also taken into consideration. The results provide a practical guideline to design and fabricate high efficiency and cost effective NH textured Si thin film solar cells.

For the device fabrication part, a large-area, simple fabrication method without additional mask is introduced for the first time to make NH textured solar cells with radial p - n junctions. Fabrication of large-scale Si NH with controllable diameter and

density via laser annealed silver particles catalytic wet etching is demonstrated. Laser annealing is used to produce Ag particles as etching catalyst on a silicon surface, which enables controllable fabrication of large-scale nanohole array surface texturing without using a mask. Hemispherical Ag particles with variable size and distribution are achievable by tuning the laser annealing parameters and metal film thickness, and the underlying physics is discussed. The nanohole array in silicon can then be realized by selective etching of silicon under the Ag particles array. Spin-on doping is applied to form radial p - n junctions, which can better utilize the strong light trapping of nanohole structures than planar junction configuration. A nanohole textured Si solar cell with 9.5% efficiency and a total cell area of 3 cm² is achieved.

To further investigate the potential of nanohole structure, a low aspect ratio nanopit array is preliminary studied. Based on simulation result, the hemispherical nanopit array texture also possesses great light trapping capability. Moreover, its low aspect ratio feature may reduce surface defect density and ease the corporation of anti-reflection coating and top electrode, which making it more feasible for practical application.

In summary, this thesis addresses the software simulation, device fabrication and characterization of Si solar cell with nanohole textured surface. The work done will offer opportunities or approaches to further improve the device performance, especially for thin film PV applications. A comprehensive study of the well-established NH fabrication process and its advantages leads to a new technique producing Si NH thin film solar cells.

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ABBREVIATIONS

AFM	Atomic force microscopy
AM 1.5G	Air Mass 1.5 Global
ATG	Asaro-Tiller-Grinfeld
CVD	Chemical vapor deposition
DD	Drift-Diffusion
EBE	Electron-Beam Evaporation
E_g	Energy band gap
FEM	Finite element method
FE-SEM	Field emission scanning electron microscope
FF	Fill factor
IPCE	Incident photon-to-electron conversion efficiency
ITO	Indium tin oxide
I-V	Current-Voltage
J_{sc}	Short-circuit current density
LA	Laser annealing
LD	Exciton diffusion length
PCE	Power conversion efficiency
PSG	Phosphosilicate glass
PvPh	Poly 4 vinyl phenol
PV	Photovoltaic
RCA	Radio Corporation of America
RTP	Rapid thermal anneal
SAM	Self-assembled monolayer
SEM	Scanning electron microscope
SiNC	Silicon nanocone
Si NH	Silicon nanohole
SiNP	Silicon nanopillar

SiNW	Silicon nanowire
V_{bi}	Built-in voltage
VLS	Vapor-liquid-solid
V_{oc}	Open-circuit voltage
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZnO	Zinc oxide

1. INTRODUCTION

1.1 Background of Clean Energy Technologies

Recent years, people talk more and more about the energy crisis issue, especially fossil energy. The energy needs of the planet are projected to continue growing in the foreseeable future, largely due to the population growth and the rapid economic development. The oil price once peaked at 147 USD/barrel. Although in past a few years the oil price dropped due to the worldwide financial crisis (about 100 USD/barrel), we will still have to face the issue when economy eventually returns to normal. The long-term dependence on these non-renewable resources is obviously non-sustainable. Moreover, the emission of the so called “greenhouse” gases such as CO₂ during consuming carbon based fossil energy has raised negative impact to the global environment including worldwide observations of the shrinking of sea ice, the retreating of glaciers, the rising of ocean levels, the bleaching of coral reefs, and the increases in strong storms and floods.

To combat the potential energy crisis and climate change, the renewable and carbon-free energy technologies need to be urgently developed. The technical report of Hoffert et al. indicates that 10 – 30 TW of carbon-free primary power will need to be implemented by 2050 to meet modest CO₂ stabilization target [1]. A number of clean energy technologies including hydropower, wind, biomass, geothermal, and solar have been developed and are competing to meet the world’s future energy needs. A comparison between the practical potential for power generation among these clean energy resources

is highlighted in Figure 1.1 [2]. Hydroelectricity is by far the most mature and commonly used renewable energy for electricity generation. According to the World Energy Assessment, technically, there is potential of ~ 1.6 TW of hydropower, Considering that ~ 1 TW of hydropower was consumed in 2006, there is little room for this source to contribute more towards the 10 TW clean energy goal. Biomass can produce carbon-neutral energy for electricity generation and fuel, but the low power density of photosynthesis (~ 0.6 W/m²) is a limitation. Large area of land will be needed to produce energy crops, which would create competition for water, agrochemical supply, drive up global food prices, and also possess negative impact to biodiversity and landscape. There is theoretically potential of 50 TW for wind energy if the entire suitable land area were used. However, a more reasonable limit of 4% land area utilization gives a practical potential of 2 TW of wind power [3]. Energy of wind, biomass or hydropower, in one way or another, is from sun. So ultimately, the Sun is the source of most energy resources available to us, including fossil fuels. Photovoltaic works by converting sunlight directly into electrical power, which gives it enormous potential. There is an average 1.2×10^5 TW of solar energy striking the surface of the Earth [3], which means that, with the conservative restrictions of 10% conversion efficiency, only 3.4×10^5 km² area of land (about the size of Malaysia) is needed to produce enough energy to support all the human activities at our 2010 rate (16 TW). Although there are some issues with the solar resource, such as its regional variance and intermittency due to time, season, and weather conditions, its vast abundance in comparison to the other renewable energy makes it clear that solar will play a leading role in the global energy portfolio in the future.

Figure 1-1 The current market share for power generation of main energy resources [3]

Photovoltaics (PV) as a clean energy technology has been developed for decades since the first silicon (Si) solar cell was fabricated at Bell Laboratories in 1954 by Chapin et al [4]. In old days, this technology was mostly used in the space applications such as satellite, space station. The terrestrial application of PV developed at a slow pace due to the low competitiveness against traditional energy resources. Thanks to the rapid development of Si semiconductor based IC industry in the past decades, Si-based PV, considered as one of the ideal candidates of fossil energy replacement, once again gained people's attention. Compared to other emerging clean energy technologies (e.g. hydropower, biomass), PV directly converts solar energy into electricity without any negative impact to the environment. Moreover, PV is highly scalable and flexible, which can be applied broadly from grid-connected to off-grid, rural and personal applications.

Figure 1-2 Solar cell market share by technology (2010) [3]

To make the solar energy competitive, the primary concern is the cost. The first generation cell, or crystalline Si solar cell, still dominates 87% of the current PV market mainly due to its mature technology and stable performance (as shown in Figure 1-2). Crystalline silicon (c-Si) has been successful as the light-absorbing semiconductor in PV industry. However, as a material with relatively low absorption of solar radiation (as compared to other semiconductors with direct-bandgap), considerable amount of silicon material (several hundred microns) is required for efficient absorption. Currently, the typical Si thickness for monocrystalline solar cell is about 200 μm . Costly, high quality crystalline Si has to be used in order to maintain long minority carrier diffusion length for efficient carrier collection. The high cost of the crystalline silicon limits its competitiveness against other energy resources. It is believed that the record Si cell efficiency for un-concentrated sunlight, of 25%, set by UNSW in 1999 [5], will not be

significantly exceeded [6]. Thus, more efforts have been made to focusing on designs that can reduce module cost at the manufacturing level. For example, thinner Si wafer solar cell has been developed; however, the handling of such thin, brittle solar cell would become difficult and costly.

To reduce the cost, thus making solar cells more competitive in the market, second and third generation solar cells are also being actively researched. Second generation solar cells generally refer to the thin film based solar cells. By introducing materials with high absorption coefficient (e.g. a-Si, CdTe, CIGS), the required amount of material is greatly reduced for the cell fabrication, and thus the cost, as shown in Figure 1.3. Unfortunately, the path to the emerging new materials is still bumpy. One good candidate is amorphous silicon (a-Si). Amorphous silicon possesses unique properties fundamentally different from crystalline or polycrystalline silicon. It has much higher absorption coefficient than c-Si due to its inherent high disorder structure, which is giving it great potential for thin film solar cell applications. Yet the a-Si based solar cell suffers low efficiency which also comes from its disordered structure. And the light-induced degradation for a-Si solar cell (normally referred to Staebler–Wronski effect) also severely affects its long-term operation stability. CdTe is growing rapidly in acceptance and now represents the second most utilized solar cells material in the market. The major advantage of this technology is that the panels can be manufactured at lower costs than Si based solar cells. Despite its price advantage, there are some drawbacks of this type of solar cells: Tellurium is extremely rare and cadmium is extremely toxic. These two challenging issues may limit its large scale implementation in the future. CIGS solar cells

also face similar challenges as cadmium and indium elements are involved. Above all, the efficiency of these thin film solar cells is still lower than the first generation cells (Highest efficiency of CIGS: 19.6%; CdTe: 7.3%; crystalline Si: 25%, as recorded in 2012 [7]). Recorded efficiencies of other solar cells are shown in Appendix A. The third generation solar cells involve a lot of novel concepts [8-10]. By introducing advanced physical concepts such as quantum dot, hot carrier, down/up conversions for efficiently utilizing the ultraviolet/infrared photons, the third generation cell are expected to have significantly boosted power conversion efficiency (PCE) and thus reduced the PV prices [11]. But none is yet clearly established as a leader, and none of these technologies is mature for industry manufacturing.

Figure 1-3 Efficiency-cost trade-off for the three generations of solar cell technologies (2003's US dollars) [8]

In spite of the increasing of interests in the use of various emerging new materials (e.g. CIGS, CdTe, organic materials) for PV applications, Si continues to serve as the

most popular choice in the terrestrial PV market. Compared to other materials, its unique strong points are as follow: (1) Si's bandgap is almost ideally matched to the solar spectrum [12]. (2) Si is abundant, which is important for large scale solar global deployment. (3) Si is non-toxic, which makes it environmental-friendly and suitable for various applications such as roof top module, personal electronics. (4) Si is a mature technology and has been well researched. By using Si, the PV industry can benefit from the well-established microelectronics industry, exploiting the wealth of knowledge that has been developed for decades.

1.2 Motivation

C-Si has been successful in 1st generation PV market. If c-Si can be adapted to thin film, the solar cell can benefit in two ways: low cost and well developed material. The main challenge left is the light trapping of c-Si thin film. As aforementioned, c-Si has a low absorption coefficient due to its indirect bandgap nature. Several hundred microns of is needed to absorb sufficient solar energy, which limits c-Si's adoption on thin films. If a feasible way could be found to increase the light trapping capability of the c-Si thin film (normally within a few microns), the c-Si thin film might be a promising solution for the next generation solar cell. Micrometer-scale surface texturing, as the anti-reflection scheme, has been well developed for first generation Si wafer based solar cell (e.g. inverted pyramid texture developed by M. Green, as shown in Figure 1.4 [13]). As solar cell development is moving towards thin film substrate, the normal textures are too large to apply on it. New surface texture design is needed to incorporate into this few micron scale platform. Inspired from that concept, in the past decade, silicon nano-scale texturing

has attracted a lot of attention due to its prominent light trapping properties and potential optoelectronic applications, especially for PV application. Substantial efforts have been devoted to design, synthesize, and integrate various semiconductor nanostructures for photovoltaic (PV) solar cells. Nano-scale texturing, such as black silicon [14], nanopillar [15, 16], has been studied and empirically demonstrated. However, no systematic studies have been conducted yet on these nano-scale textures for optimizing light trapping and device fabrication criteria. Therefore, a guideline is urgently needed to investigate the potential performance and criteria of these nano-scale textures for thin film PV applications from both optical and electrical aspects. Several types of nano-scale textures have been explored by many research groups, such as nanopillar (NP) [15, 17-23], nanocone (NC) [24, 25]. However, nanohole (NH), inspired from porous Si [26, 27], has not received as much attention as its NP counterpart. As a concave type of morphology, NH-like structures possess much better mechanic robustness than convex NP and NC, suggesting that it may be a more feasible nano-scale texture for thin film solar cell applications.

Figure 1-4 Inverted pyramid surface texture developed for 1st generation solar cell

1.3 Objectives

The first objective of this thesis is to perform a thorough, systematic study on the optical and electrical performance of Si nanohole (Si NH) textures for thin film PV application via software simulation. We establish geometrical models to simulate the optical and electrical performance of Si thin film with NH textures. The dimensions of nano-scale textured (vertical nanohole and hemispherical nanopit) Si thin film need to be systematic analyzed for optimized light trapping (optical aspect). In addition, the electrical properties including the junction depth, doping level, surface recombination velocity need to be studied for optimal carrier collection (electrical aspect). The simulation results will serve as a guideline for solar device fabrication including texture dimensions, junction configuration, surface passivation, material quality control, etc.

The second objective is to experimentally demonstrate the Si NH and Si nanopit textures in order to verify their optical performance. New methods need to be explored, which should be able to realize these nano-scale textures on Si surface with large scale, high throughput and low cost process. Thus, traditional, time-consuming and costly

complementary metal-oxide-semiconductor (CMOS) processes such as furnace, photolithography need to be avoided. The main process is based on self-assembled patterning, wet etching, laser annealing. Fabrication and characterization of Si solar cells with nano-scale textures need to be conducted as proof of concept.

1.4 Organization of Thesis

This thesis is divided into seven major chapters. The organization of thesis is presented as follows:

- Chapter 1 provides the background, the motivation, the objectives and the contributions of this project.
- Chapter 2 is a literature review on the research work that has been done and reported for Si based solar cells with surface nano-texturing.
- Chapter 3 addresses the optical absorption optimization of the NH textured Si thin film via software simulation.
- Chapter 4 addresses the electrical simulation to optimize the carrier collection and device performance.
- Chapter 5 demonstrates the fabrication of the NH textured solar cell on Si wafer.
- Chapter 6 introduces a low aspect ratio texture – hemispherical nanopit array to address the Si thin film solar cell challenges.
- Chapter 7 concludes the thesis and discusses some challenges and expectation on the Si nano-textured solar cell.

1.5 Contribution

This thesis presents the systematic study on the optical and electrical characteristics of NH textured Si thin film solar cell. The NH structure is modeled to investigate structural dimensions for optimization of the light trapping capability. The electrical properties including the junction depth, doping level, surface recombination velocity are also studied for efficient carrier collection. It is found that Si NH structure possesses higher light trapping capability than its NP counterpart. The result serves as a guideline for fabrication of high efficiency NH textured Si thin film solar cell.

Based on the simulation result, the author demonstrated Si NH textured solar cell with maskless patterning, metal assisted chemical etching and phosphorous acid diffusion. The device exhibit excellent light trapping. A power conversion efficiency of 9.5% is achieved, which is one of the highest efficiencies achieved by NH textured Si solar cell. The fabrication techniques applied also open an opportunity for thin film applications.

For the first time, a low-aspect-ratio nanopit texture is studied. As compared to traditional nanostructures (e.g. nanopillar, nanohole), low-aspect-ratio texture is more feasible for real device application due to its lower surface defect density and relief of the top contact fabrication.

2. LITERATURE REVIEW

This chapter addresses the fundamentals of Si-based solar cell and the development of nano-scale textures related to this thesis. The first part of the chapter briefly reviews the fundamentals of Si solar cells. An overview of solar cell characterization methods used in this thesis is given. The second part of this chapter gives a historical outline of nano-scale textures from beginning to the latest investigations on its properties, preparation methods and applications.

2.1 Fundamental Physics of Semiconductor Solar Cell

Solar cell has been developed for a long time since the discovery of the photovoltaic effect by Becquerel in 19th century [28]. Semiconductor solar cells have always aligned closely with other electronic devices such as transistors, lasers, light emitting diode (LED). In its simplest form, a semiconductor solar cell is basically a PN junction with a large surface area. Thus, to understand the function of semiconductor solar cells, a precise understanding of the processes within a p-n junction is indispensable. The following review focuses on Si-based solar cell. The basic aspects of silicon material and the physical mechanisms are reviewed.

2.1.1 Si Material Properties

Silicon, used to make some of the earliest PV devices, is still the most popular material for solar cell. It can be classified as crystalline, multicrystalline, polycrystalline, microcrystalline and amorphous [29]. Each of these types has its own strengths and

drawbacks for PV applications. Crystalline silicon has an ordered single crystal structure. It therefore allows direct application of the well-established theories and techniques for crystalline material, exhibits predictable and reproducible behavior and provides excellent performance. It is, however, the most expensive type of silicon due to the costly and time-consuming manufacturing processes (Czochralski method or the float-zone technique). As the PV industry is very sensitive to cost, the cheaper materials like multicrystalline or polycrystalline silicon are therefore increasingly being used for solar cells, despite their relatively inferior qualities. Multicrystalline or polycrystalline silicon is a material composed of a number of smaller crystals with grain size that ranged from a few micrometers to a few millimeters [30]. The grain boundaries reduce the solar cell performance by degrading photo-generated carrier mobility, introducing extra energy levels in the forbidden gap, thus providing extra recombination sites and additional paths for current flow across the p-n junction. Multicrystalline silicon can be produced in several ways. The most popular commercial methods involve a process in which molten silicon is directly cast into a mold and allowed to solidify into an ingot. The starting material can be refined lower-grade silicon. The cooling rate is one factor that determines the final size of crystals in the ingot and the distribution of impurities. The solar cells made of this type of silicon are generally less efficient than that made of crystalline Si, but the cost is also lower. Amorphous silicon has irregular, short-range ordered atomic arrangement. As a result, the amorphous silicon has several interesting properties that give many opportunities for thin film photovoltaic applications. For example, unlike crystalline silicon, which has an indirect energy bandgap of 1.1 eV, the amorphous silicon

has a quasi-direct bandgap of 1.7 eV. Due to the high absorption coefficient in the visible range of solar spectrum, several micrometers thick amorphous silicon is sufficient to absorb 90% of usable solar energy, which is almost 100 times more efficient than the crystalline/polycrystalline silicon. On the other hand, the large deviation in bonding length and bonding angles between the neighboring atoms in amorphous silicon results in weak and strained bonds which are relatively easily to break. This leads to the defect formation in the atomic network, which is believed to be the main cause behind the Staebler-Wronski effect. Moreover, the extra energy levels within the forbidden gap make it almost impossible to dope a-Si or to obtain reasonable current flows in a solar cell configuration [29].

2.1.2 Absorption of photons

Solar cells are used to convert sunlight into energy. To design the solar cell for better light absorption, the solar spectrum needs to be understood. The solar energy is emitted mainly as electromagnetic radiation from ultraviolet to infrared spectral ranges. Upon reaching the earth, the intensity of solar radiation in free space has a value of 1353 W/m². As solar radiation passes through the atmosphere, the sunlight is attenuated, mainly due to water-vapor absorption in the infrared, ozone absorption in the ultraviolet, and scattering by airborne dust and aerosols. The Air Mass quantitatively evaluates the reduction in the power of light as it passes through the atmosphere and is absorbed by air and dust. It is defined as

$$AM = \frac{1}{\cos \theta} \quad (2.1)$$

where θ is the angle from the vertical (zenith angle). The secant of the angle between the sun and the zenith is defined as the AM number and it gives the atmospheric path length relative to the minimum path length ($AM = 1$ when the sun is directly overhead). The AM0 thus represents the solar spectrum outside the earth's atmosphere. The AM1 spectrum represents the sunlight at the earth's surface when the sun is at zenith, and the incident power is about 925 W/m^2 . Figure 2.1 shows the solar spectrums at various AM conditions [31]. The AM0 spectrum is used for satellite and space-vehicle applications. AM1.5G (the G stands for global and includes both direct and diffuse radiation) and AM1.5D (which includes direct radiation only) are the standard spectrum at the Earth's surface and are normally used for terrestrial applications.

Figure 2-1 The spectral irradiance as observed just outside earth's atmosphere (AM0); and after having passed through 1.5 times the thickness of earth's atmosphere with (AM1.5G) and without (AM1.5D) diffusion radiation[32].

The standard terrestrial solar spectrum is the global air mass 1.5 (AM1.5G) spectrum with a photon flux density per wavelength interval, as shown in Figure 2.2. Equation 2.2 displays the current density that a solar cell would generate if all photons with energy above E_g were converted into an electron-hole pair and all the generated carriers were collected at the junction.

$$j_{sc}(\lambda) = \frac{q}{hc} \int_0^\lambda \lambda' I_{AM1.5G}(\lambda') d\lambda' \quad (2.2)$$

where λ refers to the wavelength corresponding to the E_g , λ' refers to wavelength of photons with energy above the E_g . $I_{AM1.5G}(\lambda')$ devotes the solar energy flux density ($\text{W}\cdot\text{m}^{-2}\text{nm}^{-1}$) that is calculated in Ref.[33], c is the vacuum velocity of light and h is Planck's constant. The maximum current density is $j_{sc}(4045 \text{ nm}) = 69.9 \text{ mA cm}^{-2}$, corresponding to a photon flux integral $j_{sc}/q = 4.3 \times 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$ [34].

Figure 2-2 the solar photon flux density and the current density that a solar cell could generate under AM1.5G solar spectrum [32].

The band gap of a semiconductor is the minimum energy required to excite an electron from its bound state into a free state where it can move in conduction band. The

band structure of a semiconductor gives the energy of the electrons on the y-axis and is called a "band diagram". The band gap is the gap in energy between the bound state and the free state, between the valence band and conduction band. The band gap determines how much energy is needed from the sun for conduction, as well as how much energy is generated.

Figure 2-3 Band diagram of a silicon solar cell

Figure 2.3 illustrates the band diagram of a Si solar cell. When light incidents on Si surface, the photons with energy less than the bandgap energy pass through the material as if it were transparent. While for photons with energy greater than the bandgap energy, they interact with electrons in covalent bonds to break bonds, create electron-hole pairs and excite the electron from valence band to conduction band. How far the light of a particular wavelength can penetrate into a material before it is absorbed is determined by Beer-Lambert Law, given by [35]

$$I(x) = I_0 e^{-\alpha x} \quad (2.3)$$

where I_0 is the initial intensity. The absorption depth is given by the inverse of the absorption coefficient, or α^{-1} . The absorption depth indicates the distance into the material at which the light drops to about 36% of its original intensity, or alternately has dropped by a factor of $1/e$. The number of electron-hole pairs being generated in a solar cell can be calculated based on the above equation. Assuming that the loss in light intensity directly transfers into the generation of an electron-hole pair, the generation rate (G) of electron-hole pairs per unit volume at any depth of the material can be calculated using the formula:

$$G = \alpha N e^{\alpha x} \quad (2.4)$$

where N is the photon flux (photons per unit area per second), α is the absorption coefficient, and x is the distance from the surface [32].

The energy of an electron is a function of its quantum mechanical wavevector k . In a semiconductor, this dependence of electron energy on its wavevector forms the band structure of the semiconductor. Figure 2.4 shows the energy-band structure of Si and GaAs during photon absorption. Near the band edges, the E - k relationship can be approximated by the equation

$$E(k) = \frac{\hbar^2 k^2}{2m^*} \quad (2.5)$$

where m^* is the associated effective mass, $\hbar$ is Dirac constant and k is wavevector. The top of the valence band is degenerated at $k = 0$ (Γ point). The bottom of the conduction band can be at $k = 0$ for the case of GaAs or off center along different k axes for the case

of Si. Therefore, the conduction-band minimum can be aligned or misaligned in k -space in determining the bandgap. And this is the criteria to determine whether the material possess a direct bandgap or indirect bandgap. The difference has a great impact to the carrier generation capability of the materials. For direct bandgap material, the momentum (or k) is conserved during the energy transfer. Photons with energy greater than the bandgap can directly generate electron-hole pairs. But for indirect bandgap material, like Si, because of the momentum misalignment, additional energy (phonon) is needed to realize this process, making carrier generation more difficult. The onset of absorption at E_g is not sharp for silicon, which implies that the near-bandgap absorption is phonon-assisted. The smallest phonon-free direct band to band transition in crystalline Si is ~ 3.4 eV, corresponding to a wavelength of 360 nm.

Figure 2-4 Energy-band structures of (a) GaAs and (b) Si, where E_g is the energy bandgap. (VB, valence band; CB, conduction band) [36].

2.1.3 The P - N junction

A p - n junction is formed by joining p -type and n -type semiconductor. It is the

elementary building blocks of solar cell as well as many other semiconductor electronic devices, as shown in Figure 2.5. When p - n junction is formed, the excess electrons in the n -type material flow by diffusion to the p -type material, and holes flow by diffusion from p -type material to the n -type material owing to the carrier concentration gradients across the junction. The fixed ions (donor and acceptor) left behind during the carrier diffusion process build up an electric field ($\hat{E}$). The region near the p - n junction loses its neutrality and becomes charged, which is defined as depletion region. Depending on the materials used, a built-in potential (V_{bi}) owing to $\hat{E}$ will be formed.

Figure 2-5 Simple solar cell structure with single p - n junction. Free carriers have diffused across the junction ($x = 0$) leaving a space-charge or depletion region practically devoid of any free or mobile charges. The fixed charges in the depletion region are due to ionized donors on the n -side and ionized acceptors on the p -side

For PV application, the p - n junction works as a carrier-separation mechanism. After photon is absorbed within the material, the electric field across the p - n junction separates the generated electron-hole pairs, sweeps the electrons to the n -type side and holes to the p -type side.

The electrostatics of this situation (assuming a single acceptor and a single donor

level) are governed by Poisson's equation:

$$\nabla^2 \phi = \frac{q}{\varepsilon} (n_o - p_o + N_A^- - N_D^+) \quad (2.6)$$

where ϕ is the electrostatic potential, q is magnitude of the electron charge, ε is the electric permittivity of the semiconductor, p_o is the equilibrium hole concentration, n_o is the equilibrium electron concentration, N_A^- is the ionized acceptor concentration, and N_D^+ is the ionized donor concentration.

Carrier recombination is the reverse process of carrier generation where electrons and holes recombine and are annihilated, which need to be controlled as low as possible in the solar cell device. There are several types of recombination mechanisms related to solar cell operation, such as Shockley-Read-Hall recombination (through defects in the forbidden bandgap), radiative recombination and Auger recombination, as illustrated in Figure 2.6. In order to output power, the generated electrons and holes must be able to reach the junction before recombination occurs. Therefore, the defect density must be controlled to have a longer carrier diffusion length.

Figure 2-6 Recombination processes in semiconductor [32].

2.1.4 Operation of solar cell

A Si solar cell is basically a photodiode with a large active area. It is simply a p - n junction diode consisting of two quasi-neutral regions on either side of a depletion region with an electrical contact made to each quasi-neutral region. Typically, the more heavily doped quasi-neutral region is called the emitter (the n -type region in Figure 2.5) and the more lightly doped region is called the base (the p -type region in Figure 2.5). The base region is also often referred to as the absorber region since the emitter region is usually very thin and most of the light absorption occurs in the base. This basic structure will serve as the basis for deriving the fundamental operating characteristics of the solar cell. The basic current–voltage characteristic of the solar cell can be derived by solving the minority-carrier diffusion equation with appropriate boundary conditions.

Solar cell boundary conditions

At $x = -W_N$ (refer to Figure 2.5), the usual assumption is that the front contact can

be treated as an ideal ohmic contact. Considering the surface recombination and the antireflective coating (normally SiO₂ layer), the boundary condition at $x = -W_N$ is

$$\frac{d\Delta p}{dx} = \frac{S_{F,eff}}{D_p} \Delta p(-W_N) \quad (2.7)$$

where $S_{F,eff}$ is the effective front surface recombination velocity. Similarly, the back contact could be treated as an ideal ohmic contact as well. Considering the back surface field (BSF), which is used to keep minority carriers away from the back ohmic contact and increase their chances of being collected, the boundary condition at $x = -W_P$ is

$$\frac{d\Delta n}{dx} = -\frac{S_{BSF}}{D_n} \Delta n(-W_P) \quad (2.8)$$

where S_{BSF} is the effective surface recombination velocity at the BSF.

The boundary conditions at $x = -x_N$ and $x = x_P$ are commonly referred to as the law of the junction. The boundary conditions used at the edges of the depletion region,

$$p_N(-x_N) = \frac{n_i^2}{N_D} e^{qV/kT} \quad (2.9)$$

$$n_P(x_P) = \frac{n_i^2}{N_A} e^{qV/kT} \quad (2.10)$$

Using these boundary conditions and the generation rate equation, the minority-carrier diffusion equation can be solved. The minority-carrier current densities in the quasi-neutral regions are just the diffusion currents, since the electric field is negligible.

So a general expression for the current produced by a solar cell can be yield as

$$I = I_{SC} - I_{o1} \left(e^{\frac{qV}{kT}} - 1 \right) - I_{o2} \left(e^{\frac{qV}{2kT}} - 1 \right) \quad (2.11)$$

where I_{SC} is the short-circuit current and is the sum of the contributions from each of the three regions: the n-type region (I_{SCN}), the depletion region ($I_{SCD} = AJ_D$), and the p-type region (I_{SCP}). I_{o1} is the dark saturation current due to recombination in the quasi-neutral regions, I_{o2} is the dark saturation current due to recombination in the space-charge region.

From a circuit perspective, a realistic solar cell can be modeled by a current source in parallel with a diode, as shown in Figure 2.7. Considering the recombination within the solar cell, the current generated in a planar p - n junction solar cell can be expressed as follow:

$$I = I_{sc} - I_o \left(e^{\frac{qV}{nkT}} - 1 \right) \quad (2.6)$$

This in turn leads to the expression for open-circuit voltage:

$$V_{oc} = \frac{nkT}{q} \ln \frac{I_{sc} + I_o}{I_o} \quad (2.7)$$

where I_{sc} is the short-circuit current, I_o is the dark saturation current due to recombination in the quasi-neutral and space-charge regions, k is Boltzmann's constant and T is the temperature. n is the diode ideality factor and normally has a value between 1 and 2, with $n \rightarrow 1$ for diode dominated by recombination in the quasi-neutral regions and $n \rightarrow 2$ when dominated by recombination in the depletion region.

Figure 2-7 Simplified solar cell circuit models with/without parasitic resistance.

The current-voltage (I - V) characteristic of a typical Si solar cell with and without illumination is plotted in Figure 2.8. It illustrates several important parameters of merit for solar cells, such as short-circuit current, open-circuit voltage, and fill factor. When a small voltage is applied, the diode current is negligible and the current is dominant by the photo-generated current, I_{sc} , which is in the opposite direction of a diode working current. As the voltage increases, the diode current becomes significant, as can be seen the current increase towards positive value quickly.

Figure 2-8 I - V characteristics of solar cell

The fill factor (FF) is a measurement of the squareness of the I - V characteristic,

and can be defined as the ratio of the area of the curve under the maximum power point of the cell, $P_{max} = I_{max}V_{max}$, to the area associated with intersection points, i.e., $P = I_{sc}V_{oc}$. These parameters directly related to the power conversion efficiency, η , which is the most important index for a solar cell:

$$\eta = \frac{P_{MP}}{P_{in}} = \frac{FFV_{oc}I_{sc}}{P_{in}} \quad (2.8)$$

where P_{in} is the power of the incident light applied on the device.

The I - V characteristic can be greatly affected when parasitic resistances are taken into account. The main impact of the parasitic resistances is the reduction of FF . When series and shunt resistances are considered, the diode current equation becomes

$$I = I_{sc} - I_o \left(e^{\frac{qV}{nkT}} - 1 \right) - \frac{(V + IR_s)}{R_{sh}} \quad (2.9)$$

From the above equation, one can see that the shunt resistance, R_{sh} , has no effect on the short-circuit current, but reduces the open-circuit voltage. And the series resistance, R_s , has no impact to the open-circuit voltage, but reduces the short-circuit current. Their effect to the I - V characteristic is shown in Figure 2.9. Series resistance may come from bulk resistance of semiconductor, bulk resistance of metal electrodes and contact resistance between semiconductor and metal. Shunt resistance may come from leakage across the p - n junction around the edge and crystal defects, pinholes, impurity precipitates.

Figure 2-9 (a) Effect of series resistance ($R_s \rightarrow 0$) and (b) shunt resistance ($R_{sh} \rightarrow \infty$) on the I - V characteristic of a solar cell

In addition to measuring the I - V characteristics, another important characterization for solar cell is the quantum efficiency (QE) as a function of wavelength, which illustrates solar cell's light absorption in each wavelength. The external quantum efficiency (EQE) is the ratio of the number of charge carriers collected by the solar cell to the number of photons of a given wavelength of the incident light that reach the solar cell. Internal Quantum Efficiency (IQE) is the ratio of the number of charge carriers collected by the solar cell to the number of photons of a given wavelength that reach the solar cell and are absorbed by the cell. These two terms are related as:

$$IQE = EQE/A \quad (2.10)$$

where A refers to the absorption of light. QE data provides the spectral response of the solar cell.

2.1.5 Physical loss mechanisms

A typical single junction solar cell consists of 2 processes during its normal

operation: 1. Absorption of photons, 2. Separation and collection of the generated carriers. Figure 2.10 schematically illustrates the energy loss processes during the energy generation [8]. When sunlight is incident on a solar cell, part of the photons are reflected back, as marked by process ①. For the photons entering the solar cell, only those with the energy above E_g can be absorbed and generate electron–hole pairs. Those photons with the energy below E_g simply pass through the cell without any contribution to the power generation, as marked by process ②. For the photons absorbed by the solar cells, prior to extraction of the photogenerated carriers, the main energy loss occurs in process through the thermalization loss ③, which is due to the rapid thermal relaxation for the carriers activated by high-energy (E) photons, releasing the energy of $(E-E_g)$ in the form of phonons. During the collection of the carriers, recombination also inevitably occurs at both bulk and surface of the device (⑤). These recombinations are closely related to the material properties such as surface recombination velocity, minority carrier lifetime and diffusion coefficient. The other energy loss mechanisms include junction and contact voltage losses (④ and ⑥).

Figure 2-10 Energy loss processes in a standard single junction solar cell: ①reflected photons; ②non-absorption of sub-band gap photons; ③thermalization loss; ④junction loss; ⑤contact voltage losses and ⑥recombination loss. [8]

Among these loss mechanisms, process ① and ② together contribute ~50% of the total solar energy loss [8]. Both of these two processes are related to the semiconductor bandgap. In order to reduce the losses (①), anti-reflection coating (ARC) was developed. By introducing a transparent thin film with designated thickness, the destructive interference is produced in the reflected light and constructive interference in the transmitted light. The ARC works well for suppressing the surface reflection, but could not help to increase the absorption (②). To address both the reflection and transmission losses, surface texture is also developed. The roughened surface reduces reflection by increasing the chances of reflected light bouncing back onto the device surface. The surface texture also couple light obliquely within the solar cell, which prolongs the effective optical path to exceed the physical solar cell thickness, as shown in Figure 2.11.

Figure 2-11 Reflection and transmission of light for a pyramid-textured silicon solar cell

2.2 Si Solar Cell with Nano-textures

Surface texture developed, e.g. pyramid texture, works well on 1st generation Si solar cell. But their dimensions are too large to apply on thin film substrate, which only has a few micron thickness. Inspired from the normal textures, nano-textures are actively studied. Different from normal texture which rely on geometrical optics, nano-textures are based on wave optics, which not only reduce reflection but also boost the light absorption. Moreover, the junction configuration can also be designed with the nano-texture to significantly reduce the carrier collection path. In this section, several nano-textures including their preparation methods are introduced to give an overall image of the recent research status of nano-textured solar cells.

2.2.1 Preparation of nanostructures

As the main light harvest block of the nano-textured solar cell, various

nanostructures have been studied in recent years [24, 37, 38]. The methods to prepare nano-scale textures (e.g. nanopillar, nanocone) are generally categorized into two types: one is the “top down” [39, 40] and the other is the “bottom up” approach [41, 42]. The “top down” approach, as the term implies, generally refers to the preparation of the nanostructures using various etching process with different patterning techniques. The “bottom up” approach mainly refers to the vapor-liquid-solid (VLS) mechanism to grow nanostructures (especially SiNP) from chemical vapor deposition (CVD) with the assist of metal catalysts such as Au, Al, Cu etc [43-45]. Note that neither approach is perfect. In this section, we would highlight the approaches to prepare Si nanostructures with low costs and high controllability in terms of dimension and spatial distribution.

The VSL approach has received much attention in the past few years as one popular method to fabricate silicon nanowires. The VLS mechanism is briefly introduced as follows: Au film is annealed at temperatures higher than the Au-Si eutectic point ($\sim 363\text{ }^{\circ}\text{C}$), creating liquid Au-Si alloy particles on the Si substrate. Exposing such a substrate to a gaseous silicon precursor, such as silicon tetrachloride (SiCl_4), or silane (SiH_4), precursor molecules will break on the surface of the Au-Si alloy droplets, and Si is incorporated into the droplet. The Si supply from the gas phase causes the droplet to become supersaturated with Si until silicon freezes out at the silicon/droplet interface. The continuation of this process then leads to the growth of a wire with the alloy droplet riding on top of the growing wire, as shown in Figure 2.12. [46, 47]. One can use lithography techniques to pattern the Au film so as to obtain designated nanowire diameter and distribution in the following wire growth process.

Figure 2-12 Schematic illustration of Si whisker growth from the reaction of SiCl_4 and H_2 vapor phases.

There are several favorable features for this technique: 1. Wires grown by this technique tend to be single crystalline [47]. 2. The wire growth rate can be very high ($\sim$ several $\mu\text{m/s}$) [48]. 3. The growth of wire stems from gas phase precursors, which may reduce cost and open the possibility of in-situ doping [49]. The VSL growth of SiNW with the area of $>1 \text{ cm}^2$ has been realized on glass substrates [50]. However, Au-assisted VLS process is considered incompatible with CMOS standards due to unavoidable incorporation of deep level impurities (Au) in Si during the process. Impurities in Si can affect the carrier lifetime by acting as recombination centers, which may severely affect the electrical properties of the resulting SiNW structure [51]. The maximum possible recombination rate associated with a certain impurity depends on the energy level of the impurity within the bandgap. It critically depends on the energetic difference between the impurity level and the center of the band gap. In other words, the closer the impurity level is to the mid-band, the more efficient it acts as a recombination center [51, 52]. Figure 2.13 shows the impurity levels of several potential metal catalysts as a function of the

corresponding minimum temperature required for a VLS growth. It is seen that Au has an impurity level right at the middle of the Si band gap. Such deep level traps have to be avoided as far as possible. This is one primary drawback to limit its usage for photovoltaic applications [52].

Figure 2-13 Deep level energies of various metal impurities in Si given with respect to the middle of the Si bandgap as a function of the minimum temperature required for VLS growth. In case an impurity possesses two or more levels, these are shown connected by a line. Levels above the bandgap middle that are marked with solid symbols are donor levels, whereas open symbols indicate acceptor levels. Similarly, solid symbols below the bandgap middle are acceptor levels, whereas open symbols are donor levels. [52, 53]

The “Top down” method is the other approach that has gained a lot attention in recent years. It can be categorized into dry etch and wet etch according to the applied etching technique. With the aid of various pattern techniques, such as photolithography, nanostructures can be easily realized. However, the high cost and low throughput of the traditional lithography techniques limit their usage in photovoltaic applications. Low cost patterning methods are urgently needed for replacement.

Figure 2-14 SEM images of the close-packed SiO₂ nanosphere monolayer prepared by the Langmuir-Blodgett method on a 4" Si (100) wafer. (a) - (d) demonstrate the four different regions corresponding the symbols marked in the wafer, indicating the high uniformity over the entire wafer. [15]

Self-assembled polystyrene (PS)/SiO₂ spheres monolayer is becoming one popular method to pattern ordered nanostructure. Cui's group reported the Langmuir-Blodgett (LB) [54] assembled SiO₂ sphere monolayer as mask to fabricate Si nanopillar (SiNP). By using LB method, uniform and dense nanosphere monolayer can be obtained over a large area, as shown in Figure 2.14 [15]. After getting the close-packed SiO₂ nanosphere monolayer, reactive ion etching (RIE) can be performed to reduce the diameter of the SiO₂ nanospheres using O₂ and CHF₃ gases, as demonstrated in Figure 2.15 (a) and (b) [15]. This SiO₂ nanospheres array is then used as the hard mask to etch highly ordered SiNP array via Cl₂ based RIE (see Figure 2.15 (c)). The remaining SiO₂ on top of the SiNP is removed in HF based solution. Figure 2.15(d) shows the tilted SEM image of the resulting SiNP array. Note that the size and periodicity of the SiNP array is

transferred from that of the SiO_2 nanospheres monolayer. Thus, the dimension of the SiNP array can be controlled by selecting the nanosphere size and corresponding RIE setting. Moreover, this method is possible to be utilized to fabricate SiNP array on various substrates, such as polycrystalline Si and amorphous Si.

Figure 2-15 Schematic (left) and the corresponding SEM image (right) of the process to prepare highly ordered SiNP array with controllable array periodicity and SiNP diameter using RIE combined with the SiO_2 nanosphere Langmuir-Blodgett patterning method. [15]

Compared to dry etching which requires expensive vacuum equipment and gases, metal assisted wet chemical etching is a simpler and more cost-effective method to fabricate nanostructures. Moreover, wet etching has higher throughput (batch process), which is strongly favorable for photovoltaic applications. Metal assisted wet chemical

etching can be classified into two types: one-step process and two-step process.

Figure 2-16 (a) SEM cross-section image of SiNW arrays. (b) TEM image of an individual SiNW prepared from a p-type silicon substrate (111). (c) HRTEM image of the nanowire in (b) (the inset is the ED pattern recorded along the [110] axis). d) HRTEM image of a nanowire synthesized from a p-type (100)-oriented silicon substrate (the inset is its ED pattern recorded along the [001] axis). (e, f) SEM images of SiNW arrays prepared from a polycrystalline Si substrate [55].

One example of fabrication of SiNW using one-step process is using silver nitrate (AgNO_3) and hydrofluoric acid (HF) mixture [55, 56]. The reaction mechanism has been well studied [55, 57]. Ag^+ in the solution captures electron from Si and transfers to Ag^0

nucleation on the Si surface. The electron transfer from Si to Ag⁺ is thermodynamically preferential due to the lower energy level of the Ag⁺/Ag⁰ system than that of the Si valence band edges. At the same time, the Si underneath the Ag nucleus is oxidized and subsequently dissolved in HF. The dissolution of SiO₂ creates a pit underneath the Ag nucleus and bogs it down. The excess oxidation causes accumulation of electrons around the Ag⁰ nucleus, which leads to the growth of Ag particles and the pit underneath it. Figure 2.16 shows the SiNW structure obtained by Peng's group. The SiNW structure obtained by the one-step process exhibits great light trapping capability. However, there is drawback for this method: the SiNW has random shape, size and distribution due to the lack of a patterning step, which implies less control of the structure dimensions. The highly-disordered structure also increases the difficulty of the top electrode formation.

Two-step process separates the Ag nucleation and electroless etching [57, 58]. The process involves metal catalyst deposition/patterning and chemical etching using aqueous solution of HF/H₂O₂. Several metals are capable to serve as catalysts in this process [59]. Ag is one of the best candidates for this purpose. The following mechanism is proposed to explain the chemical reaction during process.

At noble metal:

At Si:

Over all reaction:

Figure 2-17 Illustration of Ag assisted chemical etching on Si substrate. (a) Immersion of Si wafer with Ag particles on the surface, (b) SiO₂ forms beneath the Ag particles, (c) pits form as a result of etching away of SiO₂ in HF solution, (d) Ag particles sink, new layer of SiO₂ forms and the process continues.

It is generally accepted that Ag particles rested on the Si surface have a higher electronegativity than Si [60, 61]. Thus, they are able to attract more electrons than silicon to become negatively charged. These Ag particles act as local micro-cathodes and enhance the cathodic reaction stemming from their catalytic activity [62, 63]. Therefore, O⁻ ions from H₂O₂ tend to obtain electrons from Ag particles and be reduced to O²⁻ ions. The generation of H⁺ from H₂O₂ and the reduction of H⁺ to form H₂ are facilitated by the

noble metals [62]. On the other hand, the Si underneath the Ag particles is oxidized to SiO_2 . The SiO_2 generated is subsequently etched away by the HF to create pit underneath the Ag particles and then the Ag particles fall into the pit. As the process continues, the Ag particles gradually sink into silicon to form nanostructures on the silicon substrate, as illustrated in Figure 2.17. Therefore, by patterning the metal on the Si substrate, one can easily transfer the pattern to the Si substrate.

Figure 2-18 Schematic of the process flow (left) and the corresponding SEM image (right) of each step for preparing highly ordered SiNWs array with controllable array periodicity and SiNWs diameter using the electroless etching combined with the self-assembled SiO_2 nanosphere monolayer severing as the mask [64].

One simple patterning technique is using self-assembled SiO₂ nanosphere monolayer as illustrated in Figure 2.18. The dimensions of the SiNW array can be controlled by the SiO₂ nanosphere size. The sputtered Ag film and the anisotropic metal-assisted wet etching successfully transferred the SiO₂ monolayer pattern into SiNW array. Generally speaking, to integrate nanostructures for photovoltaic applications, the trade-off between the manufacturing cost and the enhanced power conversion efficiency has to be carefully taken into consideration.

Recently, nanoimprint lithography (NIL) has been attracting attentions as another promising methods for nano-sized patterning for its low cost and simplicity [65-68]. It is a simple nanolithography process with low cost, high throughput and high resolution. It creates patterns by mechanical deformation of imprint resist and subsequent processes. The imprint resist is typically a monomer or polymer formulation that is cured by heat or UV light during the imprinting. Adhesion between the resist and the template is controlled to allow proper release. Various techniques that use different molds and precursors have been developed, such as hot embossing lithography, roller nanoimprint lithography, hydrogen silsesquioxane (HSQ) based nanoimprint lithography, and Ultraviolet (UV) nanoimprint lithography [68-70]. It has been applied to create various nanostructures for organic, polymer and silicon solar cell applications [71, 72].

Plasmonics is one other photon management techniques like plasmonics, which can be considered as a special surface texture. For thin film photovoltaic devices, micrometer-scale texturing is typically challenging. Thus, plasmonics has emerged as a promising route to advanced photon management for thin film photovoltaic applications

[73-75]. Surface plasmons can confine light in spaces significantly shorter than one-fourth of the wavelength of the light and can lead to many orders of magnitude enhancement of the optical fields - a fact exploited in analytical chemistry for surface-enhanced Raman spectroscopy. Because surface plasmon modes are highly sensitive to surface structure and the immediate surrounding dielectric environment, nanostructuring (e.g., to form nanoparticles or asperities), as well as the integration of metals with dielectric materials, can strongly influence their nature [76].

Figure 2-19 For thin film photovoltaic devices, micrometer-scale texturing is typically challenging, and alternate approaches for light trapping have emerged. (a) Metal and/or dielectric nanostructures on the device surface can scatter incident light into optical modes, labeled k_1 and k_2 in the figure, confined within the thin film semiconductor device structure. Such scattering can provide photons with dramatically increased path lengths within the device and corresponding increases in optical absorption efficiency. (b) Scattering of light into waveguide modes within a thin film device can also be accomplished with scattering structures on the back side of the device. This geometry allows scattering to be optimized for longer-wavelength light, for which optical absorption coefficients are typically lower, and enables integration of an antireflection coating on the top surface, as illustrated in the figure. [76]

2.2.2 Recent Research Status of Nano-textured Si Solar Cell

The previous section introduced several promising approaches to fabricate nanostructures. In recent years, many inspiring results have been obtained in nano-textured solar cell from many research groups world-wide. Various nanostructures such as nanopillar/nanowire, nanocone, nanohole have been studied and demonstrated to reveal their potential for light harvesting. Nanowire, as the pioneer of this family, has gain the most attention from the very beginning. The Lewis and Atwater group from CIT demonstrated the SiNW array textured solar cell in 2007 [18]. They fabricated highly ordered *n*-type SiNP array (pillar diameter $\sim 2 \mu\text{m}$, length $\sim 20 \mu\text{m}$, array periodicity $\sim 7 \mu\text{m}$) on degenerately doped *n*-type Si (111) wafer using VLS method, as shown in Figure 2.20. The *p-n* junction is formed by immersing SiNP array into the 1,1' dimethylferrocene (Me_2Fc)⁺⁰ redox system in methanol (CH_3OH). A liquid electrolyte is used to as electrode over the SiNP array to achieve uniform contact. The cell is measured under AM 1.5G with an area of 2 mm^2 . The V_{oc} and J_{sc} are $389 \pm 18 \text{ mV}$ and $1.43 \pm 0.14 \text{ mA/cm}^2$, which is much better than the control sample without SiNP array (V_{oc} : $232 \pm 8 \text{ mV}$; J_{sc} : $0.28 \pm 0.01 \text{ mA/cm}^2$).

Figure 2-20 (a) Cross-sectional (scale bar = 15 μm), and (b) 45° view (scale bar = 85.7 μm) SEM images of the Si wire array prepared by the VLS growth combined with the pre-patterned Au catalyst [18].

Yang's group from University of California reported Si-based solar cells with controllable SiNP diameter and array periodicity using the RIE based "top down" technique combined with the self-assembled SiO_2 nanosphere monolayer mask [22]. In order to minimize the PV contribution from the Si substrate underneath, a highly doped wafer with epitaxial Si on top is used. The SiNP is patterned within the epi-grown Si layer. After obtain SiNP array, boron thermal diffusion was conducted to form the radial p - n junction, followed by deposition of metal electrode. Figure 2.21 (a) and (b) respectively show the SEM images of the SiNP array (diameter ~ 400 nm, array

periodicity ~ 550 nm, length ~ 5 μm), and the optical image of the SiNP array texture over a large-scale Si substrate. The I - V characteristics measured under AM 1.5G exhibit a power conversion efficiency (PCE) of $\sim 4.83\%$ ($V_{oc} = 0.525$ V, $J_{sc} = 16.45$ mA/cm², FF = 55.9%) with the main light trapping portion consisting of the SiNP array and the 3 μm thick epi-grown Si layer underneath. Thus, they concluded that the light trapping is mainly within the SiNP array portion, and the corresponding optical path length enhancement factor is ~ 73 , which is much larger than the randomized scattering limit (~ 25 without a back reflector).

Figure 2-21 (a) Tilted SEM image of the SiNWs array after forming the radial p - n junction (the scale bar: 1 μm), and (b) the tilted optical image of the SiNWs array based solar cells on the same substrate after isolating (the scale bar: 4 cm). [22]

Si NH texture is originated from porous surface texture. Although Si NH has not gained as much attention as its SiNP counterpart, it also holds great potential for feasible nano-textured solar cell applications. Theoretical study based on optical simulation has shown that Si NH may exhibit superior light trapping capability than SiNP [77]. Moreover, the interconnected Si NH array structure is naturally more robust than the free-standing SiNP array, which is fragile and easily cracked. Nishioka et al reported the solar cells with nanohole textured surface, where the Si NH texture is fabricated by immersing Ag nanoparticle (3-5 nm in diameter) coated Si layer into the HF/H₂O₂ solution [78]. Figure 2.22 (a,b) shows the photograph of the samples with and without the Si NH texture. The dark appearance of the textured sample indicates the significant anti-reflection effect of the NH texture. Accordingly, the light absorption of the Si NH textured sample is greatly enhanced, as shown in Figure 2.22. The cell performance characterized at AM 1.5G indicates that the Si NH textured cell has a J_{sc} of ~ 31.25 mA/cm² which is much higher than the control sample's ~ 24.94 mA/cm².

Figure 2-22 Photographs of the samples (a) with and (b) without the Si NH array texture and the corresponding absorption spectra of the two samples. [78]

Peng et al reported the solar cells with ordered Si NH array texturing, where the Si NH array is fabricated by the combination of the deep ultraviolet lithography patterned Ag particles and Ag assisted Si etching in aqueous oxidizing hydrofluoric acid (HF/H₂O₂) [79]. The result obtained exhibits a highly ordered Si NH array with diameter of 700 nm and depth of 1 μ m, as show in Figure 2.23. Under 1 sun AM1.5G illumination, the SiHN textured solar cell exhibited a V_{oc} of 566.6 mV and a J_{sc} of 32.2 mA/cm² The power conversion efficiency is 9.51%, which are superior to those of its counterparts based on SiNP, planar Si, and pyramid-textured Si.

Figure 2-23 SEM images of Si NH array produced in an 8-12 Ω cm p-Si (100) wafer. (a) Top-view SEM image of ordered, shallow, flat-bottomed pits in Si formed during the initial etching stage. Silver is seen at the bottom of these pits. (b, c) Top-view SEM images of ordered silicon nanoholes with large depths after prolonged immersion in HF and H₂O₂ solution. (d) Cross-sectional view of silicon nanoholes; the hole channels are cylindrical and vertical with respect to the Si surface. [79]

Finally, it is worthy to highlight a pressing challenge that need to be addressed for the Si nanostructure textured solar cells. The high surface defect density that associated with nanostructure's large surface area during the fabrication process could severely deteriorate the performance of the resulting solar cells [80, 81].

3. OPTICAL SIMULATION OF NANO HOLE TEXTURED SILICON THIN FILM

3.1 Introduction

Silicon surface nanostructures have attracted much attention because of their unique physical properties and potential optoelectronic applications, especially in areas of photovoltaic applications [82-86]. Numerous Si nanostructures, such as porous silicon [87-89], nanocone [90] and nanopillar [82, 91] arrays have been extensively studied. As an alternative surface nanostructure for optical absorption enhancement, nanohole array decorated surface was recently reported to increase the efficiency of the Si-based solar cell. In addition, the nanohole structure has been empirically demonstrated by both wet and dry etch methods, such as inductively coupled plasma reactive ion etching, electron cyclotron resonance plasma etching and photo-assisted electrochemical etching [92-94]. Despite the experimental progress, a guideline to realize the optimal nanohole structures for maximized optical absorption is missing in literature, which is critical for photovoltaic device and other application, e.g. as anti-reflection coating layer.

In this chapter, the optical characteristics of the silicon thin film decorated with nanohole array are reported. The nanohole array structural parameters, e.g. the void ratio, the nanohole depth and the periodicity are investigated via simulation by applying the full wave finite element method (FEM) [95]. It is found that the nanohole structure embedded in the silicon thin film can significantly increase the solar energy absorption,

especially in high energy range (above 2.3 eV). The light absorption is maximized when the nanohole depth, array periodicity, and nanohole diameter/period ratio (nanohole diameter divided by array period) are set at 2000 nm, 700 nm, and 87.5% respectively. The corresponding ultimate efficiency is ~35% with a total film thickness of only 2.8 μm , including a 2 μm nanohole portion. The underlying physics is also suggested.

3.2 Simulation Modeling

ANSOFT High Frequency Structure Simulator (HFSS) from SAS IP Inc. was used to handle the optical simulation. HFSS is a high-performance full-wave electromagnetic (EM) field simulator for arbitrary 3D volumetric passive device modeling. It integrates simulation, visualization, solid modeling, and automation in an easy-to-learn environment where solutions to the 3D EM problems are quickly and accurately obtained. Ansoft HFSS employs the finite element method (FEM) to solve arbitrary 3D geometry, especially those with complex curves and shapes, which is just suitable for our nanostructure texture study. The primary advantage of the FEM for solving partial differential equations lies in the ability of the basic building blocks used to discretize the model to conform to arbitrary geometry. The arbitrary shape of the basic building block (tetrahedron) also allows HFSS to generate a coarse mesh where fewer cells are needed to yield an accurate solution, while creating a finely discretized mesh where the field is rapidly varying or higher accuracy is needed to obtain an accurate global solution [96]. The simulation process is shown in Table 3.1. Starting from Model design, the 3D nanostructure is first drawn with basic geometric blocks (e.g. cuboid,

cylinder). Materials can be defined for each block, which determines each block's optical property. With proper boundary condition setup, we can simulation the optical performance of a large array with only one unit. Excitation determines the incident electromagnetic field. The simulation is based on mesh operation, in which the model is divided into many triangular meshes for calculation. Thus, the more mesh generated, the more accurate of the result, at the expense of simulation time. More detailed discussion on the HFSS calculation is given in Appendix B.

Table 3-1 Flowchart of the HFSS simulation process

Our simulation using the FEM methodology is first verified toward the data reported by Hu and Chen [97], which is obtained by the transfer matrix method (TMM) [98, 99]. In Figure 3.1, the absorption characteristics calculated by FEM are shown based on the structures described in Ref. [97]. It is found that the optical characteristics match well with the reference data. For the case of the 2330 nm thick Si thin film, the ultimate

efficiency of ~15.25% is obtained based on Figure 3.1, which is comparable to the reported 15.50% [97]. The term ultimate efficiency is defined in detail in the following part.

Figure 3-1 Absorption spectra by FEM calculation of the 2330 nm thick Si film, and SiNP arrays with the lengths of 1160, 2330, and 4660 nm, as described by Ref. [97]

Figure 3.2 shows the schematic of the Si thin film with textured nanohole array surface investigated in the simulation. In this study, a Si thin film with Si NH array decorated surfaces is studied via simulation for solar energy absorption. It is found that the adding of the Si NH arrays to the Si thin films can significantly enhance the light absorption. Three critical structural parameters of Si NH array are investigated, i.e., the nanohole array periodicity (P), nanohole depth (H), and nanohole diameter (D). The Si and corresponding refractive index used in the simulation refer to crystalline silicon [100]. Full wave finite element method is used to solve the Maxwell's equations. The incident solar radiation is a plane wave normal to the X-Y plane and parallel to the Si nanohole

array. The interaction between the incident light field and the nanohole array structure is realized through infinitely extending the structural units along the z-axis and the dimension equals to the Si NH array periodicity in the two-dimensional space by applying the periodic boundary condition. The optical information is obtained from the spatial distribution of the energy flux, as a result of the interaction of incident light and the Si structure [95]. The incident light energy varies from 1 to 4 eV, corresponding to the wavelength from ~ 1240 nm to ~ 310 nm, which covers the main part of solar spectrum that is of interest. Note in the same figure, the effective refractive index variation (see the associated discussion in Figure 3.4) along the thickness of the Si thin film is also depicted.

Figure 3-2 Schematic of 3-D view of the nanohole structure on Si film modeled for optical simulation. The figure on the right side gives the spatial distribution of the effective refractive indices for the nanohole structure, where n_{air} and n_{Si} are the refractive indices of air and bulk Si, respectively.

3.3 Simulation Result and Discussion

Three parameters are studied for optimal light absorption of NH array, i.e. array period (P), NH depth (H) and NH diameter (D). As period and diameter are correlated to each other, their ratio (D/P) is also investigated instead of diameter itself.

1. Impact of diameter/Period ratio (D/P)

Figure 3.3 (a, b, c) illustrates the absorption, reflection and transmission spectra of a nanohole array with different nanohole diameters. In this case, the structures are set with a fixed P of 400 nm, and H of 1000 nm. The diameter varies from 100 to 400 nm. A silicon thin film with 1800 nm thickness is taken as the reference sample. It is clear that the light absorption is significantly enhanced as D increases, especially in the high energy range (> 2.2 eV), as compared to the reference Si film with the same thickness of 1800 nm. The absorption edge shifts toward low energy side with the increase in the nanohole diameter. As shown in Figure 3.3 (c), the transmissions do not have much difference for different diameters. And it is clear to see that the enhanced light absorption with the nanohole diameter mainly stems from the suppressed light reflection (Figure 3.3 (b)), which can be interpreted by the reduced refractive index of the nanohole structure [101].

Figure 3-3 (a) Absorption, (b) reflection and (c) transmission spectra. The spectra of the 1800 nm thick Si film serve as reference.

From Fresnel equations, the large refractive index difference could result in high reflection when light moving between media of differing refractive indices. In this case, the large refractive index of Si thin film causes high reflection when light is incident on the surface and thus reduce the light absorption. The effective refractive index (n') of the nanohole structure can be described as the average refractive index between air and bulk Si substrate weighted by their respective volumes, with the formula below:

$$n' = n_{\text{air}} + \left(1 - \frac{\pi D^2}{4P^2}\right) \cdot (n_{\text{Si}} - n_{\text{air}}) \quad (3.1)$$

where n_{air} and n_{Si} refer to the refractive index of air and bulk Si respectively. Note that the n' decreases with increasing D . Therefore, the suppressing of reflection with increasing D from 0 nm to 400 nm can be expected. To quantitatively evaluate the overall performance of the nanohole structures for solar energy trapping, the ultimate efficiency (η_{ulti}) under the Air Mass 1.5 direct normal and circumsolar spectrum [31] was calculated by applying the formula below [12]:

$$\eta_{\text{ulti}} = \frac{\int_{E_g}^{\infty} \frac{E_g \times I(E) \times \alpha(E)}{E} dE}{\int_0^{\infty} I(E) dE} \quad (3.2)$$

where E_g is the silicon band gap, E is the photon energy, $\alpha(E)$ is the absorption spectrum from the simulation and $I(E)$ is the solar energy density spectrum corresponding to the solar spectrum mentioned. The term ultimate efficiency is used to quantitatively evaluate the nanostructure's light trapping capability. From the formula, the ultimate efficiency is defined as the optical to electrical conversion ability, we assume that for the photons with the energy above E_g , if they can be trapped by the solar devices, all of these photons would be converted into electron-hole pairs with the energy of E_g , and all these electron-hole pairs can be completely extracted for electrical energy output. Or in another word, the internal quantum efficiency is 1 [12]. The carrier recombination processes (e.g., Shockley-Read-Hall and Auger recombination) within the nanostructure are not taken into account. In other words, the internal quantum efficiency is assumed to

be 100%. As shown in Figure 3.3, η_{ulti} increases from 15.1% to 27.4% when increasing D from 100 nm to 400 nm, almost 2 times larger than that of the 1800 nm thick Si film.

Figure 3-4 Ultimate efficiency of the structure used in simulation with different nanohole diameters of 100, 200, 300, and 400 nm. 1800 nm thick Si film serves as reference. Note that the effective refractive index is based on 589 nm incident light, in this case, $n_{si} = 3.96$ and $n_{air} = 1$ [100]

Figure 3.5 illustrate the top-view of the nanohole array with varied diameter under fixed period. When diameter is close to zero, the nanohole array would act like a flat thin film. If we further increase the diameter to make the D/P ratio larger than 1, the neighbor holes will merge and the array is not nanohole array any more. Instead, it becomes a nanopillar-like structure, which is beyond the interest of this study. Thus, we do not consider that case. Note that, η_{ulti} improvement tends to saturate when D is 350 nm. Accordingly, the diameter/periodicity ratio (D/P) is set as 87.5% as the optimized

parameter for light absorption, which would be used for the following simulations in this work, considering the pitch limitation (D/P of 100% is difficult to be empirically realized).

Figure 3-5 Schematic of the top-view of nanohole array with different D/P ratio.

2. Impact of depth (H)

The optical characteristic spectra of the nanohole structure with different H are shown in Figure 3.6, with a fixed P of 400 nm and a fixed D of 350nm. Increasing nanohole depth can also improve the light absorption. And this improvement is mainly due to the depressed light reflection, as shown in Figure 3.6 (b) and (c). Compared to the 2800 nm silicon thin film, the nanohole array structure can significantly enhance the overall light absorption even with an H of only 200 nm (with a total structure thickness of 1000nm).

Figure 3-6 (a) Absorption, (b) reflection and (c) transmission spectra of the structures used in the simulation with different nanohole depth of 200, 400, 1000, and 2000 nm. The spectra of the 2800 nm thick Si film serve as reference.

Figure 3.7 shows the η_{ulti} of the nanohole structures with different depth. It is seen that η_{ulti} improvement gradually saturated when H is beyond 2000 nm (with a total structure thickness of 2800 nm). The transmission does not have obvious change as the nanohole depth variation, thus, the absorption improvement is mainly from suppression of the reflection. Considering that making deeper holes may increase surface defects and fabrication difficulty, 2000 nm could be considered as an upper limit for nanohole fabrication. Further increasing nanohole depth beyond 2000 nm would not benefit the

solar device.

Figure 3-7 The ultimate efficiency of the structure used in the simulation with different nanohole depth from 200 to 3500 nm. The spectrum of the 2800 nm thick Si film serves as reference.

3. Impact of period P

The next important parameter is the nanohole array period P . With the other parameters fixed (D/P ratio = 87.5%, $H = 2000$ nm), P is varied from 100 nm to 800 nm. Figure 3.8 (a, b, c) show the absorption, reflection and transmission spectra of the nanohole structures with a fixed H of 2000 nm (with a total structure thickness of 2800nm) and D/P ratio of 87.5%, as a function of P , and compares with the 2800 nm thick Si thin film reference. It is seen that, for the structure with small P (for example, 100 nm and 300 nm), the light absorption enhancement mainly occurs in the high energy region, i.e., > 2.6 eV. On the other hand, with further increasing P , the light absorption enhancement in the low energy range becomes more significant, but in the meanwhile the light reflection would also be increased in the high energy region. Note that the nanohole

array with the P of 100 nm shows similar absorption spectra compared to the 2800 nm thick Si thin film sample in the low energy region; and the absorption improvement becomes stronger only when energy is higher than ~ 2 eV. The absorption for the nanohole structure with P of 300nm gives a similar trend compared to the 100nm one, but starts to improve from a much lower energy (1.2 eV).

Figure 3-8 (a) Absorption, (b) reflection and (c) transmission spectra of the structures used in the simulation with different periodicity of 100, 300, 500, and 700 nm. The spectra of the 2800 nm thick Si film serve as reference.

These observations can be interpreted from the viewpoint of remaining Si nanostructure after nanohole formation. Unlike separately standing nanopillar array, the

remaining Si structure of nanohole array is continuous, as shown in Figure 3.9 (a). One can take the nanohole array as a connected, square-like nanopillar array, as illustrated in the red dotted square in Figure 3.9 (a). Note that the remaining Si structure unit also has a periodicity of P , same as the nanohole array. This can help to understand the interaction between the incident light and the nanostructure.

Figure 3-9 (a) the top view of the nanohole array and the dimension of the remaining Si structure. (b) Ultimate efficiency of the structure (with constant $H = 2000$ nm, $D/P = 87.5\%$) used in the simulation with different periodicity of 100, 300, 500, and 700 nm.

The total top surface area/total unit area is kept constant when the diameter/period ratio is fixed based on the equation below:

$$\frac{A_{top}}{A} = \frac{P^2 - \pi r^2}{P^2} = 1 - \pi \left(\frac{r}{P}\right)^2 \quad (3.3)$$

where A is total top surface area, P is period, r is radius of nanohole. Thus, when diameter/period ratio is fixed, the total top surface area is also fixed. But for different period, the top area for a single unit is different, as illustrate in Figure 3.10. The unit with larger period has larger top area surface, as shown in Figure 3.10 (b).

Figure 3-10 Top view of nanohole array with same period/diameter but different period.
(a) small period array, (b) large period array

It is seen that with the increase of P , the light absorption edge shifts toward low energy and meanwhile the light absorption decreases in high energy region. This can be explained from the viewpoint of optical path prolongation in the remaining Si nanostructure. As illustrated in Figure 3.11, in low energy region, the light wavelength is much longer than the remaining Si nanostructure P , so the radiation can easily pass through the remaining Si nanohole array, and interact with the underlying silicon thin film. When the wavelength becomes comparable to the remaining Si nanohole array P , the light absorption would be strongly enhanced due to the strong scattering effect, which is resulted from the prolonged optical path [93]. It is thus reasonable that the absorption inflection edge to shift toward lower energy regime as nanohole array P increases due to the scattering effect, as shown in Figure 3.8 (a), and accordingly the reflectance in the higher energy regime rises, as shown in Figure 3.8 (b, c). The η_{ulti} increases from 26% to 35% with the increase of the nanohole periodicity from 300 nm to 700 nm, as shown in Figure 3.9 (b). On the other hand, η_{ulti} starts to decrease when the periodicity further

increases to 800 nm onwards, owing to the enhanced light reflection in a broader range stemming from the increased top surface of the remaining Si nanostructure, as illustrated in Figure 3.10.

Figure 3-11 Schematic of interaction between nanohole structure and incident light with different wavelength ranges.

To better illustrate the light absorption in the nanohole structures at different wavelength, the electrical field distribution is analyzed for the structures at three radiation energy, as shown in Figure 3.12. For high energy radiation (3.5 eV), the light is mainly absorbed near the surface portion of the nanohole structure. At visible light range (2.5 eV), most of the light is absorbed within the nanohole structure, which explains the high absorption at this wavelength range. And for long wavelength (1.5 eV), the radiation is able to penetrate the whole structure including the thin film substrate. This result agrees very well with the optical characteristics.

Figure 3-12 Electric fields of one face of the nanohole structure under 3 different radiation energies (1.5 eV, 2.5 eV and 3.5 eV). The simulation model consists of three portions: The center portion is silicon cuboid with a hole inside. The top and bottom portions simulate the air environment. The electric field is generated from the top surface.

The oblique light incident case is also studied to analyze the sensitivity of nanohole array (nanohole depth = 2000 nm, array periodicity = 700 nm and diameter/periodicity ratio = 87.5%) to the oblique incident light. The incident angle θ is defined as the angle between the incident light and the structure normal axis. As shown in Figure 3.13, the light absorption of the Si NH structure decreases when the incident light is oblique compared to the normal incident case. As the transmittances are almost same for different incident angles, the decrease of the absorption mainly comes from the enhanced reflection. The ultimate efficiency of the 30° and 60° light incident case is 23.9% and 16.1% respectively, which is still superior to the 2800nm thick Si thin film (15% with normal incident light).

Figure 3-13 Absorption and reflection spectra of the optimized structure with normal incident light, 30° and 60° incident light. The spectra of the 2800 nm thick Si thin film serve as reference.

3.4 Conclusion

In summary, the optical characteristics of the Si thin film with nanohole array textured surface are studied via simulation. The nanohole array parameters for effective

light absorption are optimized. The ratio of diameter/periodicity ratio around 87.5% is considered as the optimized value considering the empirical difficulty for the nanohole array fabrication. The light absorption increases significantly with the increase of the nanohole depth and saturates when the H is > 2000 nm. And the light absorption strongly depends on the nanohole periodicity. When the nanohole array periodicity is set at ~ 700 nm, the light absorption reaches maximum due to the suppressed reflection in the broad range of the solar spectrum. The further increase in the periodicity would decrease the light absorption due to the increased reflection in the energy regime below 2.5 eV. The optimal ultimate efficiency we achieved is $\sim 35\%$ when setting the nanohole depth at 2000 nm, the diameter/periodicity ratio at 87.5%, and periodicity at 700 nm. The nanohole array textured surface is believed to be promising for light absorption enhancement in silicon thin film solar cell.

4. ELECTRICAL SIMULATION OF NANO HOLE TEXTURED SILICON THIN FILM SOLAR CELL

4.1 Introduction

In this chapter, the electrical characteristics of Si NH textured thin film solar cell in terms of power conversion efficiency (PCE) (η) is investigated and optimized via software simulation, where the Si NH physical dimensions were predetermined for optimized solar-energy absorption from the aforementioned optical simulation data in the previous chapter. Several key factors affecting PCE of the solar cell, e.g., the impact of Si quality in terms of minority carrier lifetime, emitter doping level, and emitter junction depth, are highlighted, and a practical guideline to design high-efficiency Si NH textured thin film solar cell is provided. The η of the structure under investigation can be significantly boosted, compared with the to-date reported Si thin-film solar cell.

4.2 Simulation Modeling

Genius Semiconductor Device Simulator from Cogenda pte Ltd is used to conduct the electrical simulation. The simulation process flow is illustrated in Figure 4.8. The electrical simulation is conducted based on the optical data extracted from the optical simulation in Chapter 3.

Figure 4-1 Optical and electrical simulation process for nanostructure modeling

The electromagnetic field at each coordinate of the three-dimensional (3D) simulation grid obtained from optical simulation was exported for electrical simulation [102]. The current-voltage characteristics of the Si NH or SiNP cell are then obtained by solving the current continuity and Poisson's equations at each coordinate of the 3D simulation grid [103]. Drift diffusion model is applied for carrier transport within the solar cell. Three recombination mechanisms are considered in the simulation, including Shockley-Read-Hall, Auger, and direct recombination. The total recombination is considered as the sum of all. [103]. The collection of generated charge carriers depends on the diffusion length of minority carriers of both side of n^+p solar cell. For the heavily doped n^+ emitter, the minority carrier lifetime is small. The p-type base ($N_A = 10^{16} \text{ cm}^{-3}$) is moderately doped and a constant minority-carrier lifetime is assumed. The lifetime is

calculated based on the doping mobility-dependent values for crystalline Si. More details regarding the electrical simulation model can be found in Appendix C and ref [103]

The process of fundamental optical absorption in a semiconductor transfers energy from a propagating electromagnetic wave to excite a free electron-hole pair within the semiconductor. Thus, the photogeneration rate can be determined from the divergence of Poynting vector. The optical power absorbed per unit volume from a monochromatic source at angular frequency ω can be calculated from the divergence of the Poynting vector:

$$P_{abs}(r, \omega) = -\frac{1}{2} \text{Real}\{\vec{\nabla} \cdot \vec{P}(r, \omega)\} \quad (4.1)$$

which can be recast in terms of electric field:

$$P_{abs}(r, \omega) = -\frac{1}{2} \omega |E|^2 \text{image}(\omega) \quad (4.2)$$

The photon energy at frequency ω is $E_v = h\omega$. To obtain a photogenerated-carrier profile (G), the photogenerated carriers are integrated to the continuity equation. G can be calculated from the divergence of Poynting vector S which can be expressed as

$$G = \eta_{quan} \frac{\pi \epsilon_o (-\epsilon_r'') |\vec{E}|^2}{h} \quad (4.3)$$

where $|\vec{E}|$ is the electric field recorded at each simulation grid point from the previous optical simulation via FEM, ϵ_r'' is the imaginary part of the concerned material's permittivity, and η_{quan} is the ideal quantum efficiency, which considers no reflection from surface. It can be calculated as

$$\eta_{quan} = \text{step} \left(\frac{hv}{E_g} \right) \begin{cases} 0, (hv < E_g) \\ 1, (hv \geq E_g) \end{cases} \quad (4.4)$$

where E_g is the energy bandgap of the Si, hv is photon energy. The terminal I - V behavior of the semiconductor device can be obtained by simultaneously solving the electron and hole continuity equations and the Poisson equation on each 3-D simulation grid [103].

Figure 4-2 Proposed NH array textured structure Si thin film PV with planar junction configuration modeled in this study. The structural parameters are optimized based on the maximum light absorption. Note that the transparent conductor and bottom metal contact are for demonstrate only. Their optical impact are not included.

Figure 4.2 illustrates the schematic of the Si NH textured thin film solar cell for device electrical performance evaluation. The structural dimensions are taken from the previous optimized structure ($H = 2000$ nm, $P = 600$ nm, and $D/P = 87.5\%$) [102]. A planar junction configuration is employed with an n -type emitter and p -type base. The

bottom of the structure has a 50 nm heavily doped p -type layer (10^{20} cm^{-3}) as back surface field to passivate the rear surface and prevent the minority-carrier recombination at the back contact. The top surface of the Si NH arrays is covered with transparent conductive materials. The ohmic contacts are assumed to be ideal at both front and rear electrodes of the device. Note that the electrical simulation is based on the previous optical simulation data. Thus, only “intrinsic” light absorption of the Si NH array is taken into account. The front transparent conductor and the rear metal contact shown in the Figure 4.2 are for device structure demonstration only. Their impact to the device light absorption is not incorporated.

4.3 Impact of Emitter doping (N_D), emitter width (d), and minority-carrier diffusion length (L_n)

It is known that the open-circuit voltage (V_{oc}) of the solar cell is directly related to the emitter doping concentration N_D . High emitter doping N_D is required to maintain high V_{oc} and low resistive loss during extraction of the photogenerated carriers. Increasing N_D reduces the equilibrium minority-carrier concentration at the junction and hence, lowers the carrier recombination, resulting in V_{oc} improvement. However, excessive N_D reduces the minority-carrier (holes) diffusion length (L_p), which causes a decrease in short-circuit current (J_{sc}). Thus, N_D has to be compromised to optimize the solar cell performance. Figure 4.3 shows the impact of emitter doping (N_D) on V_{oc} and PCE, with emitter width (d) of 50 nm and base doping (N_A) of 10^{16} cm^{-3} . It is seen that with increasing N_D , V_{oc} increases and reaches 0.69 V when $N_D = 10^{22} \text{ cm}^{-3}$. On the other hand, when N_D exceeds

10^{21} cm^{-3} , the PCE starts to drop due to the excessive doping. PCE can reach 20.8% when N_D is 10^{21} cm^{-3} .

Figure 4-3 V_{oc} and PCE of the Si NH textured thin film solar cell as a function of Emitter doping N_D

As aforementioned, high emitter doping compromises L_p . Hence, in order to extract the photogenerated carriers (holes) in the emitter layer, the emitter width d must be kept shallow to allow the holes cross the p - n junction ($d < L_p$). Figure 4.4 shows the impact of emitter width on the J - V characteristics of the Si NH device, with N_D/N_A fixed at $10^{20}/10^{16} \text{ cm}^{-3}$ respectively. It is seen that J_{sc} increases significantly with decreasing d from 800 nm to 50 nm indicating that the majority of photo-generated carriers within the emitter may recombine within the emitter layer and thus not contribute to the output current.

Figure 4-4 J-V characteristics of the Si NH textured thin film solar cell at various emitter width d from 50 nm to 800 nm. (N_D/N_A fixed at $10^{20}/10^{16} \text{ cm}^{-3}$)

The photo-generated carrier profile is also calculated from previous optical simulation to better illustrate the carrier distribution within the Si NH structure. The photo-generated carrier profiles at two different cross section (A-A', B-B') of the Si NH array are shown in Figure 4.5. The reddish color area denotes high carrier density region. It is seen that most of carriers are generated within the Si NH region, especially near the top surface area. Therefore, keeping emitter layer shallow is particularly important for nanostructure (Si NH/SiNP) textured thin film solar cell: 50 nm is taken as optimized value considering manufacture difficulty.

Figure 4-5 Photogenerated carrier profiles of the Si NH textured silicon thin film (with optimized structural parameters) in x-z plane (a) along A-A' line passing through the NH center (b) along B-B' line

The effect of minority-carrier diffusion length (L_n) on cell performance is also investigated with $d = 50 \text{ nm}$ and N_D/N_A fixed at $10^{20}/10^{16} \text{ cm}^{-3}$. The J - V characteristics for L_n ranging from 0.01 to $10 \text{ }\mu\text{m}$ are shown in Figure 4.6. Low L_n can significantly degrade the J - V characteristics of Si NH solar cell. Both J_{sc} & V_{oc} increase with L_n and start to saturate when $L_n \geq 0.5 \text{ }\mu\text{m}$, indicating that low quality Si with relative small diffusion length (e.g. poly-Si) could be employed to further reduce the cost of Si NH textured thin film solar cell, and ease the manufacturing requirement without sacrificing the cell performance.

Figure 4-6 J_{sc} and V_{oc} of the Si NH textured solar cell at various L_n

4.4 Impact of surface recombination velocity (SRV)

Nano-textured thin film solar cell has much higher surface/volume ratio and carrier densities compared to bulk solar cell. Thus, surface recombination has greater impact on V_{oc} and J_{sc} for nanostructure textured solar cell. As shown in Figure 4.5 (b), the majority of the photogenerated carriers are near the Si NH top and sidewall surfaces region. Hence, the SRV is particularly critical to the nano-textured cell performance. SRV must be kept as low as possible to achieve a high PCE. To investigate the effect of SRV on the cell efficiency, the J - V characteristics for SRV ranging from 1 to 10^6 cm/s are simulated, as shown in Figure 4.7. The emitter width d and N_D are held constant at 50 nm and 10^{20} cm $^{-3}$, respectively. The PCE only drops from 20.5% to 20% as SRV increasing from 1 to 100 cm/s. The degradation starts to accelerate when $\text{SRV} \geq 500$ cm/s. Note that

20-100 cm/s has been reported recently for a non-doped Si nano-structure after passivation [104]. SRV < 300 cm/s could also be possible to achieve by doped Si nano-structure [105], which suggests that it is possible to keep the SRV within an acceptable range for feasible nanohole textured solar cell applications.

Figure 4-7 PCE of Si thin film solar cells with different Surface recombination velocity. The emitter width d and N_D are held constant at 50 nm and 10^{20} cm^{-3} , respectively

4.5 Comparison between Nanohole and Nanopillar arrays

Nanopillar (NP) is one of the most important nanostructures and has gained much attention in the recent years. A lot of research has been done on this structure for its potential photovoltaic applications. It is therefore necessary to make a comparison of the nanohole to its nanopillar counterpart. The structural parameters for optimized light absorption of NH array have been reported in our previous studies [95, 102]. Beside the

NH array, our group also studied the optical potential of NP array for Si thin film photovoltaic applications [95, 106, 107]. Based on these studies, the optimized structural parameters for Si NH array are $P = 600$ nm, $H = 2000$ nm and $D/P = 87.5\%$; and for SiNP array are $P = 500$ nm, $H = 1000$ nm and $D/P = 50\%$. It should be noted that further increasing the NH/NP height will neither degrade the ultimate efficiency nor affect the other optimized structural parameters [95, 102].

Figure 4-8 Schematics of the Si NH and SiNP structures for optical simulation.

Figure 4.8 depicts the schematics of both Si NH and SiNP textured thin film for optical simulation comparison. The thickness of the underlying Si film for both Si NH and SiNP is fixed as 800 nm. In order to compare the light trapping properties of Si NH and SiNP array, both nanostructures are set to have same height $H = 2000$ nm (total 2800 nm with the 800 nm Si film). For structure's parameters, based on these studies, the optimized structural parameters are applied (Si NH array are $P = 600$ nm, $H = 2000$ nm and $D/P = 87.5\%$; SiNP array are $P = 500$ nm, $H = 1000$ nm and $D/P = 50\%$). The incident light (plane wave and normal to the X–Y plane) energy varies from 1 to 4 eV, which covers the major concerned energy regime of solar spectrum. The interaction

between the incident radiation field and Si NH / SiNP is calculated by finite element method through infinitely extending the structural unit by applying the periodic boundary condition. The electromagnetic field distribution is calculated by resolving Maxwell's equations. The optical characteristics can then be obtained from spatial distribution of the energy flux within the nano-structure.

Different from the multi-reflection theory based on geometrical optics which applied on the micrometer scale surface textures such as the “inverted pyramid” array textured Si wafer-based solar cells [108, 109], the incident light interaction within the sub-wavelength surface texturing is dominated by wave optics. When the incident light wavelength is comparable to P , the scattering effect could be strongly enhanced due to the prolonged optical path and thus the improved light absorption. Therefore, the strongest absorption region corresponds to the structural array periodicity. The optimized absorption spectra of Si NH and SiNP arrays are shown in Figure 4.9. One can see that both Si NH and SiNP surface texturing can significantly boost the light absorption of the thin film, especially in visible and long wavelength region. For same periodicity ($P = 500$ nm), both Si NH and SiNP have a strong light absorption at ~ 2.3 eV. Note that Si NH has a broader absorption peak compared to SiNP, which leads to higher overall light trapping capability despite of its relatively weak absorption in high energy region. The overall light absorption capability can be quantitatively evaluated by calculating their ultimate efficiency. As shown in the inset of Figure 4.9, the Si NH array with $P = 600$ nm gives higher ultimate efficiency of 33.4% as compared to 27.6% achieved by the SiNP array. It is worth pointing out that the light absorption ability of Si NH is $\sim 20\%$ stronger than that

of SiNP, which makes Si NH a better texturing candidate for thin film PV application. Similar results were also obtained by other research groups. Recent works reported that the Si NH array (nanostructure only, without underlying Si film) possess superior light absorption as compared to SiNP one [77]. The reason behind this difference is remain unclear. Further study is needed to explain for NH's superior light absorption over NP.

Figure 4-9 Absorption spectra of the Si NH and SiNP arrays with optimized structure parameters (Si NH array are $H = 2000$ nm and $D/P = 87.5\%$; SiNP array are $H = 1000$ nm and $D/P = 50\%$). The spectra of the 2800-nm-thick Si thin film serves as reference. (Inset) The ultimate efficiency of the corresponding nanostructures.

For comparison, SiNP structure is also modeled for electrical simulation using similar approach in previous work [106]. As shown in Figure 4.10 (a), with same total thickness of $2.8 \mu\text{m}$ and optimized device parameters (L_n , N_A , N_D , d , SRV), Si NH texturing gives highest J_{sc} ($\sim 37.3 \text{ mA/cm}^2$) as compared to SiNP texturing ($\sim 31.9 \text{ mA/cm}^2$) and Si thin film reference cell ($\sim 10.5 \text{ mA/cm}^2$) owing to its strong light absorption capability. Accordingly, the PCE of Si NH textured thin film PV can reach

20.5%, as compared to 17.6% achieved by SiNP array textured one, as seen in Figure 4.10 (b).

Figure 4-10 (a) J - V characteristics of Si NH, SiNP and Si thin film (Both NH and NP are with optimized structure dimensions) (b) PCE and Ultimate Efficiency of Si thin film solar cells with and without nanostructure array surfaces textures at AM 1.5 spectrum. The 2800 nm thick Si thin film solar cell serves as reference.

In summary, we have presented our investigation of the electrical performance of the Si NH textured thin film solar cell by establishing a device physics model incorporated with structural optical properties. Our simulation results indicate that Si NH textured thin film has a strong light absorption capability than the SiNP counterpart and thus higher PCE. The impact of the emitter doping level, emitter width, minority carrier diffusion length and surface recombination velocity on the cell performance is also investigated. An optimized emitter doping N_D of $1 \times 10^{21} \text{ cm}^{-3}$ is obtained considering the compromise between obtaining high V_{oc} and degrading carrier diffusion length/reverse saturation current. Shallow emitter width d is needed for effective photogenerated-carrier collection. The result suggests that the low grade Si thin film with relative small diffusion length ($L_n \geq 0.5 \text{ }\mu\text{m}$) could be employed for thin film based solar cell to reduce the production cost and yet achieve high efficiency. On the other hand, the solubility of the dopant needs to be taken into consideration to avoid diffusion-induced dislocation. This work will be helpful in the design and fabrication of high efficiency Si NH textured thin film solar cells.

5. DEMONSTRATION OF LARGE SCALE QUASI-ORDERED NANO HOLE TEXTURE FOR SI THIN FILM PHOTOVOLTAIC APPLICATIONS

5.1 Introduction

Based on the previous chapters, the optical and electrical simulation of the NH textured silicon thin film not only reveals its light trapping potential but also provides a guideline for experiment and device fabrication. In this chapter, the author investigates the structure's feasibility for practical applications. To fabricate ordered NH array structure, one direct way is to use lithography to pattern the NH array, which provides excellent matching with the simulation. However, lithography is an expensive process with low throughput, which is not suitable for photovoltaic industrial applications. Nanohole-like structure has been empirically demonstrated by various techniques including direct electrochemical etching [110], porous alumina mask [111], and self-assembly nanosphere mask [94]. Fabrication of periodic nanohole structures for optimal light absorption, and low-cost implementation of nanoholes into photovoltaic application is still a challenge for the above mentioned methods. The author tried to find a compromise method to realize NH array with certain degree of order (quasi-ordered), and yet only employing processes of relatively low cost, high throughput and feasible for thin film photovoltaic applications.

In this chapter, large scale Si NH textured solar cell with radial p - n junctions was demonstrated via low cost, maskless methods including laser annealed Ag particles

catalytic wet etching and phosphoric acid diffusion. The quasi-ordered Si NH geometry exhibits great light trapping capability and potential of high efficiency solar energy conversion. The related fabrication techniques such as Ag assisted wet chemical electroless etch and phosphorous diffusion doping are also transferrable to thin film photovoltaic applications. Under 1 sun AM1.5G illumination, the fabricated Si NH solar cell exhibited an open-circuit voltage of 558 mV, a short-circuit current density of 29.1 mA/cm², and a remarkable power conversion efficiency of 9.5%.

5.2 Nanohole Structure Formation on Si Substrate

This section discusses the formation of NH texture on Si substrate, including the author's exploration on the preparation of Ag particles. As the main light harvest body, the nanohole structure is the key to determine the solar cell performance. There are generally two approaches to fabricate Si nanostructures, i.e. "bottom up" and "top down". "Bottom up" approach mainly refers to VLS method which can be used to grow SiNP on different substrates. The main problem with this method is the unavoidable deep level defect and metal contamination which severely affects the device's electrical properties. The "top down" approach normally refers to realizing nanostructure using different etching technique, e.g. wet etch, dry etch. Among different "top down" methods, the metal assisted wet chemical etching is strongly favored in the recent years as a promising method to form different Si nanostructures with unique optical properties, such as antireflection layer, enhanced absorption in visible and near IR spectral region, high chemical stability under atmospheric conditions [58, 64]. Moreover, compared to other etching technique, e.g. dry etch, this method is possible to meet the solar cell

manufacturing requirements, i.e. large area, and high throughput. Two-step metal assisted wet chemical etching, as mentioned in Chapter 2, provides a feasible way to fabricate Si NH structure with controllable dimension. The size and distribution of the NH array is directly related to the initial shape and distribution of the Ag particles array, which can be modulated by tuning the Ag particle formation process.

In order to fabricate ordered NH texture on Si substrate, ordered Ag particles array is required as the etching mask. Photolithography technique is obviously a direct choice to get ordered Ag particles array with designated diameter and periodicity [79]. However, the high cost, complication and low throughput strictly limit its application in the PV industry. One common method to prepare Ag particles on Si substrate is through dewetting process. Dewetting is a spontaneous process that a thin film on a surface rearranges itself into a layer of continuous clusters or separated particles. It could become a possible way to obtain Ag particles with designated size and spatial distribution from a continuous thin film. It offers the advantage of avoiding using expensive lithography technique. Moreover, it can be easily applied to large scale process to further lower down the cost and increase the throughput.

When an Ag thin film (< 100 nm) is deposited on Si substrate, the obtained film/substrate system is not in a stable status. Vacuum deposited silver films generally exhibits tensile stress [112, 113]. In other words, thermodynamically, the preferred morphology is not film but separate clusters [114]. Thus, the Ag film could transform from wetting layer to Ag particles when annealed at elevated temperatures close to its eutectic temperature with the Si substrate. It is believed that the Ag particles can be

obtained by reshaping the internally-stressed film [115]. The amorphous Ag film deposited by EBE or sputtering carries a lot of defects and internal stress. During annealing, the thermal energy is transferred to Ag atoms, and the Ag atoms gain sufficient mobility to rearrange to more favorable positions. Thus, the film starts to break into a monolayer of particles or clusters with lower local energy state [116]. The defects (grain-boundary or impurity) are generally thought to be the trigger of the de-wetting process. For example, film can retract from impurity particles, and exposing the substrate next to the impurity [117]. Figure 5.1 illustrates schematically the main driving forces involved in this process. To relax the stress built in the film during the deposition process, the film tends to “ball up” into separate particles. On the other hand, the surface energy minimization trend and the dispersion force between the top and bottom interfaces work to stabilize the film. Once the particles are formed, the repulsion force between the metal covered and exposed area will help to stabilize the particles and keep a certain distance between them. Some long-ranged forces such as dispersion force and the electrical double layers will also affect the metal particle size and location distributions [115, 118]. In this case, the electrical double layers refer to two parallel layers of charge at the interface of particle and substrate. The final morphology depends on the balance between these driving forces [118, 119].

Figure 5-1 Schematic of the main driving forces involved in the Ag particles formation process

In order to get Ag particles array with certain control of size and distribution (quasi-ordered), the annealing technique and condition must be carefully chosen to control the dewetting process. The basic experiment procedure is shown in Figure 5.2. Starting with 6" *p*-type Si wafer, after standard Radio Corporation of America (RCA) cleaning, Ag film with various thicknesses was deposited on the Si substrate by physical vapor deposition (PVD). To find a suitable annealing technique, three commonly used annealing techniques are studied: 1. Furnace annealing, 2. Rapid Thermal Annealing

(RTA), 3. Laser Annealing. Based on the simulation results in Chapter 4, the target NH array should have 600 nm period and 500 nm diameter. Thus the Ag particles array should also have the same size and distribution to match the simulation result.

Figure 5-2 Schematic of the NH structure fabrication process

1. Furnace annealing

Furnace is one of the most mature annealing techniques used in the semiconductor industry. It can process a batch of wafers at a time but each run may last several hours. For the experiment reported in this work, the wafers are coated with a thin film of Ag that is deposited by EBE. The samples are annealed in nitrogen environment under different temperature (from 200 °C to 425 °C) and time (from 30 min to 3 hours). After annealing, the sample is cooled down in furnace until 200 °C before unloaded.

Figure 5-3 SEM images of the furnace annealed Ag particles from Ag films with different thickness (a) 20 nm, (b) 30 nm (c) 40 nm (d) 50 nm. The black scale bars in the images represent a distance of 200 nm.

Ag films with different thickness (20 nm, 30 nm, 40 nm, 50 nm) are deposited on Si wafers. The samples are annealed at 425 °C for 1 hour in the N₂ environment. The results are shown in Figure 5.3. The favorable result (round particle) is from 20 nm Ag film. For very thin film, surface energy minimization trend becomes negligible. Thus, the film results in uniform, circular-like shape Ag particles after annealing, which is mainly due to the film stress relaxation and easier to achieve low local energy state. As the Ag film thickness increases, the surface energy minimization trend becomes more prominent. Thus, the resulting Ag particles become less uniform in size and more irregular in shape. When the Ag film exceeds 50 nm, only continuous Ag clusters are formed instead of separate particles. Basically, the Ag film will tend to form particles on the Si substrate

given enough time at elevated temperature when sufficient energy is transferred to the Ag atoms [120]. Generally, there are three accepted mechanisms for dewetting process, as illustrated in Figure 5.4: (1) by homogeneous nucleation of holes followed by their enlargement and coalescence, (2) by spinodal dewetting due to an instability based on the free energy for phase separation [116, 121-123] and (3) Evolution of a dewetting film by Ostwald ripening.

Figure 5-4 Top rows: schematic representation; bottom rows: experimental examples of the time evolution of ruptured thin films. (a) Dewetting by nucleation, growth and coalescence of holes. Reprinted with permission from ref. 2. Copyright (1998) by the American Physical Society; (b) spinodal dewetting. Reproduced with permission from ref. 3. (c) Evolution of a dewetted film by Ostwald ripening followed by crystallization [124, 125].

The experiment result shows reflow and breaking of Ag film, which indicate that the dominant mechanism in the formation of Ag particles through furnace annealing might be spinodal dewetting. According to the well-known Asaro-Tiller-Grinfeld (ATG) [126] instability, a continuous film can reduce its stress (which is built during the deposition) through fluctuation. And the amplitude of the fluctuation increases with time. Based on this theory, as the Ag film is annealed in the furnace, the Ag film starts to reflow. When the fluctuation amplitude exceeds film thickness, the substrate would be exposed. Eventually, the film breaks into separate particles. As the film thickness increases, the fluctuation is less able to mobilize the film to expose the substrate. Thus one can only see holes in the film instead of clusters, as shown in Figure 5.3(d). Figure 5.5 shows the size distribution of Ag particles formed by annealing Ag film with three different thickness (20, 30, 40 nm). Note that, in this study, the particles are assumed to be hemispherical shape. Thus, diameter is calculated based on the top-viewed particle area which is extracted by image processing software (ImageJ). The data of the histogram (particle size and number) comes from the SEM image. It is seen that the mean size of Ag particles (open square in the box) increase as the film thickness increase from 20 to 30 nm. However, in the case of 40 nm, the mean size drops, but with larger size variation and more large outliers, which indicates the film tend to form large, irregular shaped clusters instead of spherical particles. Increasing annealing time does not ease the situation. So further increasing the Ag particles size and distribution is proven to be difficult by furnace annealing.

Figure 5-5 Size distribution of Ag particles formed by annealing Ag film with different thickness (20 nm, 30 nm, 40 nm).

2. Rapid Thermal Annealing

Rapid Thermal Annealing (RTA) is another common annealing technique used in semiconductor manufacturing industry. Recently, RTA-like processing has attracted a lot of attention for various photovoltaic applications, such as phosphorus diffusion for *p-n* junction formation, impurity gettering, hydrogen diffusion for impurity and defect passivation, and formation of screen-printed contacts using Ag-ink for the front and Al-ink for back contacts. With high intensity lamp and water cooling system, the annealing temperature can be ramped up and down on a timescale of several seconds.

To study the RTA of Ag films (thickness = 30 nm), the samples are brought in RTP-system (JETstar-100) to various peak temperatures (400, 500, 600, 700 and 900 °C). The ramping up, annealing and ramping down time are all set at 60s. The process is conducted with nitrogen ambient gas. The results are shown in Figure 5.6. The film annealed at 400 °C only shows some scattered holes. Most part of Ag film is still continuous, implying that there is not sufficient thermal energy to mobilize the film. As the peak annealing temperature goes up from 500 to 700 °C, the Ag film is transformed from continuous clusters to separated particles with irregular shape and distribution. This implies spinodal dewetting (as shown in Figure 5.4 (b)) is the dominant dewetting mechanism involved in the process, which is the same as furnace annealing, even though its process time is much shorter. Further increasing the annealing temperature will not aid the particle formation. Instead, when temperature exceeds the Ag-Si eutectic temperature of 836 °C, the eutectic phenomenon happens [127]. The eutectic structure is formed within the Ag-Si system, as shown in Figure 5.6 (e). The melted Si recrystallize and change the surface morphology, thus, Ag particles formation is interrupted, which need to be avoided. Based on the obtained results, RTA only possesses limited control to the Ag particles formation. The short annealing time is not sufficient for Ag film to fully release the built-in stress and transform the film into hemispherical particles.

Figure 5-6 SEM images of the RTA annealed Ag particles from 30 nm Ag films at different temperature (a) 400 °C, (b) 500 °C (c) 600 °C (d) 700 °C (e) 900 °C. The black scale bars in the images represent a distance of 400 nm.

3. Laser Annealing

Laser annealing adoption is driven by the challenge of semiconductor device scaling, e.g. ultra-shallow junction fabrication. It is expected to gain more foothold in the semiconductor industry in the near future. Laser annealing is also an effective technique to dewet Ag film from Si substrate [120]. The process is conducted by exposing the Ag film to multiple laser pulses of nanosecond width. In order to obtain pre-defined Ag particles size and spatial distribution, laser annealed dewetting requires a fine control of laser energy density and film thickness. In this work, industrial KrF excimer laser from Coherent Lambda Physik (NovaLine-100) is used. This 248 nm wavelength laser system has 25 ns pulse duration and a maximum energy output of 400 mJ. The beam size selected is $3 \times 3 \text{ mm}^2$ (V×H, FWHM, typ.). The details of the laser system can be found in Appendix D. The sample holding stage is controlled by computer, so that the laser is able to scan the sample with designated area and overlapping between pulses. Unlike furnace and RTA, the laser annealing is conducted in air. To ensure that no silver oxide is formed during annealing, the Ag film is sintered with maximum energy density ($\sim 800 \text{ mJ/cm}^2$). The XRD analysis of the annealed sample is shown in Figure 5.7. It is seen that the Ag film composition does not change after the laser annealing.

Figure 5-7 X-ray Diffraction analysis of Ag film and Ag particles

For laser annealing, the size and distribution of the Ag particles are closely related to three factors, i.e., the silver film thickness, laser energy density, and laser pulse number, which would be illustrated respectively. One unique characteristic that distinguishes laser annealing from other annealing techniques is its ultra-high energy intensity and ultra-short annealing time. The pulse duration is only 25 ns. The maximum repetition rate is 250 Hz or 4 ms per pulse, which means that each pulse can be considered as a separate annealing step. Thus, laser energy density becomes a key factor to control the annealing process. Samples with 25 nm Ag film were annealed under different energy densities to study its impact on the Ag particles formation. The results are shown in Figure 5.8. At low energy density e.g., 150 mJ/cm² (Figure 5.8 (a)), the energy is insufficient to trigger the

dewetting over the film. Only some “weak points” with low activation energy, such as film defect or substrate particles, can initiate nucleation of holes. As the energy increases, more and more holes are formed at defect sites, leading to accumulation of Ag to the rim, delimiting a mosaic of holes and polygons like fishing net, as shown in Figure 5.8 (b). It is obvious to see that the dewetting mechanism at this stage is the nucleation and growth of holes (Figure 5.4 (a)). If the film gains more energy, the rim breaks into a series of droplets arranged along the rims of the net. The defects are randomly located throughout the Ag film during the deposition. Thus, if the laser energy is large enough to trigger all of them, the nucleation of holes can occur at the same time, resulting in a relatively uniform net and then an array of Ag particles with certain degree of uniformity in size and distribution. Note that, the resulting Ag particles exhibit hemispherical shape, which is highly favorable for the following Si NH array processing. Further increasing the energy density may result in larger particle size variation. This is due to the excess thermal energy passing to the film, leading to violent rim breaking and then generating a lot of tiny particles (less than 20 nm), which is undesirable for our purpose. Note that tiny particles may also come from evaporation and ablation of the film material. Therefore, a fine control of the critical laser energy and the film thickness for each material is required to obtain designated Ag particles. Similar to RTA, high energy density (e.g. $> 500 \text{ mJ/cm}^2$) may also heat up the Ag-Si system over its eutectic temperature, resulting in recrystallization of the Si substrate and diffusion of Ag into the Si (Figure 5.8 (f)).

Figure 5-8 SEM images of laser annealed 25 nm Ag film under different energy density (a) 150 mJ/cm², (b) 200 mJ/cm² (c) 250 mJ/cm² (d) 300 mJ/cm² (e) 400 mJ/cm² (f) 500 mJ/cm²

As energy density is a key factor to determine the Ag particles formation, it is necessary to check the process window. Si samples with 20 nm Ag film is annealed with different energy densities. The mean diameter and the variation of the obtained Ag

particles are calculated, as shown in Figure 5.9. It is seen that the mean size of the Ag particles is relatively stable against energy density in the range from 230 to 300 mJ/cm². This implies that the process window is still large, which is very important for manufacturing. This is also particularly important for gas lasers considering their non-stability nature.

Figure 5-9 (a) SEM image of laser annealed 20 nm Ag film with 260 mJ/cm² energy density, (b) corresponding Ag particles diameter histogram, and (c) average diameter as a function of laser energy density (error bars indicate 90% confidence interval)

The Ag film thickness is another important factor. It determines the amount of material for the Ag particles formation, which in turn affects the Ag particles size. To study the impact of film thickness on the particle formation, Ag films with thickness of 50 nm, 25 nm, and 10 nm were deposited and exposed to single laser pulse with 400 mJ/cm² laser energy density. Figure 5.10 shows the SEM images of the three samples after laser annealing. Variation in particle size is observed, which is coupled with the ultrafast cooling rate of the non-equilibrium laser process and the possible film thickness non-uniformity [128]. For thin Ag film, e.g. 8 nm as shown in Figure 5.10 (a), the resulting Ag particles have a relatively large size variation in a range from 2 to 30 nm. Thicker Ag film also results in large particle size variation, as shown in Figure 5.10 (c). Due to the excess amount of material, the Ag particles closely stick together, some even overlap. The substrate is barely exposed, which is undesirable for the subsequent wet etching process. In this case, the 25 nm gives the best uniformity. This implies that the film thickness needs to be controlled to achieve designated particle size. Note that, based on the previous simulation result, the NH diameter should be ~ 500 nm for optimized light trapping. However, due to the dewetting property of Ag on Si, there may be an upper limit for the particle size.

Figure 5-10 SEM images of laser annealed silver films with different thickness. (a) 8 nm (b) 25 nm (c) 50 nm

Pulse number is another factor involved in the laser annealing process. Figure 5.11 shows the results of single pulse and multiple pulses annealing on a 25 nm Ag film sample. Single pulse irradiation results in hemispherical particles with small size (< 30 nm). As pulse number increases to 50, small particles gradually aggregate into larger, irregularly shaped clusters. As aforementioned, each pulse can be treated as separate annealing process. From the second pulse onwards, the laser annealing is conducted on Ag particles instead of Ag film. Each subsequent pulse gives the Ag particles one more chance to reshape or reflow. Thus, the mechanism also changes from nucleation and growth of holes to evolution of a dewetted film by Ostwald ripening (Figure 5.4 (c)). The

particles originated from dewetted films are often not stable. The surface atoms of small particles experience larger stress. Larger particles are more energetically favored than smaller particles [129] due to its lower curvature. As the system tries to lower its overall energy, small particles will tend to coalescence during subsequent annealing. The process continues until an equilibrium distribution of large particles of comparable size and distance is obtained [130]. Therefore, multiple pulse annealing is one possible way to obtain larger size Ag particles, at the expense of higher cost and lower throughput. Nevertheless, single pulse annealing is still capable to obtain desirable Ag particles array by tuning the laser energy density and the film thickness.

Figure 5-11 SEM images of silver films receive different number of pulses. (a) Single pulse (b) 50 pulses

5.3 NH Structure Formation and Optical Characteristics

After the Ag particles array is obtained on Si substrate, we can fabricate Si NH structure using Ag assisted chemical etching [21, 62]. As discussed in Chapter 2, during this chemical etching process, the silver acts as a catalyst. The silicon substrate that contacts with the silver is oxidized and then removed by HF. The silicon beneath is then exposed and the process continues, as illustrated in Figure 2.18. The process is conducted at room temperature. The concentration of HF and H₂O₂ used is 4.6M and 0.44M. The self-assembled Ag particles on the silicon act as mask for the NH structure. Figure 5.12 (a) shows the SEM image of as-annealed Ag particles on Si wafer. The sample is immersed in HF/H₂O₂ solution for 30 seconds. The top-view and cross-section view of the result are shown in Figure 5.12 (b,c). It is seen that the Ag particles sink into the Si wafer. The nanoholes obtained are with vertical side walls. The nanohole diameter slightly shrinks as it goes deeper. This may be due to the reshaping of Ag particles: as the silicon is being consumed, the Ag particles are also being dissolved and re-depositing, which gradually transform the hemispherical particle into a spherical one. Thus, the diameter shrinks as it sinks, results in a nanohole with shrinking diameter.

Figure 5-12 (a) Small diameter Ag particles on Si wafer (b) plane-view and (c) cross-section view of the nanohole structure after wet etch.

From the SEM image in Figure 5.12 (a, b, c), the diameter of Ag particles are within a range of 10 – 100 nm. The result film has a rough surface morphology. This can be explained by the nature of the etching process. In this case, the Ag particles located very close to each other (distance less than their diameter). The small Ag particles may merge together or shift during the wet chemical etching, resulting in a non-uniform etch, due to their small mass and high surface reaction area. Thus, the top portion of the NH is relatively rough. Figure 5.13 (a, b, c) shows the etching result of a larger Ag particles array (diameters ranging from 200 nm to 280 nm). The particles have relatively larger separation of 1 to 2 times of their diameter. The result shows a much smoother surface,

and the diameter of the NH matches well with the corresponding value for the Ag particles. Note that, in Figure 5.13 (c), the white dots at the bottom of NH are the Ag particles residue, which can be removed by toluene and APM solution (H_2O_2 : NH_4OH : H_2O =2:1:5 by volume). The Ag particles with different diameters have similar etching rate of $\sim 1 \mu\text{m}/\text{min}$.

Figure 5-13 SEM images silver film receives different number of pulses (a) Large diameter Ag particles (b) plane-view and (c) cross-section view of the Ag particles

The Lambda 950 UV/VIS/NIR spectrometer from Perkin Elmer is used to obtain the transmission and reflection spectrum of the NH textured Si wafer in the range of 250 – 1500 nm, which is the main solar spectrum of interest. The absorption is obtained by the formula: $A + T + R = 1$. The Figure 5.14(a) shows the optical characteristics of the NH textured Si wafer. Compared to the one from blank wafer, NH structure can

significantly reduce the reflection (Figure 5.15(b)). The mean absorption of the light ranging from 1.2 eV to 5 eV is more than 94%.

Figure 5-14 Transmission, Reflection and Absorption spectra of (a) NH textured silicon wafer and (b) blank wafer (650 um thickness)

5.4 Demonstration of Si Solar Cell with quasi-ordered NH texture

In this section, the Si NH textured solar cell was demonstrated on Si wafer as a proof-of-concept study. As the ultimate goal is to adopt the NH structure on Si thin film/low cost substrate, the fabrication processes are designed to avoid using expensive and high temperature techniques. The overall fabrication process flow of the Si NH solar cell is schematically depicted in Figure 5.15. As a proof-of-concept study, 6 inch *p*-type (100) silicon wafer (thickness: 675 μm , resistivity: 1-10 $\Omega\text{-cm}$) is employed as the substrate. Standard (RCA) cleaning is applied to remove organic/metallic particles and other contamination. Ag film is deposited on the substrate by electron-beam evaporation or sputtering, followed by KrF excimer laser annealing (248 nm wavelength, 25 ns pulse duration) to produce hemispherical, quasi-ordered located Ag particles. The diameter (D) and distribution of the Ag particles can be controlled by the laser annealing energy and Ag film thickness. And the NH depth can be controlled by the wet etching time. To produce large area and uniform particles, the substrate is put on a computer controlled motorized X-Y stage. Scanning was adjusted so that each laser spot overlap to produce continuous and uniform annealed pattern over the Ag film. The patterned Ag particles serve as the catalytic wet etching mask. Nanohole texture is formed by immersing the substrate into the HF/H₂O₂ based solution. The residual Ag particles are removed in APM solution (H₂O₂:NH₄OH:H₂O=2:1:5 by volume).

Figure 5-15 Schematic of the quasi-ordered NH textured solar cell fabrication process

The radial *p-n* junction configuration is applied to better extract carriers generated within the nanostructure and ease the contact formation [107], the radial *p-n* junction was incorporated by phosphorus diffusion with phosphoric acid. After removing the phosphosilicate glass (PSG) layer formed during the dopant diffusion, a 200 nm Aluminum layer was evaporated on the backside of the sample and annealed at 600°C for 40s to form a Back side field (BSF) and ohmic contact. Then, a Ti/Pd/Ag (60/60/1000 nm) multi-layer was evaporated on the top surface through a shadow mask. Finally, the sample was annealed in N₂ atmosphere at 380°C for 3 hours to achieve good ohmic contact [131].

The surface morphology of the sample was characterized by FESEM (Leo 1550). The transmission, reflection and absorption of the resulting Si NH structures were investigated by using the UV/VIS/NIR spectrometer (Perkin Elmer Lambda 950). The power conversion efficiency (PCE) measurement of Si NH textured solar cell was

performed using an I - V setup and a solar simulator under 1 sun Air Mass (AM) 1.5 G illumination with intensity of 100 mW/cm^2 .

Figure 5-16 SEM images and size distributions of the Ag particles produced by laser annealing. (a) 174 nm mean diameter. (b) 464 nm mean diameter. (c) Histogram of 174 nm mean diameter case. (d) Histogram of 464 nm mean diameter case. Scale bar $1 \mu\text{m}$.

The self-assembled Ag particles were formed by laser annealing. The internal stress carried within the Ag film was built during the deposition process. This stress was fully released during the ultrafast laser annealing. Thus, the film broke into particles with minimum local energy state. The shapes of the Ag particles tend to be spherical stemming from the high surface energy of metal. The size and density of the Ag particles are closely related to the Ag film thickness, laser energy density. In this work, annealing parameter

and film thickness (from 20 to 60 nm) were tuned to produce Ag particles with relatively uniform size and quasi-random distribution. Two different Ag particles distributions with 174 nm and 464 nm mean diameters are shown in Figure 5.16. Note that there were tiny particles (diameter < 10% of the mean size) scattered around the large particles which may be attributed to re-deposition of Ag and the droplets broke up via the Rayleigh instability during the laser annealing [116]. These small particles normally form shallow holes and increase surface roughness during the wet etch, and most of these small holes were then eliminated during the following phosphoric acid diffusion. Thus, they are excluded from the distribution calculation. The variation of the mean diameter is about 13% ~ 20% of the mean diameter determined from several runs of experiments.

Figure 5.17 (a, b) shows the top view SEM images of the NH textured silicon surface after wet etching. It can be seen that the Si NH array distribution matches with the previous Ag particles. The mean diameters reduced by ~ 17%, which may owe to the shrinking of Ag nanoparticle during the wet etching. Depending on the size of the initial Ag particles, one can get NH array with diameter from 100 nm to 800 nm. Figure 5.18 compare the optical images of the Si NH textured wafer with the blank wafer. The dark appearance indicates the great suppression of reflection in the visible light region.

Figure 5-17 SEM images and size distributions of the 2 sets of NH produced from previous Ag particles: (a) and (b) top view SEM images after wet etching; (c) and (d) top view SEM images after removal of PSG layer; (e) and (f) cross-section view of the NH after removal of PSG layer; (g) and (h) size distributions of the NH after removing PSG layer. Scale bar 1 μ m.

Figure 5-18 Optical photograph of blank wafer (left) and wafer with NH texture (right).
(a) under daylight, (b) under directional light.

After cleaning the sample, the sample surface was spin-on coated with phosphoric acid and sent to rapid thermal processing (RTP). The phosphorus diffusion of this process can be described by a dehydration scheme and a diffusion reaction [26]

P_2O_5 is formed during the dehydration process at elevated temperature, and react with Si to generate elemental phosphorus and silicon oxide. Then phosphorous diffused into the material, leaving a phosphorous-rich SiO_2 layer known as PSG on the surface [132]. Due to the higher oxygen concentration of this phosphoric acid process, the PSG

layer is thicker than that formed in the POCl_3 diffusion process. Thus, it also has impact to the final texture morphology. Figure 5.17 (c, d, g, h) shows the top view SEM images as well as the corresponding size distribution of the NH textured surface after removing the PSG layer by dipping the sample in diluted HF solution. It is clear to see that the sample surface roughness is reduced and most of the aforementioned small holes are eliminated. The nanohole diameters are also enlarged. The mean diameters increase from 143 nm/386 nm to 182 nm/443 nm. Figure 5.17 (e, f) shows the cross section image of the NH. It is seen that the NHs with depth of 1 μm are vertically aligned beneath the surface, indicating the effectiveness of the method to fabricate large area NH with uniform depth. The depth can be well controlled by tuning the wet etching time at a rate of 30 nm/s. The doping profile was analyzed by secondary ion mass spectroscopy (SIMS) on a planar wafer. The geometry effect of the nanohole on the dopant profile and junction depth is minimized because of the relatively large dimension of nanohole structure. This is especially the case when the junction is shallow. Thus, the effective doping on the exterior portion of the Si NH was indirectly correlated using the SIMS profile collected from a doped planar Si sample. Since the boron concentration of the starting p-type Si wafer is about $5 \times 10^{18} \text{ cm}^{-3}$ (see boron profile in Figure 5.19), the *p-n* junction depth is found to be about 80 nm. Thus, the nanohole structure is confirmed to have a radial *p-n* junction.

Figure 5-19 SIMS profiles of phosphorus and boron in Si (RTP temperature: 900 °C and peak time: 5 s). The junction depth is about 80 nm. Thus, the junction depth is estimated at about 80 nm from Si NH surface.

To characterize the antireflection property of these NH textures, the optical reflection measurements were carried out over a broad wavelength range (200–1200 nm). The reflectance spectra of the NH textured surfaces are shown in Figure 5.20 (a). It is clear that the reflectance is significantly suppressed when NH is incorporated in the Si substrate. In the case of NH with 386 nm mean diameter, the average reflectance for the wavelength range of 400 - 1000 nm drops below ~ 4% which is much lower than that of blank Si wafer. According to previous studies, when the dimension of the nanostructure becomes comparable to the wavelength of incident light, strong scattering effect to the incident light occurs within nanostructure. As a result, the original optical path is prolonged, and the light reflectance is suppressed [102]. After removing the PSG layer formed during the doping process, the small dimension holes are eliminated and the surface is smoothened. Therefore, the reflectance increases a bit due to losing of these small dimension textures, especially in the short wavelength region. Even with this loss,

the average reflectance is still as low as $\sim 10\%$. Nevertheless, there is still bright side worth pointing out: the reduced surface roughness implies lower surface area, thus lower surface defect density, and also eases the contact fabrication.

Figure 5-20 (a) Reflectance (R) as a function of wavelength. Black hollow square curve, blank wafer; red solid circle curve, NH with 600 nm in diameter after wet etch; pink solid triangle curve, NH with 600 nm in diameter after removing PSG layer; blue hollow square curve, NH with 200 nm in diameter after removing PSG layer. (b) IV curves of solar cells with different dimensions under the AM1.5 illumination.

Figure 5.21 shows the optical images of the finished Si NH textured solar cells with top metal electrode. The area is $1 \times 1 \text{ cm}^2$ including metal fingers which covers $\sim 20\%$ of the surface.

Figure 5-21 Finished Si NH textured solar cells with metal finger top electrode.

To demonstrate how effectively the antireflection can improve the power conversion efficiency of NH textured solar cells, we measured the Current–Voltage (IV) curves of the NH textured solar cell with solar simulator under 1 sun AM1.5G illumination. The Si NH device shows a power conversion efficiency that is $\sim 80\%$ higher than that of the flat film devices which made under otherwise identical conditions. As shown in Figure 5.20 (b), the NH cell with 443 nm mean diameter exhibits a power efficiency of 9.52%. In accordance with the trend observed in the reflection spectra, the NH cell with 182 nm mean diameter exhibits a lower efficiency of 7.4% than the other cell, which is mainly due to its lower J_{sc} . Note that, the slope of the IV curves near the short-circuit current point is flat for both NH cells and flat cell, indicating (1) a good p-n junction is achieved by the phosphoric acid diffusion. (2) the inner walls of the NH are

fully depleted during the doping process, as otherwise, the p-n junction may be short-circuited during the top electrode metal deposition. The device results for the three types of cells are given in Table 5.1. It is worth noting that the current fabrication processes are not fully optimized, such as surface passivation and contact formation, which may be the reason behind the relatively low FF and high series resistance. As this work focus on the demonstration of NH texturing, we expect the cell performance could be further enhanced by improving the dopant diffusion, electrode contact and surface passivation.

	R(%)@550 nm (after etching)	R(%)@550 nm (after doping)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	η (%)
Blank	38.3	38.1	576	20.7	45.3	5.5
182 nm	4.0	11.1	543	26.2	50.1	7.4
443 nm	3.9	10.4	558	29.1	58.7	9.5

Table 5-1 Devices results of solar cells with different dimensions along with a control sample. Control sample has not gone through any surface texturing. (R is reflectance, V_{oc} is open-circuit voltage, J_{sc} is short-circuit current density, FF is fill factor and η is power conversion efficiency)

Table 5.2 summarizes the SiNP/Si NH textured solar cells reported to date. It is worth mentioning that the solar cell demonstrated in this work achieves the highest PCE using non-lithography technique. The demonstrated results are promising, especially for thin-film solar cells as the Si NH array act as the active absorber.

Group/Year of publication	Key Structure	J_{sc} (mA/cm ²)	PCE (%)
B. Tian, et al. / 2007[82]	VLS grown NW, D 300 nm, H 2 - 25 μ m	23.9	3.4
E. Garnett, et al. / 2010[22]	DRIE NW, D 390 nm, H 5 μ m	16.85	5.3
K. Q. Peng, et al. / 2010[79]	Chemical etch NH, D 700 nm, H 1 μ m	32.2	9.51
This work	Chemical etch NH, D 443 nm, H 1 μ m	29.1	9.5

Table 5-2 Summary of the SiNP/Si NH based solar cells reported to date

In summary, we have demonstrated for the first time that quasi-random NH textured solar cell with radial *p-n* junction can be fabricated using maskless wet etching process and low cost phosphoric acid diffusion. Under 1 sun AM1.5G illumination, the NH textured Si solar cell exhibited a V_{oc} of 558 mV, a J_{sc} of 29.1 mA/cm², and a PCE of 9.5%. The short-circuit current density can be significantly boosted by the quasi-random NH with designed mean dimensions, owing to its remarkable light trapping as well as improved junction formation and eased metal contacts deposition. This NH geometry together with the fabrication process shows potential as a low cost, high performance surface texture and is also promising for thin film based PV applications. One thing worth noting is that in this study, the Ag particle formed on a highly smooth surface (Si wafer). The particle distribution and size may be different if formed on rough surface. More study is needed to verify on other substrates.

6. EXPLORATION OF HIGHLY ORDERED AND LOW ASPECT RATIO NANOPIT TEXTURES

6.1 Introduction

In the previous chapter, the enhanced light absorption for Si solar cells with quasi-ordered Si NH array surface texture has been demonstrated. In order to get ordered NH array, additional patterning technique has to be applied. In this chapter, the author discusses his exploration to produce ordered Ag particles array by combining polystyrene (PS) nanosphere monolayer patterning and laser annealing. Next, a low aspect ratio nanopit texture is discussed for its better carrier collection ability and easier implantation for thin film solar cell applications. One possible fabrication method is introduced to obtain ordered hemispherical nanopit array textured Si thin film.

6.2 Ordered NH Array Fabrication

Based on the experiment discussed in Chapter 5, direct laser annealing of Ag film cannot fully control the size and distribution of the obtained Ag particles array. In order to fabricate ordered NH array with better control of the size and periodicity while still keeping the process attractive for thin film photovoltaic applications, a low cost pattern solution is needed. In this study, PS nanospheres monolayer is chosen as the low cost patterning solution. They have been used to fabricate ordered SiNP array, which proved to be successful in controlling the size, orientation and packing density of the nanopillar

[22, 133]. Here, it is used as the mask for the laser annealing of Ag film. The process flow is illustrated in Figure 6.1.

Figure 6-1 Schematic of the PS monolayer assisted Ag particles array formation process

First, the *p*-type (100) Si wafer is cleaned in RCA, and then treated in the piranha solution (H_2SO_4 : H_2O_2 = 3:1 by volume) at 90°C for 1 hour to make the wafer surface hydrophilic. Suspension of PS sphere (5% *V/V*) is dropped on the wafer and spin at 3000 rpm for 30 seconds to uniformly spread the PS spheres. Uniform PS monolayer coated Si substrate with an area of $3 \times 3 \text{ cm}^2$ is obtained, as shown in Figure 6.2 (a). By using this method, larger area of PS monolayer is also obtainable. The PS spheres monolayer is processed by reactive ion etching (RIE) to reduce the PS sphere diameter for substrate exposure, as shown in Figure 6.2 (b). The gas used in the RIE treatment is oxygen with a flow rate of 40 sccm and RF power of 30W. The diameter of the PS spheres can be reduced to the desired value by tuning the etching time. After RIE treatment, a layer of Ag is deposited on top of the sample by E-beam evaporation (Figure 6.2 (c)). Note that only the exposed substrate is covered with Ag film due to PVD's highly directional deposition. Finally, the sample is annealed by KrF excimer laser. PS sphere is evaporated

during the annealing along with the Ag film on its top. Ag particles are formed from the dewetting of the Ag film covering the substrate. Thus, the resulting Ag particles array distribution is highly related to the PS sphere array distribution and diameter. By carefully controlling the size of PS sphere, RIE time, Ag film thickness as well as laser energy density, ordered Ag particles array is achievable. One example is shown in Figure 6.2 (d).

Figure 6-2 SEM images of (a) PS monolayer , (b) After RIE etch (c) After Ag deposition (d) After laser annealing.

Two types of Ag particles array arrangement hypothesis are proposed, as illustrated in Figure 6.3. One is hexagonal arrangement (Figure 6.3(a)). When applied shorter RIE etching time, the separation between the two neighbor PS spheres is smaller. Thus, there is less Ag film to cover this area, while most Ag film covers the triangular

area between the three PS spheres. Therefore, during laser annealing, the preferred Ag film dewetting direction is towards the triangular area. Ag particles are forced to locate at the triangular area, so that the resulting Ag particles array exhibits hexagonal arrangement, as shown in Figure 6.3(c). If the PS spheres are etched for a longer time, the separation between two neighboring PS spheres becomes comparable to the triangular area. Thus, more area is covered by Ag, and the Ag film dewetting process is less constrained. The Ag particles formed becomes larger and is triangularly arranged, as shown in Figure 6.3 (b, d). Note that Ag residue is found after annealing, which may come from the Ag film fragment during the laser annealing. The Ag residue

Figure 6-3 Hypothesis of the Ag particles array arrangement, (a) hexagonal arrangement, (b) triangular arrangement. SEM images of the two arrangement, (c) hexagonal arrangement image, (d) triangular arrangement image.

6.3 Optical Simulation of Low Aspect Ratio Nanopit Textured Si Thin Film

Si nanostructure has shown its potential in enhancing the light absorption for photovoltaic applications. However, based on recent research results, the high light absorption of various nano-textures has not fully contributed to the electrical output. Most of recent developed Si nanostructures (e.g. SiNP, Si NH) are all high aspect ratio structure, which increases the difficulty for conformal deposition of the transparent electrodes over the nanostructure surface for efficient collection of photogenerated carrier. A high aspect

ratio nanostructure also exhibits a high surface defect density, which significantly reduces the number of carriers that are supposed to be collected [22, 134]. Moreover, current nanostructure textures normally possess a depth of several microns, which is still a bit too thick for thin film photovoltaic applications. Therefore, a novel surface texture scheme with excellent light trapping capability but a lower aspect ratio is needed for feasible Si thin film solar cells. Here we developed a low aspect ratio surface texturing scheme using hemispherical nanopit arrays. Its optical characteristics are systematically studied via the same simulation procedure as discussed in Chapter 3.

Figure 6.4 (a) illustrates the cross-sectional schematic of the proposed nanopit structure, with the top view shown as an inset. The total thickness of the Si thin film is 2 μm , including the hemispherical nanopit array texturing. Since polycrystalline Si is widely used in photovoltaic industry, especially in thin film application, polycrystalline Si is used as the substrate to make the simulation closer to reality. The optical parameters, i.e., refractive index n and extinction coefficient k are shown in Figure 6.4 (b). The normal incident light is shining on the surface with the energy ranging from 1.1 eV to 4 eV (310- 1170 nm in wavelength).

Figure 6-4 (a) Schematic of the 2 μm poly-Si film with hemispherical nanopit array textured surface. (b) the refractive index n and extinction coefficient k of poly-Si used in this simulation[100].

Note that, for hemispherical nanopit, the pit depth is equal to the pit radius. Thus, there are only two structural parameters of interested: pit diameter D and array periodicity P . First, the impact of nanopit diameter to the light trapping capability is discussed with fixed periodicity. Figure 6.5 shows the reflection spectra for the nanopit texture with different nanopit diameters (100, 200, and 300 nm) at fixed array periodicity P of 300 nm. It is clear to see that the light reflection is significantly suppressed when incorporating the nanopit texture, and the antireflection ability increases with increasing D until it is equal to P . According to Fresnel theory [135], when light transmits from one media into another, the reflection would reduce if the two medium has smaller refractive index difference. The nanopit serves as a media between air and Si substrate. With nanopit diameter increasing, the refractive index distribution between air and the underlying bulk Si becomes more continuous, resulting in lower light reflection. Thus, the following simulation is conducted with $D = P$.

Figure 6-5 Reflection spectra of the nanopit texture as a function of the pit diameter D . at The array periodicity is fixed at 300 nm. The 2000 nm plain poly-Si film serves as the reference.

With $D = P$, the optical characteristics of nanopit array with different periodicity (from 100 to 900 nm) is studied. The resulting reflection spectrum is shown in Figure 6.6. One can see the array of 300 nm periodicity gives the lowest light reflection, especially in the higher photon energy regime of the solar spectrum due to the comparable nanopit array dimensions with the corresponding light wavelength. Different from the geometrical optics based multi-reflection processes in scale textures such as for the “inverted pyramid” array textured Si wafer-based solar cells [108, 109] the interaction between the incident light and subwavelength surface texturing is dominated by wave optics. It is known that when the wavelength of incident light is comparable with the interacted structure, scattering will be significantly enhanced with the result of the prolonged optical path length and thus the enhanced light trapping. On the other hand, if the light wavelength is much shorter than the structure dimension, the reflection

process should become dominant [95].

Figure 6-6 The reflection spectra of the studied structure as functions of P . The 2 μm poly-Si film without texturing serves as the reference.

Figure 6.7 shows the absorption enhancement factor for the nanopit textured structure as compared to the reference poly-Si film. It is seen that after incorporating the nanopit texture with designated dimensions, the light trapping capability of the structure can be enhanced up to twelve times in the low energy region (around the Si band gap). This is particularly important for Si-based solar cell which has an indirect band gap. The texture is able to dramatically enhance the photon collection of Si film and thus reduce the thickness required to make crystalline/poly-Si thin film solar cell possible [136].

Figure 6-7 (a) Absorption enhancement factor and (b) ultimate efficiency of the studied structure as functions of P with $D = P$. The 2 μm poly-Si film without texturing serves as the reference.

As defined in Chapter 3, ultimate efficiency η_{ult} is used to measure the light trapping capability of the nanopit textured Si films. Figure 6.7 (b) compares the calculated η_{ult} as a function of P with $D = P$. In agreement with the variation of light absorption, η_{ult} first increases and then decreases with P . The maximum value of $\sim 35.7\%$ is achieved when $P = 700$ nm, which is more than double of that of the referenced blank poly-Si film with the same thickness of 2 μm (~ 15.9). Note that, although the light absorption for the sample with $P = 300$ nm is higher than that of $P = 700$ nm in the higher energy region, its η_{ult} is still lower. This is because the visible light range contributes most energy of the solar spectrum. As a result, the enhanced light absorption in the lower energy region can compensate the lower absorption in the higher energy region as demonstrated in the ultimate efficiency change with P . It is worth mentioning that compared to the previously studied Si NH array surface texturing, the hemispherical nanopit array texturing not only introduces the scattering effect, but also utilizes a graded refractive index profile for reflection suppression. Owing to these combined effects, the

light trapping capability of the nanopit array texturing is more superior to that of the Si NH array. Comparable η_{ult} of 35% is achieved with thinner Si film (nanopit using 2000 nm poly Si versus NH using 2800 nm) .

To summarize this section, a novel low aspect ratio hemispherical nanopit array texture is introduced for Si-based thin film solar cells. The optical simulation results indicate that the light absorption can be significantly enhanced, especially near the energy band gap region. A maximum ultimate efficiency of $\sim 35.7\%$ is achieved for the hemispherical nanopit array with $D = P = 700$ nm. It is worth noting that we focus on the intrinsic light trapping capability of the nanopit array textured poly-Si thin film, without employing additional anti-reflection coating or back reflector. Therefore, it is expected that the light absorption could be further enhanced. The low aspect ratio feature of the nanopit texture would also ease the difficulty of incorporating these additional anti-reflection schemes.

6.4 Demonstration of Hemispherical Nanopit Array Textured Si Thin Film via Layer Transfer Technique

The previous section has shown the great potential of low aspect ratio hemispherical nanopit array texture for enhancing the light trapping and easing the adoption of traditional anti-reflection schemes as well as the top electrode fabrication. Beside the many potential advantages of hemispherical nanopit texture for photovoltaic application, the fabrication of the texture itself may be a challenge to the current manufacturing industry. Cui's group reported hemispherical nanodome [25] a-Si thin film

solar cell by depositing a-Si films on top of nanocone array in 2010. Our group also managed to demonstrate nanohemisphere-array textured solar cell by depositing poly-Si on top of nanopillar array, as shown in Figure 6.8. Firstly, SiNP arrays are fabricated on Si wafers by plasma dry etching. The pillars have an array period of ≈ 400 nm and height of ≈ 100 nm but variable diameters. The pillars are then coated with crystalline Si to form the nanohemisphere-like structures. The p–n junctions are formed by phosphorus ion implantation in the top crystalline Si layer. Solar cells textured by nanohemisphere arrays with diameters D of 250, 350, and 420 nm are fabricated. Figure 6.10 (a) shows the schematic cross-section view of the nanohemispherical textured Si thin film. As previously mentioned, compared with the sharp jumps of n_{eff} in the SiNP surface, n_{eff} of the nanohemisphere surface increases continuously in the textured region from air to bulk Si. This gradual change of n_{eff} between air and the underlying bulk film is essential for suppressing light reflection. In Figure 6.10 (c), we compare the antireflection capability of the nanohemisphere-array textured surface with that of the SiNP array textured with heights of 200 and 500 nm. As can be seen, the low-aspect-ratio nanohemisphere-array textured thin film has much lower reflection than the high aspect-ratio SiNP textured one, although the height of the nanohemisphere arrays is shorter than that of the SiNP arrays. A power conversion efficiency of 11.2% is realized in association with the high J_{sc} of 37.4 mA/cm^2 (diameter 350 nm) for the solar cell with a nanohemisphere diameter of 350 nm. [137]

Figure 6-8 Process flow of the fabrication process of Si nanohemisphere-array textured solar cells: a) fabrication of SiNP arrays on Si substrate; b) deposition of a crystalline Si layer on top of the SiNP surface to form the Si nanohemisphere array; c) phosphorus ion implantation to form p-n junctions; and d) front and rear electrode fabrication. The SEM images show the corresponding structures. Scale bar = 400 nm [137].

Figure 6-9 a) Schematic of the cross-sectional view of the nanohemisphere-array textured ultrathin-film-based solar cell configuration. The inset shows the top view of the structure. b) Spatial distribution of the effective refractive indices for the Si-NP (solid line) and Si nanohemisphere cases (dashed line), where n_{air} and n_{Si} are the refractive indices of air and bulk Si, respectively. c) Comparison of the light reflection of Si-NPs (diameter 200 nm) with heights (H) of 200 and 500 nm and nanohemisphere-array textured surfaces.

As the hemisphere's counterpart, hemispherical nanopit array is trickier to fabricate. Here the author made an attempt to realize hemispherical nanopit array texture on Si thin films via layer transfer technique. Inspired from the SiO₂ sphere monolayer patterning, the Si film is deposited on top of the sphere monolayer to obtain nanopit

geometry. The film can then be transferred to another substrate. The schematic of the process is illustrated in Figure 6.9.

Figure 6-10 The fabrication process of hemispherical nanopit array textured a-Si film on glass substrate including silica ball dispersion, a-Si deposition, glass attachment, glass detachment.

Starting from p-type (100) Si wafer, after standard RCA cleaning, SiO₂ sphere (diameter of 500 nm) suspension is dropped on the Si surface and followed by spin-coating. As silica sphere is heavier than PS sphere, it is difficult to get monolayer by simple spin coating. Therefore, additive is needed to add in the silica suspension to achieve uniform, large area monolayer. The silica spheres are suspended in ethanol. Poly 4 vinyl phenol (PvPh) is added to increase solution's viscosity in order to gain better control of the sphere distribution. By carefully tuning the spin-coating speed, a uniform SiO₂ sphere monolayer is achievable. The area of the SiO₂ sphere monolayer covered Si film can be as large as 5×5 cm² (shown in Figure 6.10(a)) and is only limited by the spin-coater set-up. After obtain the silica sphere monolayer, a-Si film is deposited on the

sample by PECVD. Depending on silica sphere's diameter, a thickness of 1 - 3 μm is needed to fully cover the monolayer with lower roughness. Figure 6.10(b) shows cross-section image of a 300 nm diameter monolayer sample covered by 1 μm a-Si film. Next, the sample is bonded with glass by using epoxy resin. Finally, the sample is rinsed in buffered HF solution. When the silica sphere monolayer dissolves, the top layer is detached from the Si substrate.

Figure 6-11 (a) uniform silica sphere monolayer achieved over an area of $4 \times 4 \text{ cm}^2$. (b) Cross-section SEM image of 300 nm silica sphere monolayer covered with 1 μm a-Si.

Figure 6.11(a,b) shows the SEM images of some preliminary results. It is clear that the hemispherical morphology of the SiO_2 sphere monolayer has been successfully transferred to the a-Si film. The a-Si film remains intact after the transfer process. Note that the slits that appeared in Figure 6.11(a) were formed during the a-Si film deposition, which can be improved by tuning the PECVD parameters. The SiO_2 sphere monolayer and the deposited film possess large stress, which cannot stand thermal treatment (e.g. 1 hour annealing at 300 $^\circ\text{C}$ may cause the film to crack). Therefore, one may consider fabricating the device after the layer transfer. Figure 6.11 (c) shows the absorption spectra of the nanopit textured a-Si film on glass. It is clear to see that the nanopit can enhance

the light absorption of a-Si film in the whole spectral range. Because the substrate in this process is a-Si, which already has a high absorption coefficient, the light absorption enhancement is not as dramatic as shown in the simulation. Yet, the nanopit texture still demonstrates its light trapping potential.

Figure 6-12 SEM images of the hemispherical nanopit array: (a) top view, (b) tilt view. Scale bar = 400 nm (c) Absorption spectra of the nanopit array textured film and flat film reference.

After the layer transfer, the temperature freedom is limited by the constraints imposed by the foreign substrate and bonding layer. Laser annealing may be used as a

solution for the device treatment. This layer transfer method may become an alternative approach to fabricate nanopit structure. The experimental work in this chapter is the author's preliminary exploration beyond the traditional nanohole texture. Further investigation and study is conducting in our group to continuously explore its potential for photovoltaic applications. Our fellow students are also trying to demonstrate nanopit structure on poly-Si thin film with other approaches.

7. CONCLUSION AND FUTURE EXPECTATION

In this thesis, the author systematically studied the nanohole texture for Si-based solar cell, covered both optical characteristics and electrical properties via software simulation and experimental demonstration. Based on the obtained results, the NH structure has shown its great potential to be an excellent light trapping scheme for photovoltaic applications, which may be even superior to its SiNP counterpart. Si based solar cell with quasi-ordered NH surface texture was successfully demonstrated by combining with the laser annealing technology and metal assisted wet chemical etching. Under 1 sun AM1.5G illumination, the NH textured Si solar cell exhibited a V_{oc} of 558 mV, a J_{sc} of 29.1 mA/cm², and a PCE of 9.5%. To make the nano-texture more feasible for practical application, a low-aspect-ratio nanopit texture is developed. Based on simulation, despite of the thin absorption layer, the nanopit texture still exhibits comparable light trapping capability with SiNP and Si NH. This work provides a guideline for design and fabrication of nanohole-like texture for both bulk and thin film solar cells. Not only that, the demonstration in this work also opens an opportunity for feasible application of these promising solar cells.

Despite of the great potential held by Si NH textured solar cells, the currently reported PCE record in literature is still too low as compared to the mainstream Si wafer cells. To further improve the PCE of stand-alone Si NH based solar cells, the following challenges need to be addressed:

1. Structural optimization of Si NH (based on the optical and electrical calculations)

Si NH-like textures provide another option for the photovoltaic manufacturers. Its robustness eases the fabrication and makes it closer to practical applications as compared to its SiNP counterparts. However, the nano-textures' device performance is still far from traditional Si solar cells despite the possession of high light absorption, which means that the excellent light trapping capability cannot fully contribute to the power output. The structural parameters need to be fine-tuned with the photogenerated carrier collection process. Compromised design has to be made to balance the trade-off between the light absorption and the carrier collection for practical device fabrication. For example, the nanostructures prepared by various etching process normally possess [138] high surface defect density, which may lead to degradation in V_{oc} [17]. Deeper structure may increase light absorption but also induce more surface defect states, which may eventually compensate the benefit.

2. Passivation of surface defect states

Although the radial p - n junction design eases the material requirement for nano-textured solar cell, the high surface defect density of nanostructure still needs to be deal with. The surface defects can become the recombination centers for the photogenerated carriers when collecting the carriers to output circuit, and hence deteriorating the device performance [19, 139]. Therefore how to effectively reduce the nano-textures surface defect density remains challenge to utilize the nano-textured solar cells potential.

3. Optimization of top transparent electrodes

The top transparent electrode is commonly used in PV industry. It yet becomes a

challenge for nano-textured solar cell. Especially for SiNWs based solar cells, high contact resistance needs to be addressed through optimizing the nanoscale region design/process. The conformal deposition of the top transparent electrode to uniformly cover the SiNWs surface is necessary to effectively extract the photogenerated carriers.

Another thing worth mentioning here is the terminology of “nano”. The term “nano” has become a hot keyword in the photovoltaic area in the past decade. It is generally accepted that nanostructure refers to a structure with at least one dimension in the range of 1-100nm. Apparently many papers do not strictly follow this rule. Based on the finding of this thesis, it is not the smaller the better. To achieve the best light absorption, the structure dimensions have to be comparable with the targeting light wavelength. In this case, the precise term should be sub-micron or sub-wavelength structure.

APPENDIX A

Classification ^a	Effic. ^b (%)	Area ^c (cm ²)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF ^d (%)	Test centre ^e (and date)	Description
Silicon							
Si (crystalline)	25.0 ± 0.5	4.00 (da)	0.706	42.7 ^f	82.8	Sandia (3/99) ^g	UNSW PERL [12]
Si (multicrystalline)	20.4 ± 0.5	1.002 (ap)	0.664	38.0	80.9	NREL (5/04) ^g	FhG-ISE [13]
Si (thin film transfer)	19.1 ± 0.4	3.983 (ap)	0.650	37.8 ^h	77.6	FhG-ISE (2/11)	ISFH (43 µm thick) [14]
Si (thin film submodule)	10.5 ± 0.3	94.0 (ap)	0.492 ⁱ	29.7 ⁱ	72.1	FhG-ISE (8/07) ^g	CSG Solar (1–2 µm on glass; 20 cells) [15]
III-V Cells							
GaAs (thin film)	28.8 ± 0.9	0.9927 (ap)	1.122	29.68 ^j	86.5	NREL (5/12)	Alta Devices [3]
GaAs (multicrystalline)	18.4 ± 0.5	4.011 (t)	0.994	23.2	79.7	NREL (11/95) ^g	RTI, Ge substrate [16]
InP (crystalline)	22.1 ± 0.7	4.02 (t)	0.878	29.5	85.4	NREL (4/90) ^g	Spire, epitaxial [17]
Thin film chalcogenide							
CIGS (cell)	19.6 ± 0.6 ^k	0.996 (ap)	0.713	34.8 ^l	79.2	NREL (4/09)	NREL, on glass [18]
CIGS (submodule)	17.4 ± 0.5	15.993 (da)	0.6815 ⁱ	33.84 ⁱ	75.5	FhG-ISE (10/11)	Solibro, four serial cells [19]
CdTe (cell)	17.3 ± 0.5	1.066 (ap)	0.842	28.99 ^j	75.6	NREL (7/11)	First Solar, on glass [4]
Amorphous/ nanocrystalline Si							
Si (amorphous)	10.1 ± 0.3 ^m	1.036 (ap)	0.886	16.75 ^f	67.0	NREL (7/09)	Oerlikon Solar Lab, Neuchatel [20]
Si (nanocrystalline)	10.1 ± 0.2 ⁿ	1.199 (ap)	0.539	24.4	76.6	JQA (12/97)	Kaneka (2 µm on glass) [21]
Photochemical							
Dye sensitised	11.0 ± 0.3 ^o	1.007 (da)	0.714	21.93 ^h	70.3	AIST (9/11)	Sharp [22]
Dye sensitised (submodule)	9.9 ± 0.4 ^o	17.11 (ap)	0.719 ⁱ	19.4 ⁱ	71.4	AIST (8/10)	Sony, eight parallel cells [23]
Organic							
Organic thin-film	10.0 ± 0.3 ^o	1.021 (ap)	0.899	16.75 ^p	66.1	AIST (10/11)	Mitsubishi Chemical [24]
Organic (submodule)	5.2 ± 0.2 ^o	294.5 (ap)	0.689	11.73 ⁱ	64.2	AIST (3/12)	Sumitomo (15 series cells) [5]
Multijunction devices							
InGaP/GaAs/InGaAs	37.5 ± 1.3	1.046 (ap)	3.015	14.56 ^j	85.5	AIST (2/12)	Sharp [6]
a-Si/nc-Si/nc-Si (thin film)	12.4 ± 0.7 ^q	1.050 (ap)	1.936	8.96 ^h	71.5	NREL (3/11)	United Solar [25]
a-Si/nc-Si (thin film cell)	12.3 ± 0.3% ^r	0.962 (ap)	1.365	12.93 ^p	69.4	AIST (7/11)	Kaneka [26]
a-Si/nc-Si (thin film submodule)	11.7 ± 0.4 ⁿ	14.23 (ap)	5.462	2.99	71.3	AIST (9/04)	Kaneka [27]

^aCIGS = CuInGaSe₂^bEffic. = efficiency^c(ap) = aperture area; (t) = total area; (da) = designated illumination area^dFF = fill factor^eFhG-ISE = Fraunhofer Institut für Solare Energiesysteme; JQA = Japan Quality Assurance; AIST = Japanese National Institute of Advanced Industrial Science and Technology^fSpectral response reported in Version 36 of these Tables^gRecalibrated from original measurement^hSpectral response and current-voltage curve reported in Version 38 of these TablesⁱReported on a 'per cell' basis^jSpectral response and/or current-voltage curve reported in present version of these Tables.^kNot measured at an external laboratory^lSpectral response reported in Version 37 of these Tables^mLight soaked at Oerlikon prior to testing at NREL (1000 h, one sun, 50 °C)ⁿMeasured under IEC 60904-3 Ed. 1: 1989 reference spectrum^oStability not investigated. References [28] and [29] review the stability of similar devices^pSpectral response and current-voltage curve reported in Version 39 of these Tables^qLight soaked under 100 mW/cm² white light at 50 °C for over 1000 h^rStabilised by manufacturer^sStabilised by 174 h, one sun illumination after 20 h, five sun illumination at a sample temperature of 50 °C.

APPENDIX B

Calculation Procedure for TFR1:

Before calculating the result – check:

HFSS → Fields → Edit Sources → Total Fields

HFSS → Fields → Calculator $\int_{-}^{+}$

Quantity → Poynting

Complex → Real

Geometry → Surface → Rectangle 1

Normal $\int$

Solution → Sweep → select the respective frequency → Eval

Pop to calculate next frequency.

Calculation Procedure for TFR2:

Before calculating the result – check:

HFSS → Fields → Edit Sources → Total Fields

Same as above, except Geometry → Surface → Rectangle 2

APPENDIX C

Physics in Device simulation

Drift-diffusion model (DD model) is the basic model that applied in this simulator. Since Gummel's original work, the drift-diffusion model has been widely used in the semiconductor device simulation. It is now the defacto industry standard in this field.

The original DD model can be achieved by following approximation from hydrodynamic model:

- Light speed is much faster than carrier speed.
- All the collision is elastic.
- Bandgap does not change during collision.
- Carrier temperature equals to lattice temperature and keeps equilibrium.
- The gradient of driving force should keep small.
- Carrier degenerate can be neglected.

Level 1 DD model is the fundamental solver of simulation code for lattice temperature keeps constant though out the solve procedure.

The primary function of DD model is to solve the following set of partial differential equations, namely Poisson's equation, along with the hole and electron continuity equations:

$$\nabla \cdot \epsilon \nabla \psi = -q(p - n + N_D^+ - N_A^-)$$

where, ψ is the electrostatic potential of the vacuum level. This choice makes the description of metal-oxide-semiconductor contact and heterojunction easier. n and p are the electron and hole concentration, N_D^+ and N_A^- are the ionized impurity concentrations. q is the magnitude of the charge of an electron.

The continuity equations for electrons and holes are defined as follows:

$$\begin{aligned}\frac{\partial n}{\partial t} &= \frac{1}{q} \nabla \cdot \vec{J}_n - (U - G) \\ \frac{\partial p}{\partial t} &= -\frac{1}{q} \nabla \cdot \vec{J}_p - (U - G)\end{aligned}$$

where $\sim J_n$ and $\sim J_p$ are the electron and hole current densities, U and G are the recombination and generation rates for both electrons and holes. The current densities $\sim J_n$ and $\sim J_p$ are expressed in terms of the level 1 drift-diffusion model here.

$$\begin{aligned}\vec{J}_n &= q\mu_n n \vec{E}_n + qD_n \nabla n \\ \vec{J}_p &= q\mu_p p \vec{E}_p - qD_p \nabla p\end{aligned}$$

where μ_n and μ_p are the electron and hole mobility. E_n and E_p are the effective driving electrical field to electrons and holes, which related to local band diagram.

The Level 2 DD model considers the influence of lattice temperature by solving the extra thermal equation simultaneously with the electrical equations. Also, the formula of drift-diffusion equation should be modified accordingly [140]. The details of level 2 DD model can refer to ref. [103].

APPENDIX D

NovaLine 100 High Power KrF Excimer Laser System

	Specification
Wavelength (nm)	248
Max. Stabilized Energy (mJ)	400
Max. Stabilized Average Power (W)	100
Max. Repetition Rate (Hz)	250
Energy Stability (1 sigma) (%)	<2
Pulse Duration (FWHM, typ.) (ns)	25
Beam Dimensions (V × H, FWHM, typ.) (mm ²)	29 × 4
Divergence (V × H, FWHM, typ.) (mrad ²)	<4×1.5
Beam-Pointing Stability (V × H, mrad ²)	<0.4×0.15

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