Materials and Light Management for High-Efficiency Thin-Film Silicon Solar Cells

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Materials and Light Management for High-Efficiency Thin-Film Silicon Solar Cells

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door

Hairen TAN

Master of Engineering, Chinese Academy of Sciences
geboren te Jiangxi, China
To my daughters Shiya (Erin) and Shiqi (Emily)
For their endless joy given to papa and mama

To my wife Minyan
For her kind support and assistance for my life
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Chapter 1

Introduction to thin-film silicon solar cells

Direct conversion of sunlight into electricity is one of the most promising approaches to provide sufficient renewable energy for human beings. Solar cells are such devices which can efficiently generate electricity from sunlight through the photovoltaic (PV) effect. Depending on the type of materials used as absorbers, solar cells can be divided into several categories: crystalline silicon (c-Si) solar cells, III-V solar cells, thin-film silicon (TF-Si) solar cells, organic solar cells, copper indium gallium selenide (CIGS) solar cells, quantum-dot solar cells, cadmium telluride (CdTe) solar cells and perovskite solar cells as emerging recently. Currently the c-Si solar cells dominate the PV market, with a market share higher than 90%. However, the c-Si solar cells need to use thick high-quality wafers (~200 µm). Meanwhile, thin film solar cells with an absorber layer less than a few micrometers have been widely studied in the past few decades, aiming for lower cost and simpler processing. Thin-film silicon solar cells are one of the promising thin-film PV technologies, which have been studied extensively in the past 40 years. This thesis is within the research field of thin-film silicon solar cells, and it focuses on the development of advanced materials and novel light-trapping structures to increase the power conversion efficiency.

1.1 Thin-film silicon solar cells

Thin-film silicon solar cells are a type of PV devices which use chemical-vapor-deposited hydrogenated amorphous silicon (a-Si:H) and nanocrystalline silicon (nc-Si:H) and their alloys as the absorber layers and doped layers. The first a-Si:H solar cell with an initial conversion efficiency of 2.4% under AM 1.0 illumination was demonstrated by Carlson and Wronski in 1976 [1]. Since then, the efficiency has been progressing step by step with new materials, new device construction and new light trapping structures. Details of this PV technology can be found in a nice book written by Shah et al [2].

Due to the structural disorder, thin-film silicon materials have a high density of midgap defect states and bandtail states, resulting in a low charge carrier mobility and a short diffusion length [2]. Because of these less ideal electrical properties compared to crystalline and polycrystalline semiconductors, thin-film silicon solar cells cannot use the conventional p-n junction structure due to the very short diffusion length in doped materials. Instead, the solar cells have a p-i-n device structure as shown in Figure 1.1. The intrinsic absorber layer is sandwiched between the much thinner p-doped and n-doped layers to guarantee efficient charge carrier collection from the absorber layer to electrodes. As doped layers have two or more orders of magnitude higher defect density than the intrinsic layers, the light absorption and charge generation in the doped layers does not contribute to the photocurrent in the solar cells and is thus considered as loss.
Chapter 1 Introduction to thin-film silicon solar cells

Figure 1.1 Schematic device structures of \( p-i-n \) (superstrate-type) and \( n-i-p \) (substrate-type) configured TF-Si solar cells. The \( p-i-n \) configuration is adapted for transparent glass substrate while the \( n-i-p \) configuration can be used on flexible opaque substrates.

Depending on the deposition sequence, two device configurations, \( p-i-n \) and \( n-i-p \), are used in thin-film silicon solar cells. The \( p-i-n \) (also called superstrate type) configuration, starting from the p-layer deposited on the front transparent conductive oxide (TCO) layer, is usually used for devices with transparent glass as substrate. On the other hand, opaque flexible substrates use the \( n-i-p \) (also called substrate type) configuration, where the n-layer is the firstly deposited silicon layer in the solar cell. In this thesis, both configurations were used for different purposes. In chapters 2-4, single-junction a-Si:H and nc-Si:H solar cells with an \( n-i-p \) device structure were deposited to study the performance of plasmonic back reflectors. In chapters 5-7, the \( p-i-n \) configured single-junction or multijunction solar cells were deposited to study other advanced light trapping structures and novel silicon materials.

The materials used for thin-film silicon solar cells are divided into four main categories: substrate, TCO materials, doped and intrinsic silicon materials, and back contacts. For large-scale PV installation (TW scale), the abundance of the materials and their impact on environment (e.g. toxicity, \( \text{CO}_2 \) emission during production) have to be considered, in addition to the cost of raw materials and processing. Compared to other PV technologies, thin-film silicon solar cells have several important advantages.

1. All the materials used are abundant and non-toxic, as shown in Table 1.1 and Figure 1.2. Cheap substrates, such as glass, plastic foil and steel, are used. The main elements for the photoactive layers and contact layers are Si, C, O, H, B, P and Zn (also Al or F if ZnO:Al or SnO:F is used for TCO). All the elements are earth-abundant, and all the functional materials in the solar cells are non-toxic.

2. The processing temperature for the photoactive layers and contacts is low, and the energy payback time is short. The temperatures of all the production steps for silicon layers and TCO materials can be below 200 °C.
3. The large-area manufacturing techniques are very mature. As can be seen from Figure 1.3, the efficiency loss of thin-film silicon technology is smaller than all other technologies for the upscaling from small-area laboratory cells to large-area modules. The large-area industrial deposition of thin-film silicon is very reproducible and controllable, in contrast to CIGS and CdTe technologies.

4. The energy yield, defined as produced energy (in Kwh) per installed capacity (in Kw), is higher than c-Si and other thin-film solar cells.

5. TF-Si module can be deposited on flexible substrates with roll-to-roll processing. Most importantly, the encapsulation cost (main cost in a flexible module) can be lower than other flexible technologies such as CIGS and OPV due to the better resistivity against moisture.

<table>
<thead>
<tr>
<th>Table 1.1 A list of materials used for thin-film silicon solar cells.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Materials</strong></td>
</tr>
<tr>
<td>Substrate</td>
</tr>
<tr>
<td>TCO</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>p-layer</td>
</tr>
<tr>
<td>absorber layers</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>n-layer</td>
</tr>
<tr>
<td>Back contact &amp; reflector</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

WP: white paint. SiOx:H refers to nanocrystalline silicon oxide, a material with mixed phases of nanocrystalline silicon and amorphous silicon oxide.
Figure 1.2 Abundance of the chemical elements in Earth upper continental crust as a function of atomic number. The elements marked in red are commonly used for TF-Si solar cells, either used in the p-i-n layers or other supporting layers. Figure is adapted from ref. [3] and the Solar Energy MOOC of Dr. Arno Smets [4].

Figure 1.3 State-of-the-art certified efficiencies of different PV technologies, plotted with respect to the size of cells and modules [6]. Note that the TF-Si solar cells and modules are reported after light-induced degradation. The perovskite, organic, CIGS, and CdTe solar cells and modules are reported with their initial performance, and they are subjected to stronger degradation than Si-based solar cells. (Courtesy of Dr. Arno Smets)
Despite the many advantages mentioned above, thin-film silicon technology is suffering from the drop in the PV market share. Many production companies have been bankrupted during the past few years as the price of multicrystalline silicon modules drops quickly. The main challenge of this technology, as compared to c-Si, CIGS, and CdTe, is the relatively low efficiency due to the high $E_g-V_{oc}$ loss (~50%), light-induced degradation [5] and incomplete absorption of light with photon energy above the bandgap. Table 1.2 summarizes the performance of different types of thin-film silicon solar cells and modules. As of 2015, the highest cell efficiency and module efficiency are 13.6% (triple-junction) and 12.3% (tandem), respectively. In contrast, mc-Si, CIGS and CdTe have a module efficiency of ~16%. To make thin-film silicon technology competitive with other thin-film technologies, the efficiency has to be further increased significantly. This thesis will discuss several key strategies to increase the efficiency by developing highly efficient light-trapping structures and advanced materials.
Chapter 1 Introduction to thin-film silicon solar cells

Table 1.2 Highest certified efficiency of thin-film silicon solar cells and modules in various configurations as of 2015. The module efficiency is total area efficiency, while the small cells are reported with active area efficiency. Adapted from ref. [6] and results reported in the 6th World Conference on Photovoltaic Energy Conversion, Kyoto, 2014.

<table>
<thead>
<tr>
<th>Cell structure</th>
<th>Area (cm²)</th>
<th>Substrate</th>
<th>Efficiency (%)</th>
<th>Vₒc (V)</th>
<th>Jₒc (mA/cm²)</th>
<th>FF (%)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si (pin)</td>
<td>1</td>
<td>Asahi-VU</td>
<td>10.2</td>
<td>0.896</td>
<td>16.36</td>
<td>69.8</td>
<td>AIST, triode PECVD, 2014</td>
</tr>
<tr>
<td>nc-Si (nip)</td>
<td>1</td>
<td>HC/Ag</td>
<td>11.8</td>
<td>0.548</td>
<td>29.38</td>
<td>73.1</td>
<td>AIST, 1 nm/s for i-layer, 2014</td>
</tr>
<tr>
<td>nc-Si (pin)</td>
<td>1</td>
<td>ZnO:B</td>
<td>10.7</td>
<td>0.549</td>
<td>26.55</td>
<td>73.3</td>
<td>EFPL, 0.3nm/s for i-layer, 2013</td>
</tr>
<tr>
<td>a-Si/nc-Si (pin)</td>
<td>1</td>
<td>ZnO:B</td>
<td>12.7</td>
<td>1.342</td>
<td>13.45</td>
<td>70.2</td>
<td>AIST, triode PECVD for a-Si, 2014</td>
</tr>
<tr>
<td></td>
<td>14300</td>
<td>ZnO:B</td>
<td>12.3</td>
<td>1.429</td>
<td>12.36</td>
<td>69.9</td>
<td>TEL Solar, G5 module, 2014</td>
</tr>
<tr>
<td>a-Si/a-SiGe/nc-Si (pin)</td>
<td>14300</td>
<td>ZnO:B</td>
<td>10.5</td>
<td></td>
<td></td>
<td></td>
<td>LG Electronics, G5 module, 2012</td>
</tr>
<tr>
<td>a-Si/nc-Si/nc-Si (nip)</td>
<td>1</td>
<td>HC/Ag</td>
<td>13.6</td>
<td>1.901</td>
<td>9.92</td>
<td>72.1</td>
<td>AIST, triode a-Si:H, 1 nm/s nc-Si:H, 2015</td>
</tr>
<tr>
<td>a-Si/nc-Si/nc-Si (pin)</td>
<td>1</td>
<td>etched AZO</td>
<td>13.4</td>
<td>1.963</td>
<td>9.52</td>
<td>71.9</td>
<td>LG Electronics, 2012</td>
</tr>
</tbody>
</table>
1.2 Light trapping for thin-film silicon solar cells

Light trapping is an essential part for all the high-efficiency thin-film silicon solar cells. The thin-film silicon materials have a low absorption coefficient near the bandgap. For a-Si:H solar cells it is necessary to keep the intrinsic layer thin (~250 nm) to reduce the light-induced degradation. However, such a thin absorber layer can only absorb a small part of light in the wavelength range above 600 nm if there is no light trapping in the solar cells. Similarly for nc-Si:H solar cells, the intrinsic layer should be kept as thin as possible (usually 1-3 µm) to get good electrical performance. The thin nc-Si:H layer is also a weak light absorber in the wavelength above 700 nm due to the indirect bandgap of the nanocrystalline grains. To achieve sufficient light absorption in the absorber layers, implementation of light-trapping structures in the solar cells is crucial. Refer to two recent review articles for more details [7-8].

Light scattering at the nano-textured interfaces between two materials with different refractive indices $n$ is the most successful and widely implemented light-trapping scheme in thin-film silicon solar cells. As shown in Figure 1.4, light passing through the absorber layer without being absorbed in the first two passes will come out of the solar cells if all the interfaces in the solar cells are flat. When solar cells are deposited on the textured substrates, the light scattering at the TCO/Si and Si/BR interfaces will result in significantly prolonged light path in the Si layers and thus increase the photocurrent. In $p$-$i$-$n$ type solar cells, randomly nano-textured front TCO layer is commonly used to obtain effective light trapping. Typical TCO materials are self-textured fluorine-doped tin oxide (FTO, for example Asahi-VU substrate) or boron-doped ZnO (BZO ) deposited by low-pressure CVD techniques [9-10], and sputtered-etched Ga- or Al-doped ZnO (GZO or AZO) [11]. The self-textured FTO and BZO have pyramid-like surface morphologies.

Figure 1.4 Schematic of thin-film silicon solar cells without light trapping (all flat interfaces) and with light trapping by scattering at randomly rough interfaces.
whereas the wet-etched GZO or AZO has a crater-like surface textures. In \( n-i-p \) type solar cells, light trapping is achieved mainly by using a rough back contact layer [12-14]. The nano-textures can be generated either directly from the reflecting metallic layers (e.g. textured Ag layer) or from the pre-textured underlying substrate (e.g. textured plastic foil).

The upper limit for the absorption enhancement in a thin film by textured interfaces is \( 4n^2 \) (often called Yablonovitch limit), where \( n \) is the refractive index of the semiconductor slab [15]. The \( 4n^2 \) limit is achieved when surface primary reflection \( R \) is zero, light is fully Lambertian scattered at the interfaces and an ideal back reflector (\( R=1 \)) is applied. To further increase light absorption various more exotic light-trapping schemes have been proposed such as plasmonic nanostructures [16-20], periodic gratings [21-24], nanowires and nanorods [25-27], nanodomes and nanocavities [28-29]. Many publications also claim that such novel nanophotonic light trapping can go beyond the \( 4n^2 \) limit and enable ultra-thin high-efficiency thin film solar cells [27, 30-32]. Unfortunately, none of those light-trapping schemes has led to state-of-the-art efficiency in any type of solar cell. Their implementation into a practical solar cell is usually difficult, and the material quality of the photoactive layers always drops if sharp structures such as nanowires are introduced into the devices. Furthermore, additional parasitic absorption losses from the light-trapping structures themselves or other supporting layers will greatly reduce the light-trapping capabilities of the novel nanophotonic structures [33-34]. In the following, a brief introduction to plasmonic light trapping with metallic Ag nanoparticles will be given as a short introduction to chapters 2-4.

The nanoparticles of noble metals such as Ag, Au and Pt are highly efficient light scatterers due to the excitation of the localized surface plasmon resonance. The scattering properties depend on the size, shape, surrounding media and interaction of the nanoparticles. Among the metals, Ag is the most widely used and the most promising one for PV devices due to its better abundance, larger scattering cross-section and lower plasmonic absorption. In this thesis, only Ag nanoparticles will be used and discussed. Depending on the device structure and light management purpose, the Ag nanoparticles can be placed in the front, inside the absorber layer or at the rear side of the solar cell, as shown in Figure 1.5. Nanoparticles placed in the front are commonly suggested for c-Si solar cells. The nanoparticles can reduce the surface reflection as well as scatter the incident light into the absorber layer. However, we should note that the Ag nanoparticles will induce significant parasitic absorption losses especially in the visible spectral range. Moreover, the anti-reflective effect is not as good as the conventional anti-reflection coating. Therefore, state-of-the-art light-trapping performance has never been experimentally demonstrated in this configuration. Integrating the nanoparticles inside the absorber layer is even more challenging. Firstly it is difficult to practically implement such a structure in a device. Moreover, the metal nanoparticles will reduce the material quality and the metal/semiconductor interfaces are recombination sites for charge carriers. For thin-film silicon solar cells, integrating the Ag nanoparticles into the back reflector is the most promising approach. The Ag nanoparticles can be fabricated over large-area at a low cost with the self-assembling method as presented in Figure 1.6. Details of the implementation into \( n-i-p \) type solar cells will be discussed in chapters 2-4.
1.2 Light trapping for thin-film silicon solar cells

![Diagram of light trapping geometries](image)

**Figure 1.5** Plasmonic light-trapping geometries for thin-film solar cells. The plasmonic Ag nanoparticles (NPs) can be placed in the front, inside the absorber, and at the back of a solar cell. Light trapping is achieved due to the light scattering by the Ag nanoparticles.

![Fabrication process](image)

**Figure 1.6** The fabrication of self-assembled Ag nanoparticles used for this thesis work. A thin layer of Ag film is evaporated on the Ag/ZnO coated glass substrate. A layer of Ag nanoparticles is then formed on the substrate by thermal annealing at a high temperature in a high-vacuum chamber.

1.3 Other requirements for high-efficiency thin-film silicon solar cells

High-efficiency solar cells demand both optimal optical and electrical performance. To design an effective light-trapping scheme for solar cells, the following aspects should always be kept in mind in addition to the light-trapping ability.

1. The light-trapping structure itself should not give additional parasitic absorption losses, or this loss should be minimized as much as possible. For example, plasmonic nanostructures not only scatter the incident light but also absorb light. Optical simulation studies often show that plasmonic nanostructures can result in very strong absorption enhancement, or even go beyond the 4π² limit [31-32]. However, the optical properties of the fabricated metal nanostructures in reality are far inferior to the perfect nature
assumed in the simulation. Minimizing the parasitic losses is crucial to get high-performance plasmonic light trapping in solar cells, as will be discussed in chapters 2-4.

2. The morphology of the light-trapping substrate should be suitable for the growth of high-quality materials. The introduction of metal nanoparticles or rough interfaces should not deteriorate the electrical performance of solar cells. Otherwise, the gain from light trapping will be offset by the drop in electrical performance. This issue will be addressed throughout the whole thesis work, especially in chapters 5 and 7.

3. Absorption losses in the supporting layers such as front electrodes, doped layers and back reflectors should be minimized. The use of more transparent TCO materials and more transparent doped layers will definitely result in a higher efficiency. If metal back reflectors such as Ag are used in solar cells, the plasmonic absorption loss can be significantly reduced by adding a low-refractive-index layer between the metal and Si layers [35-36]. Photonic structures with a high aspect-ratio such as nanowires and nanocavities will significantly induce additional absorption losses in the supporting layers, thus limiting its potential for practical applications.

1.4 Goals and outline of the thesis

The aim of this thesis is to investigate novel light-trapping structures and advanced materials to improve the efficiency of thin-film silicon solar cells, especially in the following points.

1. Evaluate the potential of plasmonic light trapping for thin-film silicon solar cells.
2. Develop highly transparent doped layers to reduce optical losses in solar cells and develop a-Si:H absorber materials with tunable bandgap for applications in multijunction solar cells.
3. Develop advanced light-trapping substrates which can provide both efficient light trapping and a suitable morphology for the growth of high-quality thin-film silicon materials in multijunction solar cells.

This thesis is divided into two parts. The first part (Part I, including chapters 2, 3, and 4) is Plasmonic light trapping for thin-film silicon solar cells. In chapter 2, the fabrication of plasmonic back reflectors (BRs) based on self-assembled Ag nanoparticles and the application in a-Si:H solar cells are presented. The combined optical and electrical design of plasmonic back reflectors follows in chapter 3. The design routes of plasmonic back reflectors based on self-assembled Ag nanoparticles are discussed in detail. The application of the plasmonic back reflector to low-bandgap nc-Si:H solar cells is discussed in chapter 4. The light trapping performance is improved by using plasmonic BR with a broad angular scattering and a low parasitic absorption loss through tuning the size of silver nanoparticles.

The second part (Part II, including chapters 5, 6 and 7) is Materials and light management for high-efficiency multijunction thin-film silicon solar cells. In chapter 5, micro-textures with large opening angles and smooth U-shape morphology are proposed and applied to nc-Si:H solar cells for the first time. The micro-textures can provide both
efficient light trapping and suitable morphology for the growth of high-quality nc-Si:H materials under a high deposition rate. The use of micro-textures paves the road to develop multijunction solar cells with a higher efficiency as will be shown in chapter 7. In chapter 6, the mixed-phase p-SiOx films are investigated and used as window layer in high $V_{oc}$ a-Si:H $p-i-n$ solar cells. Chapter 7 presents the implementation of highly transparent modulated-surface-textured (MST) front electrodes as light-trapping structures in multijunction thin-film silicon solar cells. Efficiencies of 14.8% (initial) and 12.5% (stable) have been achieved for a-Si:H/nc-Si:H tandem solar cells with the MST front electrode, surpassing efficiencies obtained on state-of-the-art LPCVD ZnO substrates.

Chapter 8 gives a short summary of this thesis. Perspectives to further improve the performance of thin-film silicon solar cells will be suggested based on the research works in this thesis project.

### 1.5 Contribution of this thesis to the research field

This thesis project has contributed to the developments of thin-film silicon solar cells in several aspects.

1. High-performance plasmonic back reflectors were designed and fabricated, experimentally demonstrating light-trapping performance comparable to state-of-the-art random textures without obvious deterioration of electrical performance in solar cells [37-39]. Plasmonic flat light-scattering back reflector was proposed and experimentally realized, resulting in superior materials quality in nc-Si:H solar cells.

2. High quality a-Si:H absorber layers with tunable bandgap were obtained under high deposition-pressure regime (7-12 mbar). This work gives high flexibility to select a-Si:H with suitable bandgap as the top cells in multijunction solar cells. With the highly transparent p-SiOx as window layer, a-Si:H solar cells with a high initial $V_{oc}$ of 1 V and good FF (>70%) were demonstrated, showing promising application in triple-junction or quadruple-junction solar cells [40].

3. Micro-textures were firstly introduced and investigated to mitigate the trade-off between light-trapping and electrical performance in nc-Si:H solar cells [41]. The well-designed micro-textured substrates were able to provide both efficient light trapping and high $V_{oc}$*$FF$ product even in thick nc-Si:H solar cells, paving the road to very-high-efficiency multijunction solar cells. This work also contributed to several other studies in the group [42-43].

4. Highly transparent modulated-surface-textured front electrodes were investigated and fabricated. This novel substrate can decouple the light trapping and growth of high-quality materials for each subcell in multijunction solar cells. Both optical and electrical improvements were demonstrated in tandem and triple-junction solar cells, compared to the state-of-the-art single-textured LPCVD ZnO substrates. A record-high initial efficiency of 14.8% and a high stabilized efficiency of 12.5% have been achieved in a-Si/nc-Si tandem solar cells with this new type of light-trapping substrate [44].
5. High-efficiency hybrid a-Si:H/OPV multijunction solar cells were designed and fabricated. The thick nc-Si:H junction was replaced by a thin low-bandgap polymer solar cell. Record high efficiencies of 11.6% and 13.2% have been achieved in a-Si:H/OPV tandem solar cells and a-Si:H/a-Si:H/OPV triple-junction solar cells. The details of the study will not be presented in this thesis. This configuration of hybrid solar cells will be mentioned in chapter 8.

References


Chapter 1 Introduction to thin-film silicon solar cells


Part I: 

*Plasmonic light trapping for thin-film silicon solar cells*

This part includes following three chapters:

**Chapter 2.** Plasmonic light trapping in thin-film silicon solar cells with self-assembled silver nanoparticles

**Chapter 3.** Design of plasmonic back reflector for thin-film silicon solar cells

**Chapter 4.** Plasmonic back reflector for thin-film nanocrystalline silicon solar cells
This chapter is based on the following publication:


**Preface:**

Plasmonic metal nanoparticles are of great interest for light trapping in thin-film silicon solar cells. In this chapter, we demonstrate experimentally that a back reflector with plasmonic Ag nanoparticles can provide light-trapping performance comparable to state-of-the-art random textures in $n$-$i$-$p$ amorphous silicon solar cells. This conclusion is based on the comparison to high performance $n$-$i$-$p$ solar cell and state-of-the-art efficiency $p$-$i$-$n$ solar cells deposited on the Asahi VU-type glass. With the plasmonic back reflector a gain of 2 mA/cm$^2$ in short-circuit current density was obtained without any deterioration of open circuit voltage or fill factor compared to the solar cell on a flat back reflector. The excellent light trapping is a result of strong light scattering and low parasitic absorption of self-assembled Ag nanoparticles embedded in the back reflector. The plasmonic back reflector provides a high degree of light trapping, with a haze in reflection greater than 80% throughout the wavelength range 520-1100 nm. The high performance of plasmonic back reflector is attributed to improvements in the self-assembly technique, which results in a lower surface coverage and fewer small and irregular nanoparticles.
Chapter 2 Plasmonic light trapping in TF-Si solar cells

2.1 Introduction

Advanced light trapping concepts are crucial to achieve high-efficiency thin-film silicon (TF-Si) solar cells due to the low absorption coefficient of silicon in the near-infrared region. Light scattering at randomly textured interfaces is currently the standard light trapping scheme and has resulted in state-of-the-art efficiency of TF-Si solar cells [1-6]. In the past few years, subwavelength plasmonic metal nanoparticles have attracted much attention for effective light trapping because they can induce localized surface plasmons and strongly scatter incident light into the absorber layers, thereby increasing the average light path length inside solar cells [7-11]. The optical properties of metal nanoparticles are sensitive to their size, shape, surface coverage on the substrate, surrounding medium, etc [11-15]. The light can be either scattered or absorbed by metal nanoparticles [14,15]. Therefore, the metal nanoparticles must be well designed to maximize the scattering and to minimize absorption across the wavelength range of interest in solar cells. Silver nanoparticles (Ag NPs) are commonly used because of their large scattering cross-section and potential for low absorption in the visible and near-infrared spectrum [11, 15].

Metal nanoparticles placed on front or rear sides of a solar cell can lead to preferential scattering of light into the semiconductor layers. However, metal nanoparticles are better to be placed at the rear side to avoid the suppression of photocurrent at wavelengths below the surface plasmon resonance [16-19]. In TF-Si solar cells the metal nanoparticles can be embedded in the back reflector and scatter the incident light which is not absorbed during the first pass. Moulin et al. and Eminian et al. demonstrated that the Ag/ZnO back reflector (BR) with random arrays of Ag NPs could significantly enhance the photocurrent in n-i-p hydrogenated amorphous Si (a-Si:H) and microcrystalline Si (nc-Si:H) solar cells compared to cells on the flat BR without Ag NPs due to the strong scattering of Ag NPs [20-22]. We refer to the back reflector with Ag NPs as a plasmonic BR. Recently, the plasmonic BR has also been shown to exceed the randomly textured BR in nc-Si:H solar cells, where the textured BR has similar roughness as the plasmonic BR [23]. However, the achieved light trapping capacity of the plasmonic BRs in those solar cells is still below what can be achieved by state-of-the-art random textures used in the same type TF-Si solar cells.

In the meantime, periodically patterned plasmonic back contacts have been implemented in TF-Si solar cells, in which the light absorption can be improved by coupling the incident light into waveguide modes or surface plasmon polariton modes [24-29]. Ferry et al. designed nanopatterned Ag/ZnO plasmonic BR by nanoimprint lithography, and showed that the nanopatterned plasmonic BR resulted in better light trapping than Asahi U-type glass in ultrathin n-i-p a-Si:H solar cells, where the thickness of intrinsic a-Si:H layer (i-layer) is no more than 160 nm [24-26]. However, the spectral response of such ultrathin plasmonic solar cells is far below that of p-i-n type a-Si:H solar cell with state-of-the-art efficiency [30]. Asahi U-type glass is optimized for p-i-n a-Si:H solar cell with an i-layer thickness around 300 nm, and it has not been demonstrated that the nanopatterned plasmonic BR can exceed Asahi glass in a-Si:H solar cells with i-layer of the optimal thickness [24-26]. In some works where high performance plasmonic a-Si:H solar cells were reported from current-voltage (J-V) measurements, the provided
short-circuit current densities obtained from $J-V$ measurements are much higher than that from external quantum efficiency (EQE) measurements, and the reference device does not have reasonably good performance [26,31]. Thus far, there is no conclusive experimental evidence that plasmonic nanostructures can lead to comparable or even better light trapping performance than state-of-the-art random textures in TF-Si solar cells, even though theoretical studies indicate that plasmonic light trapping has the possibility of exceeding the classical $4n^2$ limit [32,33].

In this chapter, we demonstrate experimentally that the plasmonic BR with random arrays of Ag NPs can provide comparable light trapping performance to state-of-the-art random textures in $n-i-p$ a-Si:H solar cells. The conclusion is based on the comparison to high performance $n-i-p$ a-Si:H solar cells and state-of-the-art efficiency $p-i-n$ solar cells deposited on Asahi VU-type glass. The Ag NPs were fabricated by self-assembling of metal island films, the most common method for fabricating random Ag NP arrays in TF-Si solar cells [16-23,34,35]. This method is a simple and cheap technique which can easily be applied to the large-area production of solar cells. However, the Ag NP arrays obtained by self-assembly in previous works always have many small (diameter<100 nm) and aggregated nanoparticles and relatively high surface coverage (>30%), which are reported to result in undesired parasitic absorption loss and weak scattering [34,35]. The light-trapping performance can be further improved by reducing the surface coverage and by eliminating small and irregular nanoparticles. We show that increasing the annealing temperature up to 400 °C can significantly improve the morphology of Ag NPs, resulting in a surface coverage less than 20% and particle size larger than 100 nm. The obtained Ag NPs have strong scattering and low parasitic absorption.

### 2.2 Experiments

The structure of the plasmonic BR studied in this chapter is shown in **Figure 2.1a**. It consists of a stack of glass/Ag (100 nm) /AZO (60 nm) /Ag NPs/AZO (30 nm) layers. The planar Ag layers on glass and Al-doped ZnO (AZO, ZnO:Al) layers were deposited by magnetron sputtering. The thicknesses of the two ZnO:Al layers below and above the Ag NPs are $d_1$ and $d_2$ as indicated in Figure 2.1a, respectively. The $d_1$ was chosen to completely cover the Ag film and to form Ag NPs with uniform distribution, and the $d_2$ was chosen to avoid the direct contact between Ag NPs and a-Si:H layer. However, here the thicknesses of the ZnO:Al layers were not fully optimized. The Ag NPs were formed by thermal evaporation of a thin Ag film with a mass thickness of 12 nm onto the Ag/AZO layers followed by one hour anneal at 400 °C in a vacuum oven. The deposition rate of the thin Ag film was less than 0.1 nm/s. Half of the substrate was covered by a mask during the deposition of the thin Ag film, and this masked area serves as the flat BR reference as shown in Figure 2.1b. Note that the flat BR was processed exactly the same way as the plasmonic BR except for the deposition of the 12 nm thick Ag film. The processing of plasmonic BR is prior to the deposition of silicon layers, thus the higher temperature for Ag NPs formation would not constrain the following device fabrication at a lower temperature. The textured BR as presented in Figure 2.1c was obtained by depositing Ag/AZO layers on the Asahi VU-type glass. The textured BR was completed
without further high-temperature annealing in order to keep the conformal morphology of the Asahi substrate after deposition of the Ag/AZO layers.

The $n$-$i$-$p$ a-Si:H solar cells as shown in Figure 2.1 were deposited at 180 °C onto the three BRs using plasma-enhanced chemical vapor deposition. The thickness of the intrinsic absorber layers (i-layer) was 300 nm. The solar cells were completed by sputtering a 75 nm thick ITO layer (4×4 mm$^2$) as top electrode. The values of short-circuit current density ($J_{sc}$) reported in this work were calculated from EQE measured without bias in the spectral range from 300 to 800 nm using the AM1.5G spectrum. This widely adopted standard method for determining the $J_{sc}$ of lab-scale TF-Si solar cells excludes errors in the determination of $J_{sc}$ due to spectral mismatch between the AM1.5G spectrum and light source(s) and inaccurate determination of the active area of solar cells in $J$-$V$ measurements. This method is essential in evaluating light trapping and its effect on device performance in solar cells. The open-circuit voltage ($V_{oc}$) and fill factor ($FF$) were determined using $J$-$V$ measurements under 100 mW/cm$^2$ illumination (AM1.5G, Oriel Newport). A well-defined 3×3 mm$^2$ hole mask was used in $J$-$V$ measurements to more accurately define the active area of solar cells. By using the hole mask we found that the discrepancy of $J_{sc}$ between $J$-$V$ and EQE measurements is below 3%.

### 2.3 Results and discussion

Figure 2.2a presents a scanning electron microscopy (SEM) image of self-assembled Ag NPs formed at 400 °C. This image clearly shows that Ag NPs are well-separated and have relatively round shape. The average circularity is 0.86, where circularity is calculated using $(4\pi \times \text{area})/\text{perimeter}^2$. Nanoparticles are randomly and uniformly distributed on the BR and no aggregation of nanoparticles is observed. The Ag NPs arrays have a surface coverage of around 16% and an average equivalent area diameter of 205 nm, as determined from SEM images taken in five different positions on the substrate. The size distribution given in Figure 2.2b shows that there are almost no particles smaller...
2.3 Results and discussion

Figure 2.2 The morphology of flattened self-assembled Ag NPs formed at 400°C without the AZO layer on top. SEM image (a) and size distribution (b) of Ag NPs. AFM height image 2×2 µm² (c) and typical AFM scan profile (d) of single Ag NP across the centre. The diameter in Figure 2b is calculated by \((4A/\pi)^{1/2}\), where \(A\) is the lateral area of Ag NP. The maximal height of Ag NPs in Figure 2c is 100 nm.

than 100 nm. Regularly-shaped Ag NPs with diameter larger than 100 nm exhibit negligible parasitic absorption loss and strong localized surface plasmon scattering over a broad wavelength range of interest in TF-Si solar cells [34-36]. Atomic force microscope (AFM) images in Figure 2.2c and d show that Ag NPs have a flattened hemispherical shape with heights less than 100 nm. The plasmonic BR has a root-mean-square roughness of ~22 nm, which is much smaller than that of textured BR (~36 nm). We also note that the textured BR has a higher peak-to-peak height (maximal 260 nm) than the plasmonic BR (maximal 100 nm).

The Ag NPs formed at 400 °C here have obvious improvements compared to the Ag NPs formed at 200 °C and the reported self-assembled Ag NPs on Ag/AZO stacks used in a-Si:H or nc-Si:H solar cells and on completed thin-film crystalline Si solar cells [16-23,34,35]. These improvements include more regular shape, absence of small nanoparticles, narrower size distribution, and much lower surface coverage. These Ag NPs with more regular shape, larger size and lower surface coverage can result in lower parasitic absorption; whereas Ag NPs with larger size and narrower size distribution have stronger broadband scattering in the red and infrared wavelength range. We attribute the improvements to the higher annealing temperature of 400 °C and favourable formation of Ag NPs on the surface of AZO. The formation of Ag NPs from a continuous thin Ag film under heat treatment depends on the process parameters, such as annealing temperature, thickness of Ag film, and type of substrate. When the temperature increases, the individual small size particles have higher mobility on the substrate surface, thus
higher probability to agglomerate into larger particles. The higher temperature is also beneficial to form more regularly shaped particles due to increased atomic diffusion at higher temperature. We also fabricated self-assembled Ag NPs on a c-Si wafer under the same processing conditions. However, the average diameter of Ag NPs is smaller (~67 nm), and the surface coverage is higher (~33%). This indicates that the surface properties of AZO also play a crucial role in the formation of large size and low surface coverage Ag NPs.

The function of BRs is to scatter and reflect light that has not been absorbed in a single pass, back into the absorber layer of the solar cells. The light scattering properties of BRs, which are correlated with the light trapping capacity in solar cells, are usually characterized by the descriptive scattering parameters: haze in reflection (ratio of diffuse to total reflection) and the angular intensity distribution (AID) of the reflected light. These parameters were measured for the three different BRs using an Integrating Sphere and Angular Resolved Transmittance/Reflectance Analyzer in PerkinElmer Lambda 950 spectrophotometer. Experimental details of the measurements can be found elsewhere [37,38]. As shown in Figure 2.3, the haze parameter of the flat BR is zero, as expected. The

![Figure 2.3 Total reflectance R (a) and haze in reflection (b) of flat, plasmonic, and textured BRs.](image)
2.3 Results and discussion

haze of the textured BR is high for the short wavelengths, but strongly decreases with increasing wavelength above 600 nm. By contrast, the haze of the plasmonic BR formed at 400 °C is above 80% throughout the wavelength range 520-1100 nm, which is higher than the plasmonic BR formed at 200 °C (now shown here) and the plasmonic BR in other reports. This high haze across a broad wavelength range indicates that the plasmonic BR is not only suitable for a-Si:H solar cells (requiring light trapping up to 750 nm), but also for other TF solar cells based on lower bandgap absorbers (e.g. nc-Si:H, a-SiGe:H, and CIGS).

To obtain excellent light trapping it is desirable to scatter light into larger angles as much as possible. The haze parameter indicates the fraction of light that is scattered, but it does not indicate the angle into which this light is scattered. For this, the AID of plasmonic and textured BRs were measured in air at wavelengths $\lambda$ of 600, 700 and 800 nm. The results are presented in Figure 2.4a and b, respectively. The AID of the two BRs is similar in shape, and for both BRs the intensity of scattered light decreases with increasing scattering angle at each wavelength. However, the intensity of the scattered light from plasmonic BR is higher than that from textured BR at each wavelength and increases with wavelength.

![Figure 2.4 Angular intensity distribution of light scattered by plasmonic (a) and textured (b) back reflectors at wavelength of 600, 700, and 800 nm. The arrows indicate the trend from short to long wavelength. The scattered intensity of plasmonic BR increases with wavelength while the textured BR shows the opposite trend.](image-url)
As shown in Figure 2.3 and 2.4, the haze and AID of the plasmonic and textured BRs reveal a significant difference in the wavelength dependence of scattering. In contrast to the conventional textured BR, the haze of the plasmonic BR does not decrease monotonically with increasing wavelength and remains high in the wavelength from 600 to 1100 nm; while the AID increases with increasing wavelength from 600 to 800 nm. The different scattering behaviors of plasmonic and textured BRs mainly are a result of differences in the fundamental scattering mechanisms. For randomly textured substrates, the scattering properties heavily rely on surface roughness, and the haze and AID reduce with increasing wavelength for a given roughness and feature size [39]. To estimate to which extent roughness-induced light scattering plays a role in the plasmonic BR, we used a validated optical model to calculate the texturing induced haze parameter.Input of the morphology for the simulation is the AFM scan of the plasmonic BR shown in Figure 2.2c. The texturing induced haze in the plasmonic BR is much lower than the measured haze values shown in Figure 3b for wavelengths longer than 500 nm (results not shown here), indicating that roughness-induced light scattering does not play a significant role for light scattering in the plasmonic BR. This confirms that the plasmonic BR derives its scattering properties from the localized surface plasmon resonance of Ag NPs, a mechanism which is not directly related with surface roughness. Due to the broadband large scattering cross-section of Ag NPs, the plasmonic BR can have strong light scattering across the whole spectrum for TF-Si solar cells, even though it has smooth surface features and moderate roughness as indicated in Figure 2.2.

For conventional light trapping based on texturing, substrates with high roughness and feature sizes comparable to the wavelength are necessary to trap long-wavelength infrared light. However, substrates with large scale surface texturing can induce defects within silicon layers grown on them and thus deteriorate photovoltaic performance [41-43]. In addition, the textured metal films suffer from parasitic surface plasmon absorption, resulting in large optical losses during multiple reflections [44,45]. As a result of these constraints, the degree of light trapping that can be achieved by textured substrates remains significantly below the theoretical limit [46]. The plasmonic BR, which has low roughness and smooth features, can provide both excellent light trapping and a good base for the growth of high quality silicon layers on top, indicating a great potential to eliminate the constraints of conventional light trapping [47,48].

To evaluate the light trapping of the plasmonic BR, n-i-p a-Si:H solar cells as shown in Figure 2.1 were deposited onto the three BRs. Figure 2.5 shows the EQE curves and the total device absorption (defined as unity minus the total reflectance from the device, 1-R) of the solar cells deposited on the flat and plasmonic BRs. Compared to the cell on flat BR (flat cell), a significant enhancement in the EQE is observed for the solar cell on the plasmonic BR (plasmonic cell) in the wavelength range 620-800 nm. The increased EQE of the plasmonic cell clearly corresponds to the enhanced absorption of incident light in solar cells. Overall, the \(J_{sc}\) increases from 13.1 mA/cm\(^2\) for the flat cell to 15.1 mA/cm\(^2\) for the plasmonic cell. A gain of 2 mA/cm\(^2\) is obtained with the plasmonic cell in reference to the flat cell due to effective light scattering by the Ag NPs embedded in the BR. To our best knowledge, the \(J_{sc}\) of 15.1 mA/cm\(^2\) is the highest reported \(J_{sc}\) value confirmed by EQE measurements for plasmonic a-Si:H solar cells. The plasmonic BR formed at 400 °C also resulted in higher EQE than that formed at 200 °C (EQE not shown here, \(J_{sc}=14.1\) mA/cm\(^2\)).
The improvements of EQE in TF-Si solar cells with plasmonic BR have also been reported in previous works [20-22]. The comparison of the plasmonic solar cell with a flat reference cell is interesting to demonstrate the enhancement mechanism. However, in order to evaluate the potential of plasmonic light trapping in TF-Si solar cells, it must be compared to state-of-the-art random textures. Figure 2.6a presents the EQE curves of a-Si:H n-i-p solar cells deposited on the plasmonic and textured BRs (textured solar cell). As we can see, the EQE curves of these two solar cells are nearly the same. In the range of 550-650 nm, the EQE of textured solar cell is slightly lower than that of plasmonic solar cell, possibly due to plasmonic absorption in the textured Ag film. Overall, the $J_{sc}$ of the plasmonic solar cell (15.1 mA/cm$^2$) is slightly higher than that of the textured solar cell (14.8 mA/cm$^2$). We can conclude that the self-assembled Ag NP based plasmonic BR can at least rival a textured BR in n-i-p a-Si:H solar cells.

It is important to note that the Asahi VU-type glass is designed and optimized for use as superstrate p-i-n solar cells. Hence, for a fair comparison the EQE curve of a textured p-i-n a-Si:H solar cell deposited on the Asahi VU-type glass with 300 nm thick i-layer is also included in Figure 2.6a as well. The $J-V$ curves of different solar cells investigated in this work are summarized in Figure 2.6b. The textured p-i-n solar cell with power conversion efficiency ($\eta$) of 11.1% shows significantly better blue spectral response ($\lambda<550$ nm) than n-i-p solar cells. The main reason is that n-i-p solar cells have a higher surface reflectance, higher absorption losses in the thicker p-layer, and non-optimized i/p interfaces. Since the light with $\lambda<550$ nm is absorbed during the first pass through the silicon layers, the spectral response in the blue range is not related to light trapping from the back reflector. To evaluate the light trapping effects, the photocurrent generated by
light with $\lambda>550$ nm ($J_{sc}>550\text{nm}$) can be compared. The $J_{sc}$ and $J_{sc}>550\text{nm}$ values of different solar cells are presented in Table 2.1. The $J_{sc}>550\text{nm}$ of the plasmonic $n$-$i$-$p$ solar cell is only 0.3 mA/cm$^2$ lower than that of the textured $p$-$i$-$n$ solar cell. This is due to a slightly lower $EQE$ in the range of 600-700 nm maybe resulting from the destructive interference between incident and back scattered light [17], which might be avoided by further optimization of the optical layers between $n$-doped layer and Ag NPs which will be done in the next chapter. In all, we can conclude that the plasmonic BR can lead to light trapping performance comparable to state-of-the-art random textures in a-Si:H solar cells.

![EQE curves](image)

**Figure 2.6** (a) The $EQE$ curves of the plasmonic and textured $n$-$i$-$p$ a-Si:H solar cells and the textured $p$-$i$-$n$ a-Si:H solar cell fabricated on the Asahi VU-type glass. (b) The $J$-$V$ curves of flat, plasmonic, and textured $n$-$i$-$p$ a-Si:H solar cells, and the textured $p$-$i$-$n$ a-Si:H solar cell.
The plasmonic BR has a moderate surface roughness (~22 nm) and can result in textured interfaces in solar cells which might contribute to the light trapping. Thus one could argue that the excellent light trapping of the plasmonic solar cells may be due to the roughness-induced light scattering and not mainly due to the plasmonic effects. The moderate roughness in the plasmonic BR cannot give rise to significant light scattering for wavelengths above 500 nm as we discussed before. The ITO/a-Si:H interface has an even lower roughness than the BR, and thus at the front side of an n-i-p solar cell the light scattering does not play an important role either. Therefore, the light trapping in plasmonic solar cells is mainly attributed to the plasmonic light scattering, which is consistent with other works on this topic [11,12,22,23,26].

To achieve high-efficiency TF-Si solar cells using plasmonic light trapping, the electrical performance ($V_{oc}$ and $FF$) of the solar cells should be preserved or even improved in addition to the increase in photocurrent. Deterioration of $V_{oc}$ and/or $FF$ after the integration of self-assembled Ag NPs was commonly reported in plasmonic TF-Si solar cells [20-23]. Here we show that the electrical performance of the plasmonic solar cell did not deteriorate. Both $V_{oc}$ and $FF$ of plasmonic solar cell improved compared to flat solar cell, and are almost the same as textured n-i-p solar cell. After high-temperature annealing at 400 °C, the conduction of AZO film decreases and the flat solar cell had slightly lower $FF$ (0.603) than that without high-temperature annealing (0.625); while the $V_{oc}$ and $J_{sc}$ did not change. Incorporation of Ag NPs into the BR can increase the conduction of AZO layer and thus lead to higher $FF$. On the other hand, the $FF$ and especially $V_{oc}$ of the n-i-p solar cells are lower in comparison to the textured p-i-n cell. The reason is that the i/p interfaces in the n-i-p devices are not optimized. Provided that the p/i interfaces are further improved, state-of-the-art efficiency above 10% should be possible to achieve in plasmonic n-i-p solar cells.

### 2.4 Conclusions

In conclusion, we have experimentally demonstrated that self-assembled Ag NPs based plasmonic BR can provide light trapping performance comparable to state-of-the-art random textures in a-Si:H solar cells. The conclusion is based on the comparison to
high performance $n$-$i$-$p$ solar cells and high efficiency $p$-$i$-$n$ solar cells deposited on Asahi VU-type glass. The plasmonic BR has a haze in reflection above 80% in the wavelength range 520-1100 nm, and can provide efficient light trapping over broad spectral range. The high performance light trapping of plasmonic BR has been demonstrated in $n$-$i$-$p$ a-Si:H solar cells, resulting in a short circuit current as high as 15.1 mA/cm$^2$, without any deterioration of $V_{oc}$ or $FF$. The excellent light trapping is a result of strong light scattering of Ag NPs. By self-assembling of Ag NPs at 400 °C, the high surface coverage and the formation of small and irregular particles can be avoided. Our promising results open the route to use plasmonic metal nanoparticles to obtain high efficiency and low-cost TF-Si solar cells.

References

Chapter 2 Plasmonic light trapping in TF-Si solar cells


Chapter 3

Design of plasmonic back reflector for thin-film silicon solar cells

This chapter is based on the following publication:


Preface:

The plasmonic back reflector (BR), as introduced in Chapter 2, is further optimized in this chapter. We will present the design routes of plasmonic BR based on self-assembled silver nanoparticles (Ag NPs) for high-efficiency thin-film silicon solar cells. Both optical and electrical effects on solar cells are considered. The shape of Ag NPs, the thickness of ZnO:Al spacer layers, materials on top of Ag NPs and nanoparticle size are crucial for the performance of plasmonic BR. Increased annealing temperature lead to the formation of more appropriate shapes (more spherical and regular shapes) for a good light scattering and, thus, increase the photocurrent. The ZnO:Al layer between the Ag NPs and the Ag planar film has an optical effect on solar cells, while the ZnO:Al layer between the Ag NPs and the doped a-Si:H has both optical and electrical influence on the device. Larger NPs have less parasitic absorption and can preferentially scatter light into larger angles, thus increasing the spectral response in the solar cell. However, for larger Ag NPs the fill factor deteriorates due to the rougher surface in the plasmonic BR, indicating a compromise between light trapping and electrical performance. Following the design routes, we obtained 8.4% efficient plasmonic a-Si:H solar cell.


Chapter 3 Design of plasmonic back reflector

3.1 Introduction

Effective light trapping is an essential part for high-efficiency thin-film silicon (TF-Si) solar cells in order to absorb long-wavelength photons with $\lambda>600$ nm. The common way to realize light trapping is to use textured front transparent conductive oxides for p-i-n solar cells [1] or textured back reflectors for n-i-p solar cells [2]. Recently, plasmonic metal nanoparticles have attracted much attention for light trapping since they can strongly scatter the light into nearby absorber layers [3-6], with the promise of exceeding the $4n^2$ limit for enhancement [7]. Silver nanoparticles (Ag NPs) are commonly used due to their large scattering efficiency and potential for low absorption in the visible and near-infrared spectrum [4, 5]. Several techniques have been explored to fabricate the plasmonic Ag NPs for TF-Si solar cells, such as self-assembling of metal island films [8-10], nanoimprinting lithography [11, 12], chemical synthesis [13], and aerosol deposition [14]. Among these techniques, the self-assembling of Ag NPs is most commonly used due to its low-cost and large-area processing which is compatible with TF-Si depositions [8-10, 15-17]. In the self-assembly method, the size and surface coverage of Ag NPs can be controlled through the mass thickness of the deposited silver film. However, it remains difficult to obtain large and regularly shaped Ag NPs with low surface coverage which are necessary to reduce the parasitic absorption in metal nanoparticles.

In TF-Si solar cells, Ag NPs can be placed on front of the device, leading to preferential scattering of light into the high-index semiconductor layer [3, 4]. However, recent works indicate that Ag NPs are preferred to be placed at the back reflector of a solar cell in order to avoid the suppression of photocurrent caused by parasitic absorption and Fano-resonance at wavelengths below the surface plasmon resonance [3,8-10]. The back reflector (BR) with embedded plasmonic nanoparticles, which we refer to as plasmonic BR, can scatter back the incident light which is not absorbed during the first pass through the silicon layers. This concept has been demonstrated to significantly improve the light absorption and spectral response in TF-Si solar cells [15-17]. However, a deterioration of electrical performance, i.e., open circuit voltage ($V_{oc}$) or fill factor ($FF$), was commonly observed after the integration of Ag NPs, which indicates the need for combined optical and electrical design of the plasmonic BR. In our recent work, we have demonstrated that the plasmonic BR based on relatively smooth self-assembled Ag NPs with a moderate surface roughness (~22 nm) would not deteriorate the $V_{oc}$ and $FF$ [18]. This plasmonic BR can result in light trapping capacity comparable to state-of-the-art surface textured substrates. The Ag NPs in our works were formed in a vacuum chamber and were covered by a layer of ZnO without a vacuum breaking between these two steps. This prevents the surface oxidization of Ag NPs, which might improve the scattering of the Ag NPs and the electrical performance of solar cells as well. However, the plasmonic BR with a larger surface roughness (~40 nm) would also result in lower $FF$ as will be discussed later in this work.

Previous works on plasmonic BR mainly focus on the demonstration of plasmon-enhanced absorption [8-18]. A few other works have studied the optical design of plasmonic BR by optical simulation [19, 20]. However, thus far combined optical and electrical design of plasmonic BR has yet been carried out experimentally. In this work, we will systematically study the design routes of plasmonic BR based on self-assembled
Ag NPs in hydrogenated amorphous Si (a-Si:H) solar cells, where both optical and electrical effects are considered. The shape of Ag NPs, the thickness of ZnO:Al spacer layers, materials of spacer layer on top of Ag NPs, and particle size are found to have a significant influence on the performance of a solar cell. The plasmonic BR should provide both efficient light trapping and a good base for the growth of high quality silicon layers on it. We will demonstrate the combined optical and electrical design routes that lead to high-efficiency plasmonic a-Si:H solar cells.

### 3.2 Experimentals

The structure of the plasmonic BR is shown in Figure 3.1. The plasmonic BR consists of the following layer stack glass/Ag/AZO/Ag NPs/AZO. The planar Ag layer on glass and Al-doped ZnO (AZO, ZnO:Al) layers were deposited by RF-magnetron sputtering. The Ag NPs were formed by thermal evaporation of a thin Ag film followed by one hour annealing in a vacuum oven. The deposition rate of the thin Ag film was kept below 0.1 nm/s. Unless otherwise stated the Ag NPs were formed from 12 nm Ag and annealed at 400 °C. In addition, the thickness of ZnO:Al layers between planar Ag film and Ag NPs ($d_{Ag-NPs}$) and the thickness between Ag NPs and n-doped a-Si:H layer ($d_{NPs-Si}$) were 60 and 30 nm, respectively.

The total reflection and haze in reflection of the plasmonic BRs with $d_{Ag-NPs}$=60 nm and $d_{NPs-Si}$=30 nm were measured using the integrating sphere in PerkinElmer Lambda 950 spectrophotometer. The angular intensity distribution of reflected light was measured with the Angular Resolved Transmittance /Reflectance Analyzer integrated in

![Figure 3.1 Schematic device structure of an n-i-p a-Si:H solar cell with plasmonic BR. The plasmonic BR is a stack of glass/Ag /AZO /Ag NPs/AZO layers.](image-url)
the spectrophotometer. Experimental details of the measurements can be found elsewhere [21, 22]. The size of the Ag NPs was measured by a Hitachi 4800 scanning electron microscopy (SEM). The surface coverage, NP size distribution, and circularity (defined as 4π-area/ perimeter²) were determined from the SEM images using image processing software ImageJ [23]. The surface morphology of Ag NPs was also characterized by an NT-MDT atomic force microscopy (AFM).

The n-i-p a-Si:H solar cells as shown in Figure 3.1 were deposited onto the BRs at substrate temperature of 180 °C using multi-chamber plasma-enhanced chemical vapor deposition system. The thickness of the n-i-p layers was 20, 300 and 15 nm, respectively. The values of short-circuit current density (J_sc) were calculated from external quantum efficiency (EQE) measured under short-circuit condition in the range from 300 to 800 nm by integration over the photon flux of the AM1.5G solar spectrum. The Voc and FF were determined from J-V measurements under 100 mW/cm² illumination (AM1.5G, Oriel Newport).

3.3 Localized surface plasmon resonance in metal nanoparticles

Metal nanoparticles can strongly scatter or absorb light through the excitation of localized surface plasmons (LSPs), depending on the size, shape, and surrounding medium of the nanoparticles [24]. Small nanoparticles have their resonance in a narrow spectral band and are dominated by strong parasitic absorption, whereas large nanoparticles have strong scattering and low absorption over a broad spectral range. The LSP induced light scattering by large metal nanoparticles is of great interest for light trapping in solar cells.

We illustrate the size dependent scattering and absorption of Ag NPs using Mie theory [24], which gives an analytical solution for spherical particles in a uniform medium. Figure 3.2a shows the scattering efficiency Q_{scat} and absorption efficiency Q_{abs} of Ag NPs embedded in ZnO:Al with different diameters D. The Q_{scat} and Q_{abs} are defined as the scattering and absorption cross-sections normalized by the geometric cross-section. The radiative efficiency is defined as Q_{rad}/(Q_{scat}+Q_{abs}). Ag NPs with D of 50 nm have large Q_{scat} in a narrow spectral range around 530 nm. However, such small nanoparticles also have large Q_{abs} and low radiative efficiency and thus are not suitable for light trapping in TF-Si solar cells.

As the diameter increases, additional multipolar resonances appear in the spectrum and the radiative efficiency increases as depicted in Figure 3.2a and b. Note that the radiative efficiency shown in Figure 3.2b is integrated over the AM1.5G spectrum from 500 to 1100 nm. For large Ag NPs with D of 200 nm, the radiative efficiency approaches unity. These large NPs also have broadband scattering over the spectral range 500-1100 nm relevant for TF-Si solar cells. Plasmonic Ag NPs exhibit large scattering cross-section, which may be several times their geometrical cross-section. For example, Ag NPs with D of 200 nm have an averaged Q_{scat} of about 4, thus a surface coverage of ~25% (1/Q_{scat}) is sufficient to scatter all the incident light. We emphasize that Figure 3.2b shows the radiative efficiency of a perfectly spherical Ag NP in a uniform medium. In real Ag NPs
imperfections such as the aggregation of nanoparticles, sharp corners and edges, oxidization of the surface, and high surface coverage can induce parasitic absorption which reduces the radiative efficiency \[4, 25\].

3.4 Optical and electrical design of plasmonic back reflector for amorphous silicon solar cells

3.4.1 Effect of the shape/morphology of Ag NPs

Self-assembled Ag NP arrays used in previous works were usually formed at low annealing temperature (around 200 °C) \[8-10, 15, 16\]. As shown in Figure 3.3a, the metal
island film formed from 12 nm Ag at 200 °C has many small size (D<100 nm) NPs, a high surface coverage (~34%), irregular shape with sharp edges and corners (circularity<0.6), and aggregation of NPs. When the annealing temperature is increased to 400 °C, however, small NPs are almost absent. The obtained NPs have large diameter (~200 nm on average) and low surface coverage (~20%). The Ag NPs have regular and round shape (circularity≈0.86). The random NPs arrays are uniformly distributed on the back reflector, and aggregation of NPs is not observed. AFM measurements indicate that the Ag NPs induce only a moderate surface roughness on back reflector, with a root-mean-square (RMS) roughness of 22 nm as shown in Chapter 2. The plasmonic BR have flattened surface feature with a particle height less than 100 nm, providing a good base for the growth of high quality silicon layers on top [18]. Since the plasmonic BR is processed prior to the deposition of silicon layers, the high temperature used for Ag NPs formation would not affect the following deposition of a-Si:H layers at lower temperature.

As shown in Figure 3.3b, increasing the annealing temperature also results in higher total reflection and larger haze factor over a broad spectral range from 550 to 1100 nm. The improved optical performance is attributed to the formation of large size and regularly shaped Ag NPs, which increases the scattering and reduces the parasitic absorption in Ag NPs. Due to the strong light scattering of Ag NPs formed at 400 °C, the plasmonic BR has a haze factor above 80% throughout the spectral range 550-1100 nm, where light trapping from the BR is essential for TF-Si solar cells. The broadband high haze value corresponds well to the broad scattering of Ag NPs with D of 200 nm shown in Figure 3.2a.

Figure 3.3c presents the EQE curves and total device absorption (1-R) of a-Si:H solar cells co-deposited on the plasmonic BRs formed at 200 and 400 °C. The $J_{sc}$ of the solar cells increases from 14.1 to 14.7 mA/cm² when the annealing temperature is increased from 200 to 400 °C. The EQE significantly improves at the long wavelengths (550-800 nm). The decrease in cell absorption (for Ag NPs annealed at 400 °C) indicates that the increase in EQE is predominantly due to the smaller parasitic absorption in the Ag NPs and that the enhanced light scattering at the NPs might contribute to the gain in EQE as well. We note that there is no obvious difference in $V_{oc}$ and $FF$ of the solar cells with plasmonic BRs formed at 200 or 400 °C.
Figure 3.3 (a) SEM images of Ag NPs formed at 200 and 400 °C. (b) Total reflection (Total R) and Haze in reflection (Haze R) of plasmonic BRs with Ag NPs formed at 200 and 400 °C. (c) EQE curves and total device absorption (1-R) of solar cells deposited on plasmonic BRs with Ag NPs formed at 200 and 400 °C.
3.4.2 Effect of the spacer layer between Ag film and Ag NPs

As indicated in Figure 3.1, the ZnO:Al layers in a plasmonic BR can be divided into two parts. One layer is below the Ag NPs, separating the Ag planar film from the Ag NPs, with a thickness \( d_{\text{Ag-NPs}} \). We measured the size and shape of Ag NPs formed on different \( d_{\text{Ag-NPs}} \) by SEM (not shown here), and we found that the \( d_{\text{Ag-NPs}} \) had no effect on the morphology of Ag NPs for \( d_{\text{Ag-NPs}} \) from 30 to 300 nm. The other layer is above the Ag NPs, separated the Ag NPs from the n-doped a-Si:H layer, with a thickness \( d_{\text{NPs-Si}} \). The two ZnO:Al layers in the plasmonic BR are also referred to as spacer layer in previous works since the layers can tune the optical properties of the Ag NPs [8]. We will first discuss the effect of \( d_{\text{Ag-NPs}} \) on the performance of solar cells. The effect of the other spacer layer will be shown in the next section.

Figure 3.4 shows the EQE and total device absorption of plasmonic solar cells with \( d_{\text{Ag-NPs}} \) of 60, 120, and 240 nm. From the EQE curves we can see two interference fringes (marked 1 and 2) at wavelengths around 650 and 750 nm, respectively. The \( d_{\text{Ag-NPs}} \) has influence on the EQE and absorption at the two fringes. We changed the \( d_{\text{Ag-NPs}} \) from 30 to 300 nm and found maximal \( J_{\text{sc}} \) at \( d_{\text{Ag-NPs}}=240 \) nm. When \( d_{\text{Ag-NPs}}=240 \) nm, the EQE improves compared with \( d_{\text{Ag-NPs}} \) of 60 or 120 nm. The improved EQE in fringes 1 and 2 is clearly related with the increase of absorption in solar cells as indicated in Figure 3.4.

The difference in EQE and absorption may be related to the difference of the intensity of electrical field which drives LSP induced scattering in Ag NPs [8]. The total intensity of the driving field for a Ag NP is the sum of the fields of the incident light throughout the a-Si:H layers and the light reflected back by the reflector. For Ag NPs on the Ag/ZnO:Al stacks, additional phase shift of electrical field is introduced by the ZnO:Al spacer layer when light is incident on nanoparticles, resulting in constructive or destructive interference between incident and reflected fields. If the constructive interference

![Figure 3.4](image-url)
3.4 Design of plasmonic back reflector for a-Si:H cells

happens, for example at $d_{Ag-NPs}=240$ nm as shown in Figure 3.4, the stronger driving field results in larger scattering efficiency and thereby improved light trapping in solar cells. While the spacer layer has an optical effect on the solar cells, the electrical performance, such as $V_{oc}$ and $FF$, is hardly affected. A detailed study of the driving field in plasmonic BR can be found in our recent publication [29].

3.4.3 Effect of the spacer layer between Ag NPs and n-doped a-Si:H layer

Next we study the effect of different materials on top of the Ag NPs on the performance of solar cells. Three commonly used materials: n-doped a-Si:H, hydrogenated nanocrystalline silicon oxide (nc-SiOx:H), and ZnO:Al, were studied. The nc-SiOx:H, which has lower refractive index and absorption coefficient than a-Si:H [26], is widely used in the back reflector and intermediate reflector in TF-Si solar cells. ZnO:Al is the most commonly used in the back reflector of TF-Si solar cells and has an even lower refractive index and extinction coefficient. As shown in Figure 3.5a, the plasmonic solar cell without spacer layer, i.e. with n-doped a-Si:H directly deposited on top of the Ag NPs, has significantly lower EQE than those with a nc-SiOx:H or ZnO:Al spacer layer. Compared with the nc-SiOx:H spacer layer, the ZnO:Al spacer layer results in a higher EQE for $\lambda>600$ nm.

The increased EQE for the ZnO:Al spacer layer compared to without and nc-SiOx:H layer can be attributed to less parasitic absorption losses in Ag NPs and stronger scattering by Ag NPs. It was reported that replacing ZnO:Al by higher refractive index materials (such as nc-SiOx:H and especially a-Si:H) will shift the absorption dominated resonance to higher wavelengths ($\lambda>550$ nm) [4, 24], resulting in higher absorption loss in Ag NPs and lower scattering efficiency at wavelengths (600-800 nm) of which the light trapping is important for solar cells. The reduced scattering efficiency is well indicated by the stronger interference fringes of the 1-R curve in Figure 3.5a for cells with nc-SiOx:H or a-Si:H on top of Ag NPs. The averaged total absorption in solar cells with the three different spacer layers is similar, indicating that higher refractive index materials on top of Ag NPs result in more parasitic absorption. The similar cell absorption also suggests that the Ag NPs with lower refractive indices on top have better light scattering at long wavelengths. Otherwise the cell absorption with lower refractive indices would be lower, given that the parasitic absorption is lower.

Figure 3.5b shows the EQE and photovoltaic parameters of plasmonic solar cells with different thickness of ZnO:Al spacer layers on top of the Ag NPs. When the $d_{NP-Si}$ is increased from 30 nm to 60 nm, the $J_{sc}$ increases from 14.7 to 15.1 mA/cm². Meanwhile the $V_{oc}$ improve significantly which may be ascribed to improved surface morphology which is beneficial for the growth of dense a-Si:H material with less defective zones. The thicker ZnO:Al layer on the Ag NPs could possibly flatten the sharp surface features (especially around the edges of NPs) which often cause cracks or defective areas in a-Si:H layer and thus deteriorate the $V_{oc}$ and $FF$ [27, 28]. Further improvement is not observed as the thickness is increased beyond 60 nm. From this we can conclude that the spacer layer between the Ag NPs and n-doped a-Si:H layer should be optimally designed to provide a good surface to grow high quality a-Si:H materials and to avoid the low scattering and strong parasitic absorption of Ag NPs at the long wavelengths.
3.4.4 Effect of the size of Ag NPs

The size of self-assembled Ag NPs can be tuned by the initial Ag mass thickness. The thicker the Ag film is, the larger the NPs are. Here we will discuss how particle size influences both the optical and electrical performances of plasmonic solar cells. From the inset SEM image of Figure 3.6a, we can clearly see that Ag NPs formed from 21 nm Ag have larger diameter than those formed from 12 nm Ag shown in Figure 3.3a. The Ag NPs have an average diameter of ~400 nm, particle height lower than 250 nm, RMS roughness of ~40 nm, and surface coverage of ~19%. Similar to the NPs formed from 12
The NPs formed from 21 nm Ag have relatively smooth top surface as well.

Figure 3.6 (a) Total R and haze R of plasmonic BRs with Ag NPs formed from 12 and 21 nm Ag. The inset shows the SEM image of the Ag NPs formed from 21 nm Ag. (b) Angular resolved scattering of plasmonic BRs with Ag NPs formed from 12 and 21 nm Ag measured at wavelengths of 600, 700, and 800 nm. (c) EQE and 1-R curves of plasmonic solar cells with Ag NPs formed from 12 and 21 nm Ag.
As shown in Figure 3.6a, the total reflectance of plasmonic BR formed from 21 nm Ag is higher, possibly due to the lower parasitic absorption by larger Ag NPs. The haze factor, however, is lower than that of BR formed from 12 nm Ag because of the smaller scattering efficiency for larger nanoparticles as shown in Section 3.3. The haze parameter indicates the fraction of light that is scattered, but it does not indicate the angle into which the light is scattered. To obtain efficient light trapping it is desirable to scatter light into larger angles as much as possible. The angular resolved scattering (ARS) of plasmonic BRs formed from 12 and 21 nm was measured in air at wavelengths of 600, 700 and 800 nm, and the results are presented in Figure 3.6b. The ARS intensity is the scattered light intensity at angle θ multiplied by sinθ, where θ is the scattering angle in reference to the surface normal. Thus the ARS curve shown in this figure denotes the most probable angle of scattering. The larger Ag NPs have stronger scattering at larger angles, which is beneficial for light trapping in solar cells.

The EQE curves in Figure 3.6c clearly show that the plasmonic solar cell with larger Ag NPs has higher EQE in the long wavelengths, due to the preferential light scattering into larger angles and the less parasitic absorption in Ag NPs as indicated by the reduced 1-R. The $J_{sc}$ of 15.6 mA/cm$^2$, to the best of our knowledge, is the highest reported value for plasmonic a-Si:H solar cells. Although the spectral response improves for larger NPs, the FF decreases significantly which results in lower efficiency. The larger NPs induce rougher surface and larger feature size in the back reflector, which deteriorates the FF of TF-Si solar cells [27, 28]. Therefore, a compromise should be considered between the light trapping and electrical performance when choosing the particle size. However, a robust n-doped layer (such as a-SiC:H) and a buffer layer at the $n/i$ interface might improve the FF of solar cells with rougher plasmonic BR [27].

### 3.5 Conclusions

The design parameters of plasmonic BR with self-assembled Ag NPs, such as annealing temperature which modifies the size and especially the shape of the NPs, spacer layer, and particle size, have been systematically studied. Increased annealing temperature can improve the morphology and the optical performance of Ag NPs, thereby increasing the photocurrent of solar cell. The higher annealing temperature of 400 °C does not affect the $V_{oc}$ and FF. The design of ZnO:Al spacer layers has to be divided into two parts. The ZnO:Al layer between Ag NPs and Ag planar film has only optical effect on the solar cells. The driving field that affects the scattering efficiency should be considered when designing this layer. The spacer layer between Ag NPs and doped a-Si:H has both optical and electrical influence on the device. Lower refractive index materials are favored on the top of Ag NPs to reduce the parasitic absorption loss and to enhance light scattering. It is also found that thicker ZnO:Al spacer layer on top of Ag NPs can significantly improve the $V_{oc}$ and FF. The light scattering behavior of plasmonic nanoparticles depends on their size. Larger NPs have less parasitic absorption and can preferentially scatter light into larger angles, thereby increasing the spectral response in the solar cell. However, for larger NPs the FF of the device deteriorates due to the rougher surface, indicating a compromise between light trapping and electrical
performance. This work points out the important routes for the design of plasmonic BR. Following these routes, we have obtained high efficiency a-Si:H solar cells with plasmonic light trapping. Although the design routes here are discussed for Ag NPs based back reflector, they are also useful for the design of periodically nanopatterned Ag film based plasmonic back reflector.

References


Chapter 4

Plasmonic back reflector for thin-film nanocrystalline silicon solar cells

This chapter is based on the following publication:


Preface:

In the previous two chapters, the plasmonic back reflectors (BRs) were studied and applied to amorphous silicon solar cells. In this chapter, we will extend the application of plasmonic BRs in thin-film hydrogenated nanocrystalline silicon (nc-Si:H) solar cells. We show experimentally that the photocurrent of nc-Si:H solar cells can be enhanced by 4.3 mA/cm² with a plasmonic BR in reference to the flat BR. The light trapping performance is improved by using plasmonic BR with a broader angular scattering and a lower parasitic absorption loss through tuning the size of silver nanoparticles. The nc-Si:H solar cells deposited on the improved plasmonic BR demonstrate a high photocurrent of 26.3 mA/cm² (absorber layer 2 µm) which is comparable to the state-of-the-art textured Ag/ZnO BR. The commonly observed deterioration of fill factor is avoided by using nc-SiO: H as the n-layer for solar cells deposited on plasmonic BR.

NOTE: The EQE curves in Figure 4b as published in Tan et al., Appl. Phys. Lett. 102, 153902 (2013) were overvalued due to the degradation of calibration diode. The diode has been calibrated by Fraunhofer ISE again after the publication. Data shown in Figure 4b and Table 1 in this thesis has been corrected from the publication, according to the new calibration file. However, conclusions claimed in the publication are still supported and remain unchanged.
4.1 Introduction

Effective light trapping in thin-film nanocrystalline silicon (nc-Si:H) solar cells is crucial to obtain high photocurrent and to reduce the absorber layer thickness, which in state-of-the-art devices is commonly realized by using randomly textured substrates [1-5]. Recently, plasmonic metal nanoparticles have attracted extensive interest to further improve the light trapping in solar cells since metal nanoparticles can efficiently scatter the incident light into absorber layer [6-14]. Enhanced solar cell performance has been demonstrated by using periodic metallic gratings and random metal nanoparticles as rear reflectors, which here we refer to as plasmonic back reflector (BR). By depositing nc-Si:H solar cells on periodic metallic reflector, Paetzold et al. demonstrated that the photocurrent can be increased to 21.0 mA/cm², compared to 17.7 cm²/cm² for a planar cell [12]. Bhattacharya et al. also reported that the photocurrent increased to 21.5 mA/cm² by incorporating a photonic-plasmonic BR in the nc-Si:H solar cells [13]. Chantana et al. demonstrated that the photocurrent of nc-Si:H solar cells can be increased to 22.3 mA/cm² by the plasmonic BR with a random array of silver nanoparticles (Ag NPs) [14].

Although plasmon enhanced light trapping has been demonstrated in reference to the flat devices, so far the plasmonic light trapping capability in nc-Si:H solar cells remains considerably below the levels attained by state-of-the-art textured substrates [11-14]. One of the main reasons is the considerable parasitic absorption in the plasmonic BR. Scattering mainly into low angles (close to the surface normal) is another possible factor limiting the light trapping performance. The effects of plasmonic losses and the angular resolved scattering of the plasmonic BR on the light trapping performance in solar cells have not received much attention to date. In this work, we will investigate the correlation between the size of Ag NPs and the parasitic absorption and angular scattering of the plasmonic BR. We show that the plasmonic light trapping can be improved by the plasmonic BR which has a broader angular scattering and a lower parasitic absorption. Accordingly, in a 2 µm-thick nc-Si:H solar cell the improved plasmonic BR results in a high photocurrent of 26.3 mA/cm², which is comparable to the state-of-the-art textured Ag/ZnO BR.

4.2 Experiments

The structure of the plasmonic BR studied in this chapter is shown in Figure 4.1a. It consists of glass/flat Ag (100 nm)/AZO (60 nm)/Ag NPs/AZO (30 nm) layers, where AZO stands for Al-doped ZnO (ZnO:Al). The Ag NPs were formed by a self-assembly method, and the size of the Ag NPs can be tuned by the initial thickness of as-deposited Ag film and annealing temperature. Experimental details can be found in our previous works [9,15]. The reflection of plasmonic BRs was measured with the PerkinElmer Lambda 950 spectrophotometer. Angular resolved scattering was measured with an Angular Resolved Analyzer integrated in the spectrophotometer as discussed in Ref.16. The n-i-p substrate-type nc-Si:H solar cells with ~2 µm intrinsic absorber layer were fabricated on the BRs by plasma enhanced chemical vapor deposition. The solar cells were completed by sputtering an 80 nm-thick ITO layer and Ag grids as top electrode. The Ag grids have
4.3 Results and discussion

Plasmonic Ag NPs can scatter and absorb light through the excitation of localized surface plasmons, which depends on the size and shape of the NPs \([7,17]\). Larger NPs will have plasmonic resonance at longer wavelengths. Meanwhile, the parasitic absorption by Ag NPs decreases as the size increases. According to Mie-theory the multipolar resonances appear if the wavelength is larger than the diameter of spherical Ag NPs increases. Therefore, broadband light scattering can be achieved by tuning the size of the Ag NPs and the size distribution of the NPs. The Ag NPs with diameter larger than 100 nm have broadband scattering over the spectral range (up to 1100 nm) relevant
for nc-Si:H solar cells. Here we choose three plasmonic BRs containing Ag NPs with average lateral diameters of 150, 350, and 600 nm as shown in Figure 4.1b-d, respectively. These Ag NPs with different sizes have similar surface coverage of ~20% and circularity of ~86%. A lateral diameter of 600 nm is significantly larger than the size typically used for plasmonic a-Si:H solar cells. The larger Ag NPs are expected to have lower parasitic absorption as well as efficient light scattering over a broad wavelength range.

From Figure 4.2a it can be seen that the measured reflectance of the plasmonic BRs increases by increasing the size of Ag NPs, indicating that the parasitic absorption loss reduces with the increase of size. When the size increases from 150 to 350 nm, the average reflectance in the range of 600-1100 nm significantly improves from 57% to 84%. Further increase of the size to 600 nm improves the average reflectance to 88%. However, the reflectance of the plasmonic BR is still lower than the flat BR whose reflectance is higher than 95% at wavelengths from 600 to 1100 nm. Nevertheless, it should be noted that the reflectance of the plasmonic BR in real solar cells will be higher than the measured reflectance in air since the light trapped within the ZnO will enter into the silicon when solar cells are made on the BRs. Measurements of haze in reflection (shown in Figure 4.2b) reveal that the size of Ag NPs has great influence on the scattering properties of the plasmonic BRs. The increase of size shifts the plasmon-resonance peaks to longer wavelengths. In the crucial wavelength range for light trapping in nc-Si:H solar cells (700-1000 nm), the three plasmonic BRs have reasonably high haze values. A higher surface coverage is needed to achieve 100% haze in reflection. However, it is difficult to control the surface coverage for self-assembled Ag NPs.

Although the haze parameter is commonly used to evaluate the light trapping potential, recent studies also emphasize the importance of the angular intensity distribution (AID) of the scattered light to achieve efficient light trapping [16,18]. Light scattered into large angles, i.e. above the critical angle, is preferred since this light can be trapped inside the absorber layer by total internal reflection or by coupling into guided modes. The maximum absorption enhancement of $4n^2$ ($n$ is the refractive index of the absorber layer) for random textures is derived under the assumption of an ideal Lambertian scattering with an AID following a cosine distribution. Figure 4.3 shows the AID of the reflected light from the plasmonic BRs at the wavelengths of 700 and 800 nm measured in air. For comparison, the AID of a Lambertian reflector is also shown. As the size of Ag NPs increases from 150 to 600 nm, incident light is reflected into larger angles more efficiently. The preferential scattering into larger angles by larger Ag NPs shown here might be due to the excitation of additional higher-order localized surface plasmon modes and resonant surface plasmon polaritons modes, which scatter light into large angles more efficiently than the dipole modes (dominant in small metal nanoparticles) [19-20]. Overall, the broader angular scattering of plasmonic BR with larger Ag NPs is useful to increase the optical path length within the absorber layer of nc-Si:H solar cells and enhance the total internal reflection at the interface between the nc-Si:H film and the ITO top electrode. For the plasmonic BR with Ag NPs size of 600 nm, the AID is close to the Lambertian distribution.
4.3 Results and discussion

Figure 4.2 Total reflection (a) and haze in reflection (b) of the flat BR and the plasmonic BRs with Ag NPs size of 150, 350, and 600 nm.

Figure 4.3 The AID of the plasmonic BRs with Ag NPs size of (a) 150, (b) 350, and (c) 600 nm measured at wavelengths of 700 and 800 nm in air. The AID of a Lambertian reflector normalized to the highest intensity at the angle of 5 degree is also shown for comparison.
To investigate the light trapping performance of the three plasmonic BRs, the n-i-p structured nc-Si:H solar cells were processed at TU Delft on the BRs in the same deposition run. Figure 4.4a shows the EQE curves and the total device absorption (1-R) of corresponding solar cells. The positions of the maximal EQE are not the same due to small variation in the ITO thickness. Over the wavelength range between 600-1100 nm, the EQE increases as the Ag NPs size increases from 150 to 600 nm, indicating improved light trapping for the plasmonic BR with larger Ag NPs. The improvement of EQE can be attributed to two aspects. Firstly, the larger Ag NPs have lower parasitic absorption, leading to less optical losses for the solar cells. The total device absorption in the three solar cells is almost the same, also indicating lower parasitic absorption losses in solar cells for larger Ag NPs. Secondly, light is preferentially scattered into larger angles for plasmonic BR with larger Ag NPs, which more efficiently enhances the optical path length in the nc-Si:H absorber layer. Especially for light scattered beyond the critical angle, it will be trapped in the absorber layer by total internal reflection.
To demonstrate the plasmon enhanced light trapping, nc-Si:H solar cells were deposited on the flat BR and the plasmonic BR with Ag NPs size of 600 nm using improved deposition recipe, where high-transparency nanocrystalline silicon oxide (nc-SiOx:H) was used as doped layer. Figure 4.4b shows the EQE curves of corresponding solar cells. At short wavelengths (300-550 nm) where light trapping does not play a role, the EQE of the two solar cells is the same. For wavelengths above 550 nm, the EQE of the solar cell deposited on the plasmonic BR is significantly enhanced in comparison to the planar cell. The improved EQE can be attributed to the strong scattering of light by the Ag NPs in the plasmonic BR, which increases the optical path length in the photoactive layer compared to the flat BR. The corresponding photocurrent increases considerably from 20.0 to 24.3 mA/cm², resulting in a significant increase of the power conversion efficiency (η) from 6.0% to 7.4%.

To evaluate the light trapping capability of the plasmonic BR, it should be compared to the state-of-the-art textured Ag/ZnO BR which is well-known to have high-performance light trapping in nc-Si:H solar cells. For this purpose, the nc-Si:H solar cells were deposited at United Solar on the plasmonic BR with Ag NPs size of 600 nm and on the state-of-the-art textured Ag/ZnO BR using the base-line processing. The textured BR consists of textured Ag layer on the stainless steel substrate and a thin ZnO (110-140 nm) layer, which is optimized for both good light trapping and for the growth of high-quality nc-Si:H materials on top [3,21,22]. The EQE spectra of the two solar cells are compared in Figure 4.5. As shown, the plasmonic solar cell exhibits slightly higher EQE than the textured solar cell at short wavelengths from 350 to 600 nm, possibly due to two reasons. Firstly, the solar cells deposited on the plasmonic BR have much smoother top surface than cells on the highly textured BR, which can improve the i/p interface and thus enhance the carrier collection at those short wavelengths range. Secondly, the thickness of ITO in plasmonic solar cell might be smaller than the textured solar cells, which shifts lowest surface reflection peak to shorter wavelengths and thus higher EQE in plasmonic cell at the short wavelengths range. In the wavelength range from 700 to 1100 nm, the EQE of the plasmonic solar cell is slightly lower than the textured solar cell. For the textured BR, the incident light is almost completely scattered. However, for the plasmonic BR the incident light is not completely scattered as indicated by the haze curve in Figure 4.2(b), which results in the stronger interference and slightly lower EQE than the textured BR. Further increase of the surface coverage of Ag NPs would lead to higher haze value and higher EQE. Overall, the plasmonic BR results in a high photocurrent of 26.3 mA/cm² which is comparable to the textured BR (26.7 mA/cm²). The photocurrent of 26.3 mA/cm² achieved here is considerably higher than those reported in the previous works on plasmonic light trapping [11-14], thanks to the low parasitic absorption and broad angular scattering distribution.

To illustrate the effects of plasmonic BR on the electrical performance of the nc-Si:H solar cells, the photovoltaic parameters are summarized in Table 4.1. For solar cells deposited at TU Delft or United Solar, the Voc of solar cell deposited on the plasmonic BR is almost the same as the solar cell deposited on the flat BR or the textured BR, respectively. The effect of plasmonic BR on the FF, however, is different between solar cells deposited at TU Delft and United Solar. For devices deposited at United Solar where hydrogenated amorphous silicon (a-Si:H) n-layer was used, the FF of the plasmonic solar cells (0.575) is
Figure 4.5 EQE spectra (measured at bias of -3V) of nc-Si:H solar cells deposited at United Solar on the plasmonic BR and on state-of-the-art textured Ag/AZO BR using the baseline deposition recipe.

Table 4.1 Photovoltaic characteristics of solar cells deposited at TU Delft on the flat BR and the plasmonic BR, and solar cells deposited at United Solar on the plasmonic BR and the state-of-the-art textured BR.

<table>
<thead>
<tr>
<th>Device</th>
<th>BRs</th>
<th>n-layer</th>
<th>$V_{OC}$ (V)</th>
<th>$FF$ (%)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$I_{PLAS-3V}$ (mA/cm$^2$)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>TU Delft</em></td>
<td>flat</td>
<td>nc-SiO$_2$:H</td>
<td>0.479</td>
<td>66.3</td>
<td>18.9</td>
<td>20.0</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>plasmonic</td>
<td>nc-SiO$_2$:H</td>
<td>0.485</td>
<td>66.2</td>
<td>23.1</td>
<td>24.3</td>
<td>7.4</td>
</tr>
<tr>
<td><em>United Solar</em></td>
<td>textured</td>
<td>a-Si:H</td>
<td>0.493</td>
<td>69.4</td>
<td>26.3</td>
<td>26.7</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>plasmonic</td>
<td>a-Si:H</td>
<td>0.498</td>
<td>57.5</td>
<td>25.5</td>
<td>26.3</td>
<td>7.3</td>
</tr>
</tbody>
</table>

lower than that of textured solar cells (0.694). Such a deterioration of $FF$ was also commonly observed in other reports [10-14]. Although the top surface of the Ag NPs is flattened, the edges of the Ag NPs are still relatively steep. The sharp valleys around the Ag NPs can create cracks (porous defective material) near the n/i interface and inside the nc-Si:H intrinsic layer [23]. Such cracks act as shunting paths which could reduce the $FF$ of solar cells, making the cell efficiency (7.3%) much lower than the efficiency of solar cells deposited on the textured BR (9.0%). Therefore, suppressing the formation of cracks inside the nc-Si:H intrinsic layer or preventing the deterioration of $FF$ by proper interface treatment is a key point to achieve high-efficiency solar cells deposited on the plasmonic BR. One possible route is to deposit a thicker ZnO:Al layer on top of the Ag NPs and then
polish the surface to be flat, as demonstrated by other groups [24-25]. Another alternative method is to use a nc-SiO\textsubscript{x}::H n-layer which enables $FF$ and $V_{oc}$ more robust to the cracks than the conventional a-Si:H or nc-Si:H doped layers [26-27]. As demonstrated, the deterioration of $FF$ is not observed for the solar cells deposited at TU Delft which deploy a nc-SiO\textsubscript{x}::H n-layer instead of the conventional a-Si:H n-layer. There are two possible reasons why the $FF$ of the plasmonic solar cell with a nc-SiO\textsubscript{x}::H n-layer is not degraded. Firstly, the nc-SiO\textsubscript{x}::H layer can quench the shunting paths created by the cracks near the n/i interface or inside the i-layer. Secondly, the mixed-phase nature of nc-SiO\textsubscript{x}::H can act as a barrier to the in-diffusion of contamination atoms from the underlying layer into the nc-Si:H intrinsic layer.

### 4.4 Conclusions

In conclusion, the photocurrent of the nc-Si:H solar cells can be significantly enhanced by a plasmonic BR due to the efficient scattering of incident light by metal nanoparticles. The light trapping performance is improved by using a plasmonic BR with a broader angular scattering and a lower parasitic absorption loss through tuning the size of the plasmonic nanoparticles. The improved plasmonic BR results in a high photocurrent of 26.3 mA/cm\textsuperscript{2} which is comparable to the state-of-the-art textured Ag/ZnO BR. One potential drawback of using plasmonic BRs is a deterioration of $FF$. However, we show here that this can be avoided by using a nc-SiO\textsubscript{x}::H n-layer instead of the conventional a-Si:H n-layer.

### References


Part II:

*Materials and light management for multijunction thin-film silicon solar cells*

In previous part, plasmonic light trapping was studied in thin-film silicon solar cells. In this part the focus is on the more conventional roughness-induced light trapping. Advanced materials and novel light-trapping substrates are developed for high-efficiency multijunction solar cells. This part includes following three chapters:

**Chapter 5.** Micro-textured glass as light-trapping substrate for nanocrystalline silicon solar cells

**Chapter 6.** Wide bandgap p-type nanocrystalline silicon oxide as window layer for high $V_{oc}$ a-Si:H solar cells

**Chapter 7.** Highly transparent modulated-surface-textured front electrodes for multijunction thin-film silicon solar cells
Chapter 5

Micro-textured glass as light-trapping substrate for nanocrystalline silicon solar cells

This chapter is based on the following publication:


**Preface:**

In this chapter, micro-textures with large opening angles and smooth U-shape are developed and applied to nanocrystalline silicon (nc-Si:H) solar cells, to mitigate the trade-off between the light trapping and electrical performance. The micro-textured substrates result in higher open-circuit-voltage ($V_{oc}$) and fill-factor ($FF$) than nano-textured substrates. For thick solar cells, high $V_{oc}$ and $FF$ are maintained. Particularly, the $V_{oc}$ only drops from 564 to 541 mV as the solar cell thickness increases from 1 to 5 μm. The improvement in electrical performance of solar cells is ascribed to the growth of dense nc-Si:H layers free from defective filaments on micro-textured substrates. Thereby, micromorph tandem solar cells with an initial efficiency of 13.3%, $V_{oc}$=1.464V, and $FF$=0.759 are obtained.
5.1 Introduction

Hydrogenated nanocrystalline silicon (nc-Si:H) is widely used as absorber layer in the bottom cell of multijunction thin-film silicon solar cells [1-5]. The nano-textured substrates with morphology features in the order of 1 μm are commonly used to achieve efficient light trapping in the state-of-the-art devices [4-10]. However, the nano-textured substrates deteriorate the electrical performance of solar cells by decreasing the open-circuit voltage \((V_{oc})\) and fill factor \((FF)\) compared to flat substrates [7,11-12]. Furthermore, the \(V_{oc}\) and \(FF\) of nc-Si:H solar cells show a considerable drop as the cell thickness increases [9,13-16], while a thick nc-Si:H absorber layer (typically 2-3 μm or even thicker) is required to achieve high current density. In addition, for economically viable nc-Si:H solar cells deposited at high deposition rates, the \(V_{oc}\) and \(FF\) are even more sensitive to the substrate textures and absorber layer thickness than the counterparts fabricated at a low deposition rate [17-19].

The decrease in \(V_{oc}\) and \(FF\) is commonly ascribed to the creation of porous and defective “cracks” in the absorber layer at concave or sharp valleys [11-12]. Here we use the term defective filaments to describe the physical nature of such porous and defective regions. The defective filaments are created at the sharp valleys even when the absorber layer is thinner than 1 μm [20]. As the thickness increases, the defective filaments generate even on the smooth valleys [14]. The deterioration of \(V_{oc}\) and \(FF\) in relatively thin cells can be partially mitigated by using substrates with smoother surface morphology (e.g. smooth U-shape instead of steep V-shape) [15,20], by implementing silicon oxide-based (SiOx:H) doped layers [18,21-22], and by optimizing the plasma deposition conditions [18,23-24]. However, it is still challenging to effectively maintain high \(V_{oc}\) and \(FF\) at thick absorber layers. Therefore, textured substrates which can provide efficient light trapping and maintain high \(V_{oc}\) and \(FF\) for thick absorber layers under high deposition rates are highly desirable.

Recently Sai et al. have shown that periodically-textured substrates with a μm-scale period resulted in a higher short-circuit current density \(\left( J_{sc}\right)\) and improved \(V_{oc}\) and \(FF\) in 3-μm-thick nc-Si:H solar cells compared to substrates with a sub-micro period [10,14]. Their work suggests that substrates with an even larger period, which we here refer to as micro-textures (feature size in the range of a few μm), might have the potential to maintain high \(V_{oc}\) and \(FF\) in thick cells by growing nc-Si:H material free from defective filaments. In this chapter, we explore the behavior of nc-Si:H solar cells deposited on the micro-textured glass substrates.

5.2 Experiments

Three different textured substrates as shown in Figure 5.1 were studied: (i) etched ZnO:Al (EAZO) with sub-micro features, (ii) micro-textured glass coated with as-deposited ZnO:Al, and (iii) modulated-surface-textured substrate by superposing nano-textured ZnO:Al on micro-textured glass. For simplification in the following, we refer to these three substrates as EAZO, EG, and MST, respectively. The morphological properties
Figure 5.1. Schematic structures and corresponding SEM images of nano-textured sputtered-etched AZO on flat glass (EAZO), micro-textured wet-etched glass covered by an as-deposited AZO layer (EG), and modulated surface textures superposing nano-textured AZO on micro-textured glass (MST).

Table 5.1 Root-mean-square roughness ($R_{rms}$), correlation length ($L_c$), aspect ratio ($r_{RMS}/L_c$), and haze in transmittance at wavelength of 1000 nm ($H_T@1000nm$) of different substrates shown in Figure 5.1.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$R_{rms}$ (nm)</th>
<th>$L_c$ (µm)</th>
<th>Aspect ratio</th>
<th>$H_T@1000nm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EAZO</td>
<td>227</td>
<td>1.02</td>
<td>0.22</td>
<td>0.36</td>
</tr>
<tr>
<td>EG</td>
<td>889</td>
<td>5.10</td>
<td>0.17</td>
<td>0.84</td>
</tr>
<tr>
<td>MST</td>
<td>917</td>
<td>6.59</td>
<td>0.14</td>
<td>0.86</td>
</tr>
</tbody>
</table>

obtained from AFM scans and haze in transmittance of the three substrates are summarized in Table 5.1. The micro-textures on glass were generated by wet-etching with In$_2$O$_3$:Sn as sacrificial layer in a solution composing of HF and H$_2$O$_2$ for 30min [25-26]. The AZO layers (1.5 µm for EAZO and MST, and 1 µm for EG) were fabricated by RF magnetron sputtering from a ZnO target with 2.0wt% Al$_2$O$_3$. Nano-textured AZO was obtained by wet-etching in 0.5wt% HCl for 40s. As shown in Figure 5.1, the U-shaped craters in EG are much larger than the V- or U-shaped craters in EAZO.

To evaluate the effects of the three different textures on the electrical performance and light trapping in solar cells, superstrate-type $p-i-n$ nc-Si:H solar cells (4×4 mm$^2$) were co-deposited on three substrates for each cell thickness using plasma-enhanced chemical vapor deposition (PECVD). The solar cells have a structure of $p$-SiO$_x$:H/$i$-nc-Si:H/$n$-SiO$_x$:H/Ag. Prior to the deposition of $i$-nc-Si:H layers, the $p$-SiO$_x$:H films were subjected to an air exposure for a few minutes. This surface treatment can improve the $V_{oc}$ and FF of solar cells, similar to the function of an in-situ $i$-SiO$_x$:H interface layer investigated by Bugnon et al [33]. The doped SiO$_x$:H layers were deposited with RF-PECVD and were kept...
the same in all devices. The i-layers were deposited at a rate of ~40 nm/min under high-pressure (4 mbar) and high-power (40 W) regime at 40.68 MHz, without any profiling or buffer layers. The $V_{oc}$ and $FF$ of solar cells were evaluated by current-voltage ($I-V$) measurements with an AM 1.5G solar simulator (100 mW/cm$^2$) at 25 °C. The $J_{sc}$ values were calculated from the external quantum efficiency (EQE) measurements, which exclude the overestimation of $J_{sc}$ due to the lateral current collection and any errors in the determination of active area of solar cells in $I-V$ measurements for small-area devices [1,10,14,27].

5.3 Results and discussion

Figure 5.2 summarizes the photovoltaic performance of nc-Si:H solar cells deposited on EG, EAZO, and MST. As the thickness of the i-layer ($t_i$) increases from 1 to 5 μm, the $V_{oc}$ and $FF$ decrease continuously for all the three substrates. However, the decreasing rate is different for the three textures. For cells deposited on EAZO, the $V_{oc}$ drops quickly from 558 to 487 mV as $t_i$ increases from 1 to 5 μm, which is consistent with previous experiments using nano-textured substrates [13-16]. On the other hand, the $V_{oc}$ of cells deposited on EG drops by just 23 mV as $t_i$ increases from 1 to 5 μm, and it remains high for cells with $t_i>2$ μm ($V_{oc}$ of 551 mV at $t_i=3$ μm and 541 mV at $t_i=5$ μm). The trend of the $FF$ with $t_i$ for the three substrates is similar to the one seen in the $V_{oc}$. The $FF$ of solar cells deposited on EG is higher than that of devices deposited on EAZO and MST for each thickness. Considering the $V_{oc}×FF$ product, which is important for multijunction solar cells, EG has higher values than EAZO and MST. The light trapping performance of the three substrates is indicated by the $J_{sc}$ values. As can be seen in Figure 5.2, the EAZO and MST perform similarly as both have steep features from textured AZO layer which enable efficient light in-coupling. Note that only the EAZO used for $t_i=3$ μm was annealed at 400°C to reduce the free-carrier-absorption [28], and thus higher $J_{sc}$ than MST is expected. EG can provide relatively high $J_{sc}$ values when $t_i$ is above 2 μm. Overall, EAZO and MST are superior to EG from the point of light trapping capability. It should be noted that the $J_{sc}$ of cells deposited on EG continuously increases as $t_i$ increased from 1 to 5 μm, while for cells on EAZO and MST the $J_{sc}$ either drops or saturates for $t_i>3$ μm.

When evaluating solar cells, the ultimate figure of merit is solar cell efficiency. For thin absorber layer ($t_i=1$ μm), EAZO and MST result in higher efficiency than EG, due to the better light trapping performance. This indicates that the micro-textures are not suitable for very thin nc-Si:H solar cells, as also indicated in Ref. 14. At $t_i=2$ μm, the three substrates have almost the same efficiency (~9.5%). As the thickness increases further, the efficiency of solar cells deposited on EAZO and MST drops significantly due to the vastly decreasing $V_{oc}$ and $FF$. For cells deposited on EG, the highest efficiency (10.0%) is obtained at $t_i=3$ μm. Further increase of thickness results in slightly lower efficiency, possibly due to the increased bulk recombination and resistance in the absorber layer which leads to lower $FF$. 
Figure 5.2 Photovoltaic performance of single junction nc-Si:H solar cells deposited on EG, EAZO, and MST with different i-layer thickness. Note that the EAZO used for \( t=3 \mu m \) was annealed at 400 °C to reduce the free-carrier-absorption, and thus slightly higher \( J_{sc} \) than non-annealed one is expected.

The solar cells performance is related with the density of defective filaments in the absorber layers [11]. To check the presence of defective filaments in the nc-Si:H grown on the three different textures, cross-section images of solar cells were taken by a scanning electron microscopy (SEM, Hitachi S4800) with back scattering mode. As shown in Figure 5.3, the growth of nc-Si:H layer on EG is mostly conformal. The large U-shaped craters with large opening angles allow for the growth of dense nc-Si:H absorber layers free from defective filaments in the solar cells. The high device-quality material grown on EG results in the high \( V_{oc} \) and \( FF \), which holds true for both thin and thick devices as shown in Figure 5.2. On the contrary, for the nc-Si:H solar cells grown on EAZO or MST, the defective filaments (as indicated by the arrows) are clearly observed in the regions related to the sharp features. These defective filaments have detrimental effects on the electrical performance of solar cells. The porous defective filaments are shunt paths and significantly increase the leakage current (dark current), which reduces the \( V_{oc} \) and \( FF \) of solar cells. They also make solar cells more sensitive to the oxidization and in-diffusion of impurities into the i-layer, which further reduces the \( V_{oc} \), \( FF \), and the collection efficiency of photo-generated carriers [18]. It is also observed that MST induces lower density of defective filaments than EAZO, which could explain that MST results in higher \( V_{oc}\times FF \) product and higher \( J_{sc} \) for thick absorber layers \((t>3 \mu m)\) as shown in Figure 5.2.
Chapter 5 Micro-textured glass for nc-Si:H solar cells

Figure 5.3. Cross-sectional SEM images of nc-Si:H solar cells deposited on (a) EG, (b) EAZO, and (c) MST with i-layer thickness of 3 μm. The arrows indicate the defective filaments.

The $V_{oc}$ and $FF$ of nc-Si:H solar cells are also correlated with the crystallinity (volume fraction of the crystalline phase) of the i-layer [29]. Figure 5.4 shows the normalized Raman spectra and corresponding Raman crystallinity ($X_c$) for solar cells deposited on different substrates. The measurements were done with a 633 nm laser from the $n$-side of the solar cells (n-SiO$_x$:H layers were removed by plasma etching before measurements) and the penetration depth is about 1 μm. The $X_c$ is defined by $X_c=(I_{520}+I_{510})/(I_{520}+I_{510}+0.8×I_{480})$, where $I_i$ denotes the integration area under Gaussian fitting peak centered at $i$ cm$^{-1}$ [34]. The correction coefficient of 0.8 here is due to the difference in the cross sections for phonon excitation of crystalline phase compared to that of amorphous phase. It should be noted that this cross section ratio is reported to depend on the crystallite size and varies from about 0.9 to 0.7 [35]. As can be seen from Figure 5.4a and b, it seems that the three substrates result in almost the same crystallinity for a fixed i-layer thickness, indicating that the $V_{oc}$ and $FF$ difference between different substrates is not related to crystallinity. Therefore, the presence of defective regions in the nc-Si:H film dominantly affects the $V_{oc}$ and $FF$ of solar cells deposited on different substrates, considering that the deposition processing is the same for devices on different substrates.
For the solar cells deposited on EG as shown in Figure 4c, the $X_c$ increases slightly as the i-layer grows thicker, which could partially explain the small drop of $V_{oc}$ for thicker i-layer. Optimizing the plasma deposition by H$_2$ profiling or power profiling can further increase the $V_{oc}$ and $FF$ of solar cells by keeping the $X_c$ constant throughout the i-layer [30-31].

Figure 5.4. Normalized Raman spectra of nc-Si:H solar cells deposited on EG, EAZO, and MST with i-layer thickness of (a) 1 μm, and (b) 3 μm. (c) Normalized Raman spectra of nc-Si:H solar cells deposited on EG with different i-layer thickness.
To evaluate the potential application of micro-textures in multijunction solar cells, we used the three substrates in amorphous/nanocrystalline silicon (a-Si:H/nc-Si:H) tandem solar cells. We observed that tandem solar cells deposited on MST exhibit the same $I_{sc}$ as those on EAZO but have higher efficiency due to slightly higher $V_{oc}$ and $FF$. Therefore, in the following we only compare the performance of tandem cells deposited on EG and MST. Figure 5.5 shows the $J$-$V$ curves and the corresponding cross-sectional SEM images of the devices deposited on EG and MST. Here, the top a-Si:H cells with a high $V_{oc}$ (~950 mV in a single-junction cell) were used. The two tandem cells were co-deposited and have a device structure of $p$-nc-Si:H/$p$-a-SiC:H/$i$-a-Si:H (300 nm)/$n$-a-Si:H/$n$-SiO$_x$:H/$p$-SiO$_x$:H/$i$-nc-Si:H (2.5 μm)/$n$-SiO$_x$:H/Ag. From Figure 5.5a we can see that EG results in a significantly higher efficiency than MST. The $V_{oc}$ improves by 20 mV which is mainly from the improvement in nc-Si:H bottom cell as indicated in Figure 5.2, and the $FF$ improves considerably from 73.1% to 75.9%. It should be noted that the relatively high $FF$ (73.1%) for MST is due to the large current mismatch between the top and bottom cells, while the high $FF$ (75.9%) for EG is obtained under matched current condition. The significant improvement of the $V_{oc}$×$FF$ product for EG is mainly ascribed to the better material quality of the nc-Si:H absorber layer deposited on EG. As shown in Figure 5.5b and c, the deposition on EG results in a dense nc-Si:H layer free from defective filaments, while on MST featuring nano-textures the defective filaments are observed in the nc-Si:H layer. The $J_{sc}$ of the top cell is higher on EG than that on MST because of self nano-texturing of the as-deposited AZO layer on EG which can improve the light trapping in the a-Si:H top cell. The as-deposited AZO film has small pyramid-like textures (as shown in the zoom-in image in Figure 5.5b) and a small RMS roughness of ~17 nm (growth on flat glass), which is possibly due to that our ZnO:Al target is oxygen-deficient [32]. However, such small textures of the as-deposited AZO disappear after etching in HCl solution.

The $V_{oc}$×$FF$ product (1464×0.759 mV) before light-soaking is one of the highest reported values for high-efficiency micromorph solar cells. This indicates the high potential of EG for high efficiency multijunction thin-film silicon solar cells. The limiting factor for EG is light scattering mainly into low angles with respect to the nano-textures, which makes it less efficient for light trapping. In the future, higher aspect ratio micro-textures (here the aspect ratio of EG is only 0.15-0.20) can be developed and thus significantly improve the light trapping in nc-Si:H bottom cells [10]. Due to the large size and U-shape of EG, the higher aspect ratio would not degrade the electrical performance of solar cells. Combining the small nano-textures which are suitable for light trapping in the a-Si:H top cell on EG, $J_{sc}$ of the top cell can also increase which enables a thinner top a-Si:H cell and thus higher stabilized efficiency. The small nano-textures will be flattened again after the deposition of a-Si:H top cell, and thus will not affect the growth of the nc-Si:H bottom cell [5].
5.3 Results and discussion

Figure 5.5. (a) $J-V$ curves of a-Si:H/nc-Si:H tandem solar cells deposited on EG and MST. Reported $J_{sc}$ values of the top and bottom cells refer to the EQE measurements. Cross-sectional SEM images of tandem solar cells deposited on (b) EG and (c) MST. The arrows indicate the defective filaments.
5.4 Conclusion

To summarize, micro-textures can result in higher $V_{oc}$ and $FF$ than nano-textures in nc-Si:H solar cells. High $V_{oc}$ and $FF$ are maintained for thick devices. The $V_{oc}$ only drops from 564 to 541 mV as i-layer thickness increases from 1 to 5 μm. The better electrical performance of nc-Si:H solar cells grown on micro-textures can be attributed to the improved material quality. The micro-textures with smooth U-shaped craters and large opening angels are advantageous for the growth of dense nc-Si:H layers free from the defective filaments. Finally a-Si:H/nc-Si:H tandem solar cells deposited on micro-textured substrates exhibit an initial efficiency of 13.3%, $V_{oc}$=1.464V, and $FF=0.759$, indicating the high potential of micro-textures for high-efficiency multijunction thin-film silicon solar cells.

References

Chapter 6

Wide bandgap p-type nanocrystalline silicon oxide as window layer for high Voc a-Si:H solar cells

This chapter is based on the following publication:


Preface:

High efficiency thin-film silicon multijunction solar cells require both high open-circuit voltage ($V_{oc}$) and high blue spectral response in the top amorphous silicon (a-Si:H) cell. In this chapter we investigate the mixed-phase p-type nanocrystalline silicon oxide (p-SiO$_x$) films and use this material as window layer in high $V_{oc}$ a-Si:H $p$-$i$-$n$ solar cells. The introduction of oxygen suppresses the nucleation of Si nanocrystallites. Therefore, p-SiO$_x$ film with low oxygen content should be used for the contact layer, to guarantee growth of highly conductive Si nanocrystallites in the initial few nanometers. With p-SiO$_x$ as p-layer, the optimal p-SiO$_x$ film has high oxygen content and thus high bandgap, resulting higher $V_{oc}$ and better spectral response than the standard p-type amorphous silicon carbide alloys (p-SiC) based window layer. Although the optimal p-SiO$_x$ film has very low planar conductivity (in the order of $10^{-12}$ Scm$^{-1}$), the filament-like Si nanocrystallites which grow perpendicular to the substrate enable the adequate transverse conduction for the solar cells. Consequently, a-Si:H solar cells with $V_{oc} > 1$ V and $FF > 70\%$ have been obtained. Finally, the p-SiO$_x$ window layers were successfully applied to thin-film silicon multijunction solar cells. A high initial efficiency of 14.4\% has been achieved in a-Si:H/nc-Si:H tandem solar cells on Asahi-VU substrate.
6.1 Introduction

Thin-film silicon (TF-Si) solar cells have received much attention due to the abundance of the raw materials and the potential for large-area lost-cost manufacturing. However, the efficiency should be further increased to be competitive with other thin-film PV technologies. Multijunction solar cells based on hydrogenated amorphous silicon (a-Si:H) and nanocrystalline silicon (nc-Si:H) can offer both high efficiency and good stability [1-7]. As top cell, the a-Si:H sub-cells with high $V_{oc}$ and high blue spectral response are highly desirable for high-efficiency devices. The p-type window layer and its interface with the intrinsic absorber layer play an important role to achieve high performance a-Si:H solar cells. There are several critical requirements for a promising p-doped material as window layer: (1) good ohmic contact with front TCO layer; (2) high bandgap to achieve high built-in voltage ($V_{bi}$) and thus high open-circuit voltage ($V_{oc}$); (3) good conductivity to obtain high fill factor (FF); and (4) low absorption loss over the short wavelengths range (300-600 nm). Especially for triple- or quadruple-junction solar cells, good transparency of the window layer are crucial to enable thinner a-Si:H absorber layers and thus higher stabilized efficiency.

The p-type protocrystalline silicon (p-pc-Si:H, also called microcrystalline silicon) deposited under very high hydrogen dilution is commonly used for high $V_{oc}$ n-i-p substrate-type a-Si:H solar cells [8, 9]. For superstrate-type a-Si:H solar cells, p-type amorphous silicon carbide (p-SiC) or p-SiC with embedded nanocrystalline silicon phase is traditionally used as the p-layer [1-3, 10, 11]. The optimized p-SiC films have higher optical bandgap (~2.0 eV) and lower absorption loss than p-pc-Si:H, resulting in higher $V_{oc}$ and better blue spectral response. It is interesting to note that $V_{oc}$ higher than 1 V can be achieved with oxygen- or carbon-free p-pc-Si:H in substrate-type a-Si:H solar cells [8, 12, 13]. A pure protocrystalline character is observed at the i/p interface, which results in low recombination at the i/p interface and high $V_{oc}$ [9]. However, similar high $V_{oc}$ has not yet been reported in p-i-n superstrate-type a-Si:H solar cells with p-pc-Si:H doped layers. This phenomenon indicates that both high bandgap in p-layer and low defects density at the p/i interface are crucial to achieve high $V_{oc}$ and thus high $V_{bi}$.

In this study, we aim at reaching p-i-n a-Si:H cells with high $V_{oc}$ and high blue spectral response by using p-type nanocrystalline silicon oxide (p-SiOx) as window layer. This material presents even higher bandgap and lower absorption loss than p-SiC, which makes p-SiOx an promising material for the window layer [14, 15]. Doped nanocrystalline silicon oxide is a key material for functional layers in TF-Si solar cells and modules because of its low absorption and low refractive index after incorporation of oxygen. It is a mixed phase material comprising oxygen-rich amorphous SiOx matrix with embedded nc-Si:H phase [16, 17]. The n-doped silicon oxide (n-SiOx) layers with a low refractive index are widely used as intermediate reflector and back reflector in multijunction solar cells [18-25]. The p-doped silicon oxide (p-SiOx) with relatively high crystalline fraction is also widely used as p-layer for nc-Si:H solar cells, leading to reduced optical loss and improved electrical performance compared to p-nc-Si:H [25-29]. However, the use of p-SiOx as window layer has been seldom investigated in a-Si:H solar cells [14, 15, 30-32]. Biron et al. studied the p-SiOx as window layer for high $V_{oc}$ n-i-p a-Si:H solar cells and increased the $V_{oc}$ up to 940 mV [14]. However, the increased $V_{oc}$ is commonly
accompanied with relatively low FF, which is also observed in other studies [14, 15, 30-32]. Therefore, developing p-type window layer with high transparency and good conductivity is crucial to simultaneously achieve high $V_{oc}$, high FF and high blue spectral response in a-Si:H solar cells. Here, we demonstrate that the p-SiO$_x$ window layer can result in high $V_{oc}$ a-Si:H solar cells with high FF, and excellent blue spectral response. The p-SiO$_x$ window layers were also successfully applied to high performance multijunction solar cells.

6.2 Experiments

To study the microstructure and opto-electrical properties, the p-SiO$_x$ films with a thickness of ~40 nm were deposited on the Corning Eagle XG glass using a RF-PECVD cluster tool at the frequency of 13.56 MHz. The typical deposition condition used for the p-SiO$_x$ films is presented in Table 6.1. Both planar conductivity ($\sigma$) and activation energy ($E_{act}$) were determined by the dark conductivity measurements after evaporating aluminum contacts on the layers. The refractive index and optical bandgap were determined from spectroscopic ellipsometry (SE). The optical band gap $E_0$ is determined at the absorption coefficient of $10^4$ cm$^{-1}$. The SE measurements were fitted with an effective-medium model with three materials: a-Si:H, SiO$_2$, and poly-Si. The combination of a-Si:H and SiO$_2$ resembles the a-SiO$_x$ matrix, and the poly-Si corresponds to the nanocrystalline Si phase in the film, similar to the fitting method used in Ref.17 but with minor modifications. Advantage of the method here is that we can indirectly obtain the oxygen content and crystallinity ($X_c$, volume fraction of the crystalline phase) besides the optical properties. The films were also measured by Raman spectroscopy with a 514 nm laser. The $X_c$ is defined by $X_c=(I_{520}+I_{510})/(I_{520}+I_{510}+0.8\times I_{480})$, where $I_i$ denotes the integrated area under Gaussian fitting peak centered at $i$ cm$^{-1}$. We have found that the $X_c$ determined from Raman measurements and the oxygen content deduced from X-ray photoelectron spectroscopy (XPS) are consistent with the results from SE measurements (Figure 6.3b). However, it is difficult to use Raman measurements to determine $X_c$ value when it is lower than 20%. The transmission electron microscopy (TEM) was used to study the microstructure and growth behavior of p-SiO$_x$ using a FEI-Tecnai F30 setup with incident electron energy of 200 kV. The energy-filtered plasmon imaging was acquired by a Tridiem Gatan energy filter with a slit width corresponding to 4 eV. Samples for TEM characterization have a thickness of around 100 nm.

### Table 6.1 Typical deposition condition used for the deposition of p-SiO$_x$ films.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
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</tr>
<tr>
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</tr>
<tr>
<td>Substrate temperature</td>
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<td>Pressure</td>
<td>2.2 mbar</td>
</tr>
<tr>
<td>RF power density</td>
<td>350 mW/cm$^2$</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>2 nm/min</td>
</tr>
</tbody>
</table>
Unless otherwise stated, the p-i-n solar cells were deposited on the nanotextured Asahi-VU (SnO$_2$:F) substrates. A thin layer of ZnO:Al (30 nm) was sputtered on the substrates before the deposition of the p-SiO$_x$ layers to protect the SnO$_2$:F under H-rich plasma. The single junction a-Si:H cells have a device structure shown in Figure 6.1. Note that the window layer consists of two layers, namely contact layer (the first p-SiO$_x$ layer) which makes good ohmic contact with front TCO (SnO$_2$:F/ZnO:Al here) and p-layer (the second p-SiO$_x$ layer) which enables high built-in voltage and good interface with the i-a-Si:H absorber layer. After the deposition of p-SiO$_x$ layers, H-plasma treatment for 2 minutes was applied before the deposition of i-a-Si:H. The i-a-Si:H layers were deposited using mixture gases of H$_2$ and SiH$_4$ at a pressure of 10 mbar and a power density of 100 mW/cm$^2$. The bandgap of a-Si:H can be tuned by changing the H$_2$/SiH$_4$ dilution ratio and deposition temperature [33-36]. For the nc-Si:H subcell in the tandem and triple-junction solar cells, the nc-Si:H layers were deposited at the high-pressure (4 mbar) and high-power (400 mW/cm$^2$) regime at 40.68 MHz. The deposition rate of the i-layer is ~40 nm/min, and neither profiling techniques nor buffer layers were used [25]. The area of single junction a-Si:H cells is 4×4 mm$^2$, and the area of the tandem and triple-junction cells is 1.05×1.05 cm$^2$, as defined by the back metal contacts. The silicon layers between metal contacts were removed by plasma dry etching to reduce lateral collection of current. The current-voltage (J-V) measurements of solar cells were performed in their initial state under an AM 1.5G solar simulator (100 mW/cm$^2$) at 25 °C. The short-circuit current density ($J_{sc}$) values were calculated from the external quantum efficiency (EQE) measurements by weighting with the AM 1.5G spectrum. The statistical analysis on solar cell performance was deduced from the J-V measurements over 30 dots for single junction solar cells or 6 dots for multijunction solar cells on one substrate (10×2.5 cm$^2$). The series resistance was extracted from the J-V curves near open circuit conditions. The scanning electron microscopy (SEM) cross-section images of solar cells were taken with a high resolution Hitachi S4800 setup using back scattering mode to resolve the fine cross-sectional structures of the devices.

**Figure 6.1** The schematic structure of a single junction a-Si:H solar cell with p-SiO$_x$ window layer. The window layer consists of two layers of p-SiO$_x$, namely contact layer and p-layer.
6.3 Results and discussion

6.3.1 Micro-structure and properties of p-SiO\textsubscript{x} materials

Figure 6.2 presents the electrical and optical properties of p-SiO\textsubscript{x} thin films with varying CO\textsubscript{2}/SiH\textsubscript{4} gas flux ratio from 0 to 3.75. The CO\textsubscript{2}/SiH\textsubscript{4}=0 indicates the p-type nc-Si:H. Films of p-SiO\textsubscript{x} with CO\textsubscript{2}/SiH\textsubscript{4} ratio higher than 3.75 are too resistive for solar cells and will not be shown and discussed here. For CO\textsubscript{2}/SiH\textsubscript{4} ratio increasing from 0 to 3.75, the planar dark conductivity drops by 13 orders of magnitude. Correspondingly, the activation energy (E\textsubscript{act}) increases from 33 meV to 769 meV. However, one should keep in mind that the transverse conduction (important for solar cells) can be much higher than the planar conduction as we will discuss later. With the increase of CO\textsubscript{2} flux, the optical bandgap (E\textsubscript{04}) also increases up to 2.48 eV, accompanying with the decrease of the refractive index (at wavelength of 600 nm) down to 2.11 for CO\textsubscript{2}/SiH\textsubscript{4}=3.75. As we can see in Figure 6.2b, when CO\textsubscript{2}/SiH\textsubscript{4} ratio is higher than 1.25, the optical bandgap of p-SiO\textsubscript{x} is higher than the standard p-SiC film, and consequently lower parasitic absorption loss can be expected in solar cells. The incorporation of oxygen in the material also affects the microstructure of the material as we can see in Figure 6.3. As the oxygen content increases, the nanocrystalline Si composition (X\textsubscript{c}) decreases as indicated by the Raman spectra in Figure 6.3a. The X\textsubscript{c} decreases from 55% for CO\textsubscript{2}/SiH\textsubscript{4}=0 to 15% for CO\textsubscript{2}/SiH\textsubscript{4}=3.75.
Figure 6.2 The lateral dark conductivity ($\sigma$), activation energy ($E_{act}$), refractive index at wavelength of 600 nm ($n_{@600nm}$), and optical bandgap ($E_{0.4}$) of p-SiO$_x$ layers as function of CO$_2$/SiH$_4$ ratio. The properties of standard p-SiC optimized for a-Si:H solar cells in our group is also shown in the figure.
6.3 Results and discussion

6.3.2 p-SiO$_x$ as contact layer for high $V_{oc}$ a-Si:H solar cells

It have been reported that an energy barrier for hole transport is generated between the front ZnO electrode and p-layer, which deteriorates the performance of a-Si:H solar cells [37, 38]. To solve this problem, a front contact layer with high conductivity to enable tunneling transport of holes is inserted between the front TCO and the p-layer. The p-doped nc-Si:H, nc-SiC:H and nc-SiO$_x$ layers have been demonstrated to be suitable for contact layer [37-40]. A wide bandgap of the contact layer is also favorable to reduce the optical absorption loss in the short wavelength region. With p-SiO$_x$ as p-layer, an advantage of using p-SiO$_x$ as contact layer is to reduce the parasitic absorption and to shorter the production time. Figure 6.4 shows the electrical performance of a-Si:H solar cells with the p-nc-Si:H (CO$_2$/SiH$_4=0$ in the figure) and p-SiO$_x$ contact layers. As we can

Figure 6.3 (a) The Raman spectra and (b) the crystallinity ($X_c$) and oxygen content (O at.%) of p-SiO$_x$ films deposited at different CO$_2$/SiH$_4$ ratio.
see, the $V_{oc}$ is not sensitive to the CO$_2$/SiH$_4$ ratio, and it remains around 940 mV for different contact layers. For CO$_2$/SiH$_4$ ratio higher than 2, the FF decreases considerably, due to the low conduction in the p-SiO$_x$ contact layer as indicated by the sharp increase of series resistance. By using p-SiO$_x$ instead of p-nc-Si:H as contact layer, we observe a slight improvement in EQE over wavelength range 300-450 nm as shown in **Figure 6.5**, which leads to 0.1 mA/cm$^2$ increase in current density. Overall, the best performance is achieved for the CO$_2$/SiH$_4$ ratio of 1.25, and the efficiency increases by 0.1% absolute compared to the oxygen-free p-nc-Si:H contact layer. Contact layer with a CO$_2$/SiH$_4$ ratio of 1.25 also results in the best uniformity over the whole deposition area, and thus it is used as the contact layer in the devices discussed in the remainder of this chapter.

**Figure 6.4** The photovoltaic performance of a-Si:H solar cells as a function of CO$_2$/SiH$_4$ ratio in the p-SiO$_x$ contact layers (~4 nm). The CO$_2$/SiH$_4$=0 indicates the p-nc-Si:H. Here the optical bandgap $E_{o4}$ of i-a-Si is 1.92 eV.
6.3 Results and discussion

Figure 6.5 EQE spectra of a-Si:H solar cells with different CO$_2$/SiH$_4$ ratio in the p-SiO$_x$ contact layers (~4 nm). The CO$_2$/SiH$_4=0$ indicates the p-type nc-Si:H.

6.3.3 p-SiO$_x$ as p-layer for high $V_{oc}$ a-Si:H solar cells

To study the performance of p-SiO$_x$ films as window layer in devices, the films were incorporated in $p-i-n$ a-Si:H solar cells with a high bandgap absorber layer. The optimized p-SiO$_x$ contact layer as discussed in Section 6.3.2 was used for all the devices here. Figure 6.6 shows the cell $V_{oc}$, $FF$, $J_{sc}$, efficiency, and series resistance as a function of the CO$_2$/SiH$_4$ ratio in the p-layers. The cell with p-nc-Si:H p-layer (CO$_2$/SiH$_4=0$ in the figure) is shown as well for comparison. As we can see from the figure, the $V_{oc}$ gradually increases with increasing CO$_2$ flux until CO$_2$/SiH$_4=3.5$, after which the $V_{oc}$ starts to drop again. The $V_{oc}$ is considerably enhanced with the introduction of oxygen in the p-layer. A relative gain of 18.2% is achieved from 839 mV for oxygen-free p-nc-Si:H to a maximum of 992 mV for the oxygen-rich p-SiO$_x$. As for the $J_{sc}$, it increases as we increase the CO$_2$/SiH$_4$ ratio and a maximum gain of 2.8 mA/cm$^2$ can be obtained. The corresponding $EQE$ curves in Figure 6.7 show that the gain in $J_{sc}$ is mainly in the short wavelength range between 300 and 550 nm. The improvement of the $EQE$ in this wavelength region with higher CO$_2$/SiH$_4$ ratio is attributed to the reduced parasitic absorption in the p-layer since the p-SiO$_x$ becomes more transparent with the increase of oxygen content. The $FF$ is also enhanced for p-SiO$_x$ compared to p-nc-Si:H. It maintains very high (~75%) for CO$_2$/SiH$_4$ ratio between 1.25 and 3, after which the $FF$ starts to decrease because of the higher series resistance.

The best efficiency in Figure 6.6 is obtained at CO$_2$/SiH$_4$ ratio of 3.0. The $V_{oc}$, $J_{sc}$, $FF$, and efficiency are significantly increased compared to the p-nc-Si:H. Noticeably, the $FF$ still remains higher than 74%, indicating the adequate transverse conduction of the p-SiO$_x$ even with high oxygen content in the material. Keeping the optimized CO$_2$/SiH$_4$ ratio, when we reduce the p-layer thickness by half (from 16 to 8 nm), the blue response further improves significantly, from 70% to 77% at the wavelength of 400 nm (Figure 6.8).
Meanwhile the $V_{oc}$ remains almost the same as presented in Table 6.2, and the $FF$ is still sufficiently high for multijunction solar cells. By replacing the absorptive n-a-Si:H layer at the rear side with highly transparent n-SiO$_x$ (20 nm), the $EQE$ in the long wavelength range (550-800 nm) improves significantly and highest efficiency of 10.2% is achieved, although a slight decrease in $V_{oc}$ and $FF$ is observed. Further optimization of the n-SiO$_x$ layer can still increase the cell performance. As for a-Si:H solar cells with a higher bandgap, $V_{oc}$ of 0.996 V and $FF$ of 72.3% can be obtained for cells deposited on Asahi-VU substrates. $V_{oc}$ as high as 1.006 V is reached for cells deposited on the micro-textured substrates [25] while the $FF$ is still higher than 70%.

![Figure 6.6](image-url)

**Figure 6.6** The photovoltaic performance of a-Si:H solar cells as a function of CO$_2$/SiH$_4$ ratio in the p-SiO$_x$ p-layers. Here the optical bandgap $E_{04}$ of i-a-Si is 1.96 eV.
6.3 Results and discussion

Figure 6.7 EQE spectra of a-Si:H solar cells with different CO\textsubscript{2}/SiH\textsubscript{4} ratio in the p-SiO\textsubscript{x} p-layers.

Figure 6.8 EQE spectra of a-Si:H solar cells with different p-layers. The CO\textsubscript{2}/SiH\textsubscript{4} for p-SiO\textsubscript{x} is 3.0 for all samples shown here.
Table 6.2 The photovoltaic performance of a-Si:H solar cells with p-SiO_x as p-layers.

<table>
<thead>
<tr>
<th>p-layer</th>
<th>CO_2/SiH_4</th>
<th>E_g (eV)</th>
<th>n-layer (20 nm)</th>
<th>V_oc (V)</th>
<th>J_sc (mA/cm^2)</th>
<th>FF (%)</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-SiO_x 16 nm</td>
<td>3.00</td>
<td>1.96</td>
<td>n-a-Si</td>
<td>0.977</td>
<td>12.9</td>
<td>74.9</td>
<td>9.4</td>
</tr>
<tr>
<td>p-SiO_x 8 nm</td>
<td>3.00</td>
<td>1.96</td>
<td>n-a-Si</td>
<td>0.973</td>
<td>13.3</td>
<td>71.5</td>
<td>9.3</td>
</tr>
<tr>
<td>p-SiO_x 16 nm</td>
<td>3.00</td>
<td>1.96</td>
<td>n-SiO_x</td>
<td>0.965</td>
<td>14.8</td>
<td>71.7</td>
<td>10.2</td>
</tr>
<tr>
<td>p-SiO_x 16 nm</td>
<td>3.00</td>
<td>1.99</td>
<td>n-a-Si</td>
<td>0.996</td>
<td>11.3</td>
<td>72.3</td>
<td>8.1</td>
</tr>
<tr>
<td>p-SiO_x 16 nm*</td>
<td>3.25</td>
<td>1.99</td>
<td>n-a-Si</td>
<td>1.006</td>
<td>10.8</td>
<td>70.4</td>
<td>7.7</td>
</tr>
</tbody>
</table>

*Micro-textured glass substrates coated with ZnO:Al front electrode was used for this cell, and lower J_sc is due to the less efficient light trapping performance of textured glass than Asahi-VU.

6.3.4 Growth character of p-SiO_x materials and the relationship with solar cell performance

Previous studies have shown that nc-SiO_x films deposited by PECVD are a mixed-phase material consisting of oxygen-rich a-SiO_x matrix and Si-rich nanocrystallites, in which the doped nanocrystalline phase dominates the electrical conduction in the material [16, 17]. The phase separation in the p-SiO_x film can be clearly seen from the energy filtered TEM (EFTEM) plasmon images in Figure 6.9. As shown in Figure 9a, the tiny Si nanocrystallites (bright spots) are surrounded by the a-SiO_x matrix (dark area). The filament-like agglomerates of nanocrystallites are observed from the cross-section image (Figure 6.9b). The filaments are perpendicular to the substrates. In the initial growth stage (first a few tens of nanometers) the filaments are preferentially parallel to each other, and then the filaments grow larger and interconnect with each other.

Figure 6.9 (a) Plane-view and (b) cross-section EFTEM Si plasmon images of the p-SiO_x film deposited at CO_2/SiH_4=2 (white = Si nanocrystallites, gray = a-SiO_x matrix).
The microstructure of p-SiO$_x$ films is closely related to the oxygen content in the materials. As can be observed from the cross-section HRTEM in Figure 6.10, the size of Si nanocrystallites become smaller and less nanocrystalline phase exists when more oxygen is incorporated in the films. The selected area electron diffraction pattern (SAED) images inserted in Figure 6.10 agree well with the change of crystallinity shown in Figure 6.3. The diffraction rings become weaker as more oxygen is incorporated in the material. For p-SiO$_x$ film with CO$_2$/SiH$_4$ ratio of 3.75, no obvious Si nanocrystallites are observed by HRTEM. Still the SE and Raman measurements indicate that there is a small amount of crystalline phase (~15%) in the film. This implies that the Si nanostructures in the film (CO$_2$/SiH$_4$=3.75) are mainly small Si nanoclusters and the diameter is smaller than 2 nm [16]. Therefore, the crystalline phase is too small to be identified by the HRTEM. But the SE and Raman measurements are still sensitive to those nanoclusters.

![Figure 6.10 Cross-section HRTEM images of p-SiO$_x$ films with CO$_2$/SiH$_4$ ratio of (a) 1.25, (b) 2.00, (c) 3.00, and (d) 3.75. The white lines indicate the interface between p-SiO$_x$ and glass substrate. The red shapes indicate the existence of Si nanocrystallites which can be clearly identified by the HRTEM. The inset images show the SAED patterns of the corresponding p-SiO$_x$ film. Those diffraction patterns indicate that the crystalline phase material is Si.](image-url)
Coming back to the relationship between growth character of p-SiO$_x$ and the performance in solar cells, for the very thin contact layer (3-4 nm) the nanocrystalline phase should start to grow in the first few nanometers to establish high conduction which is necessary for the tunneling transport of carriers. From the HRTEM images shown in Figure 6.10, we can see that the crystalline phase indeed starts to form even at the first few nanometers for p-SiO$_x$ films with CO$_2$/SiH$_4$ ratio of 1.25 and 2. However, for CO$_2$/SiH$_4$ of 2, fewer nanocrystallites grow in the first few nanometers. As the CO$_2$/SiH$_4$ ratio further increases, a pure amorphous incubation layer grows in the initial process. The initial growth character of p-SiO$_x$ explains why the solar cells have a low series resistance and high FF when CO$_2$/SiH$_4$ is lower than 2. For CO$_2$/SiH$_4$ higher than 2, the devices have high series resistance and the FF starts to drop quickly (see Figure 6.4).

As for p-SiO$_x$ based p-layer, it is interesting to note that the optimal p-SiO$_x$ (CO$_2$/SiH$_4$ between 3 and 3.25) films, which have a very low planar conductivity (in the order of $10^{-12}$ S cm$^{-1}$) still give rise to a high FF (>73%) in solar cells, while the conductivity should be at least on the order of $10^{-5}$ for a good device. This indicates that the transverse conductivity of p-SiO$_x$, especially for film with high oxygen content, can be many orders of magnitude higher than the planar conductivity. Such anisotropic conductivity in the film can be well explained by the growth of the filament-like Si nanostructures in the film perpendicular to the substrate as shown in Figure 6.9. Table 6.3 summarizes the properties of optimal p-SiO$_x$ used as p-layer in different studies. In this work, the high $V_{oc}$ can be achieved together with a high FF for p-SiO$_x$ with high oxygen content. In addition, the higher bandgap in this study implies that lower absorption loss can be expected. Noticeably, the crystallinity is much lower in this work, and the planar conductively is many orders of magnitude lower than the one used in other studies. However, the FF here is much higher. The large anisotropic conductivity, which might be due to that our p-SiO$_x$ has stronger phase separation and Si filaments are more perpendicularly grown to the substrate, can explain the high FF here. The phase separation between a-SiO$_x$ and nc-Si depends on the H$_2$/SiH$_4$ dilution ratio, and the higher dilution may lead to stronger phase separation and thus higher transverse conductivity [16].

Table 6.3 Summary of optimal p-SiO$_x$ based p-layers used in different studies. Note that the $\sigma_{dark}$ and $X_c$ values can be sensitive to the layer thickness as well.

<table>
<thead>
<tr>
<th>Ref</th>
<th>$E_{04}$ (eV)</th>
<th>$\sigma_{dark}$ (S cm$^{-1}$)</th>
<th>H$_2$/SiH$_4$ (-)</th>
<th>$X_c$ (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biron et. Al</td>
<td>2.28</td>
<td>$10^{-2}$</td>
<td>130</td>
<td>40</td>
<td>927</td>
<td>67.9</td>
</tr>
<tr>
<td>Sichanugrist et. al</td>
<td>2.18</td>
<td>$10^{-2}$</td>
<td>160-320</td>
<td>58</td>
<td>900</td>
<td>64.0</td>
</tr>
<tr>
<td>Sriprapha et. al</td>
<td>2.10</td>
<td>$10^{-2}$</td>
<td>70</td>
<td>50</td>
<td>900</td>
<td>65.0</td>
</tr>
<tr>
<td>this work</td>
<td>2.32</td>
<td>$10^{-12}$</td>
<td>210</td>
<td>&lt; 20</td>
<td>986</td>
<td>73.4</td>
</tr>
</tbody>
</table>
6.3.5 Performance improvement with p-SiO_x window layer in high V_{oc} a-Si:H solar cells

Table 6.4 shows the photovoltaic performance of a-Si:H solar cells with different p-layers. As can be seen, both p-SiC and p-SiO_x can improve the V_{oc} and FF compared to p-nc-Si:H as p-layer. Comparing the p-SiC and p-SiO_x shows that the V_{oc} and FF are similar if the bandgap is the same. For p-SiO_x with higher bandgap by incorporating more oxygen, the V_{oc} increases by up to 75 mV for p-SiO_x with bandgap of 2.46 eV, in comparison to p-SiC. However, the FF drops significantly for the maximal V_{oc} due to the poor electrical conduction of the p-SiO_x. For the optimal p-SiO_x with a bandgap of 2.30 eV, the V_{oc} increases by 57 mV, from 920 mV for p-SiC to 977 mV for p-SiO_x. Meanwhile the EQE also improves in short wavelength range due to the reduced absorption loss in the p-SiO_x, leading to the increase of J_{sc} by 1.1 mA/cm^2 compared to p-SiC. Overall, the efficiency increases to 9.4%, a relative improvement of 14.6% in comparison to the standard p-SiC p-layer.

The V_{oc} improvement with p-SiO_x as p-layer can be explained by the increase of the built-in voltage (V_b), which is associated with the work function of the p-layer and the conduction band offset (CBO) at the p/i interface [15, 41]. Since the majority of the p-layer is the p-doped a-SiO_x matrix, its work function and CBO with the i-layer determine the V_b. Possible reasons for the higher V_b could be a higher work function or higher CBO. As can be seen from Table 4, the increase of bandgap is comparable to the increase of activation energy, which implies that the work function should not change significantly. Results here indicate that the increase of V_b cannot be ascribed to the higher work function of p-SiO_x. Instead, the increase of bandgap in p-layer will increase the CBO at the p/i interface, regardless of the change of activation energy. Higher CBO can better repel the electrons away from the p-layer and thus reduce the recombination rate at the p/i interface, which can lead to higher V_b [15, 42]. However, further investigation is needed to precisely explain the V_{oc} improvement.

Table 6.4 The photovoltaic performance of a-Si:H solar cells with different p-layers. For cells with p-SiC as p-layer, a thin layer of intrinsic a-SiC:H (4 nm) buffer layer was used at the p/i interface to improve the V_{oc} and FF.

<table>
<thead>
<tr>
<th>p-layer</th>
<th>CO_2/SiH_4</th>
<th>E_0 (eV)</th>
<th>E_{act} (eV)</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA/cm^2)</th>
<th>FF (%)</th>
<th>Effi (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-nc-Si 16 nm</td>
<td>0</td>
<td>1.87</td>
<td>0.033</td>
<td>0.843</td>
<td>10.1</td>
<td>71.3</td>
<td>6.1</td>
</tr>
<tr>
<td>p-SiC/i-SiC 10/4 nm</td>
<td>-</td>
<td>2.00</td>
<td>0.300</td>
<td>0.920</td>
<td>11.8</td>
<td>75.1</td>
<td>8.2</td>
</tr>
<tr>
<td>p-SiO_x 16 nm</td>
<td>1.25</td>
<td>2.00</td>
<td>0.259</td>
<td>0.917</td>
<td>11.7</td>
<td>75.2</td>
<td>8.1</td>
</tr>
<tr>
<td>p-SiO_x 16 nm</td>
<td>3.00</td>
<td>2.30</td>
<td>0.724</td>
<td>0.977</td>
<td>12.9</td>
<td>74.9</td>
<td>9.4</td>
</tr>
<tr>
<td>p-SiO_x 16 nm</td>
<td>3.50</td>
<td>2.46</td>
<td>0.754</td>
<td>0.995</td>
<td>12.9</td>
<td>68.5</td>
<td>8.8</td>
</tr>
</tbody>
</table>
In many studies, a buffer layer between the p/i interface was used to improve the solar cell performance [42-44]. Here no buffer layer was used in the devices with p-SiO_x window layer. We indeed tried the use of intrinsic a-SiC:H and i-SiO_x as buffer layer (results not shown here), however, improvement in either \( V_{oc} \) or \( FF \) was not observed. We believe that further optimization of the p-SiO_x is still possible since highest efficiency is not obtained at the point with highest \( V_{oc} \) due to the limitation of film’s transverse conductivity. If we can develop a window layer with higher bandgap but adequate transverse conductivity, higher \( V_{oc} \) together with high \( FF \) can be expected in the future. For example, finely tuning of the doping ratio and using higher H_2/SiH_4 dilution can induce stronger phase separation in the films and thus higher transverse conductivity can be expected.

6.3.6. Applications of the p-SiO_x window layer in multijunction solar cells

The a-Si:H cells (\( V_{oc} \sim 0.95 \text{ V} \)) with p-SiO_x window layer were firstly applied to the a-Si:H/nc-Si:H tandem solar cells. The device structure is shown in Figure 6.11a. The comparison of different p-layers for the top cell is shown in Figure 6.11b and Table 6.5. Compared to the p-SiC window layer, p-SiO_x layer can significantly improve the \( EQE \) in the wavelength range (300-550 nm) due to the lower absorption loss, leading to the increase of \( J_{sc} \) in the top cell by 0.5 mA/cm^2. Meanwhile, the \( V_{oc} \) increases by 27 mV, resulting in an efficiency improvement from 12.9% for p-SiC to 13.6% for p-SiO_x as p-layer. In comparison to the device without top p-layer, the optical loss by p-SiO_x is 0.5 mA/cm^2. With further optimization of the thickness, lower optical loss can be realized with thinner p-SiO_x as indicated in Figure 6.8.

Although some work showed that the p-SiO_x window layer can reduce the reflection of incident light due to the lower refractive index [27, 28], we cannot observe an obvious reduction in primary reflection with p-SiO_x window layer as shown in Figure 6.11b, mainly because the rough front TCO/a-Si:H interface acts as an effective anti-reflective layer already. Only minor reduction in reflection is observed in the wavelengths range 300-400 nm. After further optimization of the device, a high initial efficiency of 14.4% has been achieved and the corresponding \( J-V \) and \( EQE \) curves of the device are shown in Figure 6.12. A commercially available anti-reflection (AR) film (InnoX Co., Ltd.) with a moth-eye structure comprising a UV-curable polymer, a polyethylene telephthalate (PET) substrate, and an acrylic adhesive film was applied at the front glass surface to minimize the reflection loss [45]. The detail of the moth-eye structure can be found in Ref. 46. The combination of highly transparent p-SiO_x window layer with an AR foil results in high blue spectral response and extremely low surface reflection (~3%) for TF-Si solar cells.
6.3 Results and discussion

Figure 6.11 (a) Cross-section SEM image of a-Si:H/nc-Si:H tandem solar cell. The p- and n-layers (some are too thin to be distinguished in the image) are indicated by the yellow and green lines, respectively. The n-SiOx n-layer (60 nm) for the top cell also functions as intermediate reflector. (b) EQE curves of tandem solar cells with different p-layers for the top a-Si:H cell. The p-SiC layer is 7 nm thick, and the p-SiOx layer is 16 nm thick. The thicknesses of i-layers in the top and bottom cells are 300 nm and 3 μm, respectively. 4-nm-thick p-SiOx contact layer was used for the three devices.

Table 6.5 The photovoltaic performance of a-Si:H/nc-Si:H tandem solar cells with different p-layers for the top cell. The parentheses indicate the average value.

<table>
<thead>
<tr>
<th>p-layer</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$J_{EQE}$ top/bottom</th>
<th>FF (%)</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no p-layer</td>
<td>1.117 (1.112)</td>
<td>13.3</td>
<td>13.3/13.3</td>
<td>66.2 (65.7)</td>
<td>9.8</td>
</tr>
<tr>
<td>p-SiC</td>
<td>1.409 (1.407)</td>
<td>12.3</td>
<td>12.3/13.3</td>
<td>74.4 (73.9)</td>
<td>12.9</td>
</tr>
<tr>
<td>p-SiOx</td>
<td>1.436 (1.433)</td>
<td>12.8</td>
<td>12.8/13.3</td>
<td>73.8 (73.2)</td>
<td>13.6</td>
</tr>
</tbody>
</table>
Figure 6.12 (a) The $J-V$ curve and (b) $EQE, 1-R$ spectra of the optimized a-Si:H/nc-Si:H tandem solar cell with p-SiO$_x$ window layer for the top a-Si:H cell. An moth-eye nanostructured anti-reflective foil was attached directly on the glass to reduce the air/glass surface reflection.

Finally, the high $V_{oc}$ a-Si:H cell ($V_{oc}$ ~0.98 V) with p-SiO$_x$ window layer was used as top cell in an a-Si:H/nc-Si:H/nc-Si:H triple-junction solar cell. The solar cell was deposited on micro-textured glass substrate coated with a thin layer of ITO (~120 nm). The initial $J-V$ curve is shown in Figure 6.13. A high $V_{oc}$ of 1.984 V and high $FF$ of 76.6% are achieved. The $J_{sc}$ value is limited by the light trapping performance of the substrate used here [25]. If substrates with better light trapping capability are used, an even higher efficiency can be expected in the future.
Figure 6.13 The $J$-$V$ curve of an a-Si:H/nc-Si:H/nc-Si:H triple-junction solar cell with p-SiO$_x$ window layer for the top a-Si:H cell.

6.4 Conclusions

Mixed-phase p-SiO$_x$ films with varied oxygen content have been investigated and applied to the window layer in high $V_{oc}$ a-Si:H solar cells. The microstructure, optical and electrical properties are closely related to the oxygen content, which can be tuned through the CO$_2$/SiH$_4$ gas flux ratio. With higher oxygen content incorporated in the films, the bandgap and activation energy increase whereas the conductivity, refractive index and crystallinity decrease. The PECVD deposited p-SiO$_x$ films have strong phase separation and perpendicular growth character as revealed by the TEM measurements. The introduction of oxygen in the film suppresses the nucleation of Si nanocrystallites in the initial growth and thus for p-SiO$_x$ contact layer lower CO$_2$/SiH$_4$ ratio is used than p-layer. Both high $V_{oc}$ and $FF$ are achieved for p-SiO$_x$ p-layer with high oxygen content in a-Si:H solar cells. The perpendicular filament-like Si nanocrystalline phase enables the adequate transverse conductivity despite of the very low planar conductivity. Compared to the standard p-SiC layer, p-SiO$_x$ improves both the $V_{oc}$ and $J_{sc}$ due to the higher bandgap and lower parasitic absorption loss in the p-layer. Finally, p-SiO$_x$ window layer was successfully applied to high performance multijunction TF-Si solar cells, leading to higher $V_{oc}$ and better blue spectral response than conventional p-SiC based window layer. With p-SiO$_x$ window layer, a high initial efficiency of 14.4% has been achieved in a-Si:H/nc-Si:H tandem solar cells with an active area of 1.1 cm$^2$.

References

Chapter 6 Wide-bandgap p-type silicon oxide for a-Si:H solar cells


Chapter 7

Highly transparent modulated-surface-textured front electrodes for multijunction thin-film silicon solar cells

This chapter is based on following publication:


Preface:

To further increase the efficiency of multijunction thin-film silicon (TF-Si) solar cells, it is crucial for the front electrode to have a good transparency and conduction, to provide efficient light trapping for each subcell, and to ensure a suitable morphology for the growth of high-quality silicon layers. In this chapter, we present the implementation of highly transparent modulated-surface-textured (MST) front electrodes as light-trapping structures in multijunction TF-Si solar cells. The MST substrates comprise a micro-textured glass, a thin layer of hydrogenated indium oxide (IOH), and a sub-micron nano-textured ZnO layer grown by low-pressure chemical vapor deposition (LPCVD ZnO). The bilayer IOH/LPCVD ZnO stack guarantees efficient light in-coupling and light trapping for the top amorphous silicon (a-Si:H) solar cell while minimizing the parasitic absorption losses. The crater-shaped micro-textured glass provides both efficient light trapping in the red and infrared wavelength range and a suitable morphology for the growth of high-quality nanocrystalline silicon (nc-Si:H) layers. Thanks to the efficient light trapping for the individual subcells and suitable morphology for the growth of high-quality silicon layers, multijunction solar cells deposited on MST substrates have a higher efficiency than those on single-textured state-of-the-art LPCVD ZnO substrates. Efficiencies of 14.8% (initial) and 12.5% (stabilized) have been achieved for a-Si:H/nc-Si:H tandem solar cells with the MST front electrode, surpassing efficiencies obtained on state-of-the-art LPCVD ZnO, thereby highlighting the high potential of MST front electrodes for high-efficiency multijunction solar cells.
7.1 Introduction

To obtain high efficiencies, a multijunction device configuration is commonly applied in thin-film silicon (TF-Si) solar cells, with tandem or triple-junction structures based on hydrogenated amorphous silicon (a-Si:H) and nanocrystalline silicon (nc-Si:H) as absorber layers [1-3]. Certified stabilized efficiencies of 12.7% and 13.4% have been achieved in small area (~1 cm$^2$) a-Si:H/nc-Si:H tandem and a-Si:H/nc-Si:H/nc-Si:H triple-junction solar cells, respectively [3-5]. A certified module efficiency of 12.3% has also been achieved recently for Gen-5 size (1.1×1.4 m$^2$) a-Si:H/nc-Si:H modules [6], indicating the high potential of the TF-Si technology for large-scale and cost-effective renewable electricity generation. However, the efficiency should be further increased to be competitive with other thin-film PV technologies. There are still several issues to be tackled for further efficiency improvement: (1) enhanced stability of a-Si:H under illumination, (2) highly efficient light management for multijunction solar cells, (3) growth of high-quality nc-Si:H materials on light-trapping substrates, especially under a high deposition rate, and (4) reduction of parasitic absorption losses in the supporting layers (transparent front electrodes, doped layers, and back reflector).

In the past decades, enormous efforts have been carried out to tackle those issues. The stability of a-Si:H can be enhanced by the triode technique, optimized deposition conditions, and thinner absorber layer with the help of efficient light in-coupling and light trapping [4,7]. Parasitic absorption losses can be reduced by using highly transparent conductive oxides (TCOs) [8-10], more transparent doped silicon oxide layers [11-14], and low-loss back reflectors. However, it is still challenging to design a light-trapping substrate for multijunction solar cells which can simultaneously provide efficient light trapping and a suitable morphology for the growth of high-quality absorber layers for each subcell. Consider a-Si:H/nc-Si:H tandem solar cells as an example. On the one hand, sharp nano-textures are necessary for the top a-Si:H junction to achieve excellent light trapping and light in-coupling and thus to enable thinner absorber layers. On the other hand, large and smooth textures promote the growth of dense and high-quality nc-Si:H layers in the bottom junction [15-18]. In the superstrate (p-i-n) configuration, single-scale nano-textured TCOs with sub-micron morphology features are commonly used as front electrodes in state-of-the-art devices to ensure efficient light trapping in individual junctions [3,4,18]. However, the relatively sharp nano-textures deteriorate the electrical performance of nc-Si:H and even a-Si:H solar cells by reducing the open-circuit voltage ($V_{oc}$) and fill factor (FF) [18,20-22]. Especially, the performance of nc-Si:H cells is more sensitive to the substrate morphology with increasing deposition rate, while high deposition rate is required for industrial manufacturing [23,24]. Currently, the trade-offs on one hand between strong light trapping and growth of high-quality silicon layers and on the other hand between transparency and conductivity of front electrodes severely constrains the efficiency improvement of multijunction TF-Si solar cells.

Here, we propose a modulated-surface-textured (MST) front electrode as light trapping structures, aiming for both superior light-trapping performance and high electrical performance in superstrate-type p-i-n multijunction TF-Si solar cells. The modulated-surface-textured (also called “multi-scale textured” or “double textured”)
substrates were proposed to improve light scattering over a broad wavelength range [25-27]. Previous studies have shown a great potential for modulated surface textures to achieve a better light-trapping performance than single-scale textures in multijunction solar cells [28-30]. To obtain high-performance MST substrates, the larger scale background textures should provide efficient light trapping and promote the growth of high-quality nc-Si:H absorber layers. Recently, crater-shaped micro-textures with morphology features in the order of a few micrometers have been demonstrated to effectively mitigate the trade-off between light trapping and electrical performance of nc-Si:H solar cells [16,18]. The well-designed micro-textures from either wet-etched glass or honeycomb textured substrates can provide both efficient light trapping and high electrical performance even for thick nc-Si:H solar cells. Tan et al. have shown that micro-textures result in a much lower decrease in $V_{oc} \times FF$ product than commonly used nano-textures, as the absorber layer thickness increases [18]. Very recently, the highest certified efficiency of 11.8% for nc-Si:H solar cells has been achieved with substrate-type $n-i-p$ configuration by Sai et al., using a micro-textured honeycomb substrate at a high deposition rate of 1 nm/s for the absorber layer [23].

In this contribution, we will present the details on the design and fabrication of highly transparent MST front electrodes based on micro-textured glass. The dedicatedly designed front electrodes can provide efficient light trapping in individual subcells, have a suitable morphology for the growth of high-quality silicon materials, and exhibit a high transparency and conductivity. The performance of MST substrates will be compared to state-of-the-art single textured LPCVD ZnO substrates.

### 7.2 Experiments

#### 7.2.1 Fabrication of highly transparent modulated-surface-textured front electrodes

The fabrication of highly transparent MST front electrodes is schematically shown in Figure 7.1a. Firstly, a thin layer of In$_2$O$_3$:Sn (ITO, 100-300 nm thick) was sputtered on clean Corning glass (Eagle XG). The crater-shaped micro-textures on glass were generated by wet-etching in an aqueous solution of HF (49wt%) and H$_2$O$_2$ (31wt%), with a volume ratio of H$_2$O:HF:H$_2$O$_2$=10:1:2. The ITO layer on glass acts as catalyst for glass etching. The etching process was stopped when the ITO layer peeled off from the glass, and the wet-etched glass (EG) was thoroughly cleaned in DI water. Then, a thin layer of highly transparent and conductive hydrogenated indium oxide (IOH, ~140 nm) was deposited on EG by sputtering [31,32]. Subsequently, a layer of non-intentionally doped ZnO (i-ZnO, 0.5-2.3 µm) was deposited on top of the IOH in an in-house developed low-pressure chemical vapor deposition (LPCVD) system. The superposition of nano-textured LPCVD ZnO on micro-textured glass forms modulated surface textures on the front electrode. The resulting layer stack had a sheet resistance lower than 30Ω/sq. To improve the electrical performance of a-Si:H solar cells, an Ar-plasma treatment of the front electrodes was applied before the deposition of solar cells. Regarding sample names, non-intentionally doped ZnO layers with a thickness $d$ (in µm) are denoted as iZ$d$ and B-doped ZnO layers are referred to as Z$d$. The plasma treatment duration $t$ (in min) is
Chapter 7 Highly transparent MST for multijunction solar cells

denoted as $t'$. For example, MST-iZ1 4' refers to an MST substrate with 1-µm-thick non-intentionally doped ZnO subjected to a plasma treatment of 4 min.

Figure 7.1 (a) Schematic illustration of the fabrication of MST front electrodes. The superposition of nano-textured LPCVD ZnO on IOH coated micro-textured glass (EG/IOH) forms the MST front electrodes. (b) SEM images of EG/IOH and MST substrate with 1-µm-thick LPCVD ZnO. (c) Schematic device structure of an a-Si:H/nc-Si:H tandem solar cell deposited on the MST front electrode.

7.2.2 Fabrication and characterization of thin-film silicon solar cells

The superstrate-type $p-i-n$ a-Si:H, nc-Si:H and multijunction solar cells were deposited using a multi-chamber plasma-enhanced chemical vapor deposition (PECVD) system. Unless otherwise stated, the solar cells were deposited at Delft at a frequency of 13.56 MHz (except for the nc-Si:H absorber layers). The single junction a-Si:H solar cells have a device structure of $p$-SiO$_x$:H (16nm)/$i$-a-Si:H/$n$-a-Si:H (20nm)/Ag-Cr-Al. A $p$-type silicon oxide ($p$-SiO$_x$:H) window layer was used to obtain higher $V_{oc}$ and better spectral response in the short wavelength range [14]. The a-Si:H absorber layers were deposited at a high pressure of 10 mbar, and the bandgap of the layers can be flexibly tuned by varying substrate temperature and H$_2$/SiH$_4$ dilution ratio [14, 33]. The nc-Si:H solar cells show the following device structure: $p$-SiO$_x$:H (20nm)/$i$-SiO$_x$:H (4nm)/$i$-nc-Si:H/$n$-SiO$_x$:H (50nm)/Ag-Cr-Al. The intrinsic nc-Si:H layers were deposited at a high-pressure and high-power regime with a generator frequency of 40.68 MHz. The deposition rate of the $i$-nc-Si:H is ~7 Å/s, and no profiling technique was used. The experimental details can be found in Ref. [14,18]. The a-Si:H/nc-Si:H tandem solar cells have a device structure as shown in Figure 1c. The active area of cells is 4×4 mm$^2$ or 1.05×1.05 cm$^2$ as defined by the metal back contacts. The silicon layers between the metal contacts were removed by plasma etching to reduce lateral current collection. The a-Si:H/nc-Si:H/nc-Si:H triple-
7.3 Results and discussion

7.3.1 Optimization of micro-textured glass for nc-Si:H solar cells

The feature size and shape of micro-textured glass have a great impact on the light-trapping performance and material quality of silicon absorber layers. By tuning the thickness of sacrificial ITO layer, the feature size of the craters on glass obtained from wet-etching can be varied from a few hundred nanometers up to a few tens of micrometers. The thicker the ITO layer is, the larger the crater size will be. Figure 7.2 shows the different types of substrates with increasing feature size for nc-Si:H solar cells. The atomic force microscope (AFM) images of Z5 45’ and wet-etched sputtered ZnO:Al (E-AZO) are given in Figure 7.2a-b, respectively. Figure 2c-f shows the AFM images of the micro-textured glass substrates with increasing feature sizes. The substrates are referred to as samples A, B, C, D, E and F, respectively. Their corresponding morphological parameters are summarized in Table 7.1. Prior to the silicon deposition,
the micro-textured glass substrates were coated with an 800-nm-thick AZO layer as front electrode by RF magnetron sputtering from a ZnO target with 2.0 wt% Al₂O₃. Single-junction nc-Si:H solar cells with an i-layer thickness of 3 µm were fabricated on those substrates. The characteristics of the solar cells are summarized in Table 7.1, and the corresponding EQE curves are presented in Figure 7.3.

Figure 7.2 AFM images of (a) LPCVD ZnO Z5 45’, (b) wet-etched sputtered AZO deposited on flat glass, (c-f) micro-textured glass with different feature sizes.
Table 7.1 Root-mean-square roughness \((R_{\text{rms}})\), correlation length \((L_c)\), aspect ratio \((R_{\text{rms}}/L_c)\) of different substrates shown in Figure 2. The photovoltaic performance of nc-Si:H cells deposited on those substrates is summarized correspondingly.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>(R_{\text{rms}}) (nm)</th>
<th>(L_c) ((\mu)m)</th>
<th>(R_{\text{rms}}/L_c)</th>
<th>(V_{oc}) (V)</th>
<th>(J_{sc}) (mA/cm(^2))</th>
<th>(FF) (%)</th>
<th>Effi (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z5 45'</td>
<td>A 126</td>
<td>0.45</td>
<td>0.28</td>
<td>0.526</td>
<td>27.7</td>
<td>51.1</td>
<td>7.4</td>
</tr>
<tr>
<td>E-AZO</td>
<td>B 178</td>
<td>1.09</td>
<td>0.16</td>
<td>0.538</td>
<td>25.8</td>
<td>68.2</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>C 370</td>
<td>2.72</td>
<td>0.14</td>
<td>0.552</td>
<td>25.6</td>
<td>72.6</td>
<td>10.2</td>
</tr>
<tr>
<td>EG</td>
<td>D 546</td>
<td>3.59</td>
<td>0.15</td>
<td>0.545</td>
<td>24.4</td>
<td>70.7</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>E 721</td>
<td>4.35</td>
<td>0.16</td>
<td>0.542</td>
<td>23.9</td>
<td>70.5</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>F 1101</td>
<td>7.49</td>
<td>0.15</td>
<td>0.546</td>
<td>24.0</td>
<td>72.6</td>
<td>9.5</td>
</tr>
</tbody>
</table>

As can be seen from Table 7.1, the nano-textured Z5 45’ with a high aspect ratio and smallest feature size (sample A) results in lowest \(V_{oc}\) and \(FF\) values. For E-AZO substrates (sample B), the surface morphology is smoother and the feature size is larger than Z5 45’. As a result, the \(V_{oc}\) and \(FF\) values are greatly improved compared to Z5 45’. As for EG substrates (samples C-F), the U-type craters have larger radii of curvature and they are larger than those of E-AZO. Consequently, the \(V_{oc}\) and \(FF\) of cells on EG are all higher than the cells on E-AZO. It is interesting to note that the best \(V_{oc}\), \(FF\), and efficiency values are obtained here when the correlation length is comparable to the thickness of the cell. A similar trend was also observed in \(n-i-p\) substrate-type solar cells deposited on the Ag-coated textured glass substrates (results not shown here). It was reported that porous and defective filaments are formed in nc-Si:H layers deposited on nano-textured substrates, especially on sharp valleys (as for Z5 45’ and E-AZO) [17,21]. The defective filaments increase the bulk recombination of charge carriers and act as shunt paths, which deteriorates the \(V_{oc}\) and \(FF\) of solar cells [20]. For EG substrates with crater-shaped micro-textures, the nc-Si:H absorber layers are grown densely without any defective filaments as shown in chapter 5 and our previous work [18]. Therefore, thick nc-Si:H solar cells still have high \(V_{oc}\) and \(FF\) values.

As shown in Figure 7.3a, the spectral response in the wavelength range between 600 and 1100 nm increases with decreasing feature size. For correlation lengths of EG much larger than the absorber layer thickness \((L_c > 4 \, \mu\text{m})\), the \(J_{sc}\) values do not differ too much (samples E and F). For correlation lengths of EG comparable to the absorber layer thickness (sample C), the \(J_{sc}\) value is comparable to the one provided by the nano-textured E-AZO (sample B). Sample A results in the highest \(J_{sc}\) value due to the better transparency of the front electrode and the better light scattering provided by the sharp surface morphology. However, the sharp surface morphology gives rise to much lower
FF in thick nc-Si:H solar cells. Coincidentally, among all the EG substrates sample C results in both optimal light-trapping performance and best electrical performance. Therefore, in the following sections sample C will be used unless stated otherwise. Efficiencies of 10.2% and 10.5% can be obtained on sample C without and with a moth-eye structured ARC on the front glass side, respectively. Here we keep the aspect ratio of samples B-F almost identical (~0.15) for a fair comparison of solar cells deposited on those substrates. The aspect ratio here was chosen to have both efficient light trapping and good electrical performance in solar cells. As revealed by previous studies, the optimal correlation length is correlated with the cell thickness and aspect ratio [16, 33-36]. Thus a careful optimization of correlation length (or pitch for periodic structures) and aspect ratio is necessary to obtain the best efficiency for a given cell thickness.

![EQE curves of nc-Si:H solar cells](image)

**Figure 7.3** EQE curves of nc-Si:H solar cells deposited on (a) substrates A-E corresponding to Table 1 and (b) etched glass D coated with either AZO (~800 nm) or IOH (~300 nm) as a front electrode.
7.3.2 Choice of transparent conductive oxides for front electrodes

To form modulated surface textures on EG, we can use either wet-etched sputtered AZO or as-grown textured LPCVD ZnO. The sharply pyramidal-like LPCVD ZnO is superior to wet-etched AZO in terms of both light trapping and transparency. Thanks to the high degree of flexibility provided by the LPCVD method, LPCVD ZnO layers with the desired surface texture can be obtained by tuning the layer thickness and the deposition parameters and by subsequently adapting the plasma treatment duration. Thus, here, we only discuss the use of LPCVD ZnO for the fabrication of MST substrates. Figure 7.4 shows the absorptance of commonly used TCO materials for TF-Si solar cells. The absorptance of the AZO film is the highest in the red and infrared part of the spectrum because of the strong free carrier absorption (FCA). The FCA of the lightly doped Z2.3 is significantly lower than AZO due to its much lower free carrier concentration. With no intentional doping during the growth of ZnO, as it is the case for iZ1, the FCA is even lower in the wavelength range relevant for TF-Si solar cells (up to 1100 nm). As its sheet resistance $R_\sigma$ exceeds 100$\Omega$/sq, iZ1 has to be combined with an additional layer of IOH with a high conductivity and low FCA to be used as a front electrode. The IOH layer has an absorptance as low as iZ1 due to its high mobility and low electron concentration. Therefore, the combination of a thin layer of IOH and non-intentionally doped LPCVD ZnO guarantees both high conduction and low absorption losses. As can be seen in Figure 7.3b, the replacement of AZO with IOH in the front electrode can significantly boost the spectral response at the long wavelengths and thus the $J_{sc}$ of nc-Si:H solar cells, resulting in a higher efficiency ($\eta=10.2\%$, $V_{oc}=0.542$ V, and $FF=69.9\%$). The cell has a slightly lower FF, mainly due to the higher sheet resistance of IOH. However, the thin layer of IOH as front electrode is conductive enough for multijunction devices.

Figure 7.4 Absorptance of different transparent conductive oxide layers. The absorption of Z2.3, iZ1 and IOH (140 nm) was measured by photothermal deflection spectroscopy, and the absorption of AZO (~900 nm) was measured by R/T of the layer with a spectrophotometer ($A=1-R-T$). All the layers were deposited directly on flat glass.
7.3.3 Growth of high-performance a-Si:H solar cells on modulated-surface-textured front electrodes

To achieve high-efficiency tandem solar cells, it is crucial to firstly obtain high performance a-Si:H solar cells on the MST substrates. Table 7.2 summarizes the performance of a-Si:H solar cells deposited on MST substrates with different ZnO thicknesses and various plasma treatment times. The purpose of Ar-treatment is to smoothen sharp features. For MST samples without Ar plasma treatment, the $V_{oc}$ and $FF$ drop quickly as the thickness of the ZnO layers increases from 0.5 to 2.3 µm. Even for the thin ZnO layer (0.5-µm-thick), the $FF$ of the cell on MST-iZ0.5 is already lower than the sample deposited on flat glass FG-iZ1. However, the $V_{oc}$ and $FF$ improve considerably by subjecting the MST substrate coated with iZ1 to a 4 minute plasma treatment (sample MST-iZ1 4'). The cells on MST-iZ1 4' and FG-iZ1 then have comparable electrical performance and light trapping. In contrast, if the ZnO is thick (i.e. 2.3 µm), the $FF$ values cannot be recovered even after a long plasma treatment of 15 min. Longer plasma treatment might be able to provide higher $FF$. However, the $J_{sc}$ will drop due to less efficient light in-coupling and light trapping. Overall, the highest efficiency is obtained for cells on MST-iZ1 4', which will therefore be used for the tandem devices in the following sections.

Table 7.2 Photovoltaic performance of a-Si:H solar cells deposited on FG-iZ1 and MST substrates with varying thickness and Ar plasma treatment time of the ZnO layers. The device structure is $p$-SiO$_x$:H 16nm/i-a-Si:H 220nm/n-a-Si:H 20nm/Ag-Cr-Al. A thin layer of IOH (140 nm) was deposited on the glass before the ZnO layer. FG is short for flat glass substrate. t': Ar plasma treatment duration.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>ZnO</th>
<th>$t'$ (min)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$FF$ (%)</th>
<th>Effi (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FG</td>
<td>iZ1</td>
<td>0</td>
<td>0.936</td>
<td>12.9</td>
<td>73.6</td>
<td>8.9</td>
</tr>
<tr>
<td>EG</td>
<td></td>
<td>0</td>
<td>0.946</td>
<td>11.6</td>
<td>70.1*</td>
<td>7.7</td>
</tr>
<tr>
<td>MST</td>
<td>iZ0.5</td>
<td>0</td>
<td>0.937</td>
<td>13.0</td>
<td>71.3</td>
<td>8.7</td>
</tr>
<tr>
<td>MST</td>
<td>iZ1</td>
<td>0</td>
<td>0.892</td>
<td>12.5</td>
<td>60.4</td>
<td>6.7</td>
</tr>
<tr>
<td>MST</td>
<td>iZ1</td>
<td>4</td>
<td>0.943</td>
<td>13.0</td>
<td>74.0</td>
<td>9.1</td>
</tr>
<tr>
<td>MST</td>
<td>iZ2.3</td>
<td>0</td>
<td>0.655</td>
<td>7.7</td>
<td>38.5</td>
<td>1.9</td>
</tr>
<tr>
<td>MST</td>
<td>iZ2.3</td>
<td>4</td>
<td>0.825</td>
<td>10.8</td>
<td>50.9</td>
<td>4.5</td>
</tr>
<tr>
<td>MST</td>
<td>iZ2.3</td>
<td>15</td>
<td>0.938</td>
<td>12.6</td>
<td>68.6</td>
<td>8.1</td>
</tr>
</tbody>
</table>

*The conductivity of IOH without the LPCVD ZnO cap layer drops after the dry etching of Si layers and after exposure to air, which might reduce the $FF$ of solar cells.
7.3 Results and discussion

Figure 7.5 (a) Schematic illustration of the inclination angle of ZnO pyramids on flat glass and etched glass. (b) The inclination angle distribution of EG and iZ1 deposited on flat glass as derived from AFM images. The inclination angle of iZ1 on EG cannot be directly obtained from AFM measurement due to the too large contrast in feature size between EG and iZ1.

The a-Si:H solar cells deposited on single-textured Z0.5, Z1 and Z2.3 4' on flat glass substrates all exhibit state-of-the-art performance. However, the superposition of as-grown pyramidal-textured ZnO layer on micro-textures deteriorates the performance of a-Si:H solar cells if no surface modification is made. As illustrated in Figure 7.5a, local facet inclination angles of the ZnO textures are significantly increased when the sharp pyramidal textures of ZnO are superposed on the micro-textured glass. Assuming the pyramid and textured glass have inclination angles of $\alpha$ and $\beta$, respectively, the inclination angle of the substrate $\theta$ will not change on flat glass and $\theta = \alpha$. If ZnO is deposited on EG, $\theta = \alpha - \beta$ for facet A (shallow slope) and $\theta = \alpha + \beta$ for facet B (steep slope), respectively. Considering the random orientation of the pyramids, the facet inclination angles will fall in the range $\alpha - \beta \leq \theta \leq \alpha + \beta$. Considering that the mean inclination angles of EG and iZ1 are 25 and 37 degree respectively as shown in Figure 7.5b, there is a considerable part of inclination angles in MST-iZ1 higher than 60 degree. As the facet inclination angles are increased, there will be several issues which can deteriorate the performance of thin-film silicon solar cells.
1. The thickness of the thin doped layers on MST substrates is severely inhomogeneous. On the surface with higher angles (e.g. facet B) the layer will be thinner, which can generate locally weak or even shunt diodes.

2. Nano- and micro-sized voids are formed in the deep valleys (formed due to the increased inclination angle), which can serve as recombination centers and form shunt paths.

3. Growth is faster on the top part of the pyramids and slower in the valleys, thus issues 1 and 2 are aggravated as the size of the pyramids become larger. This is why the performance of solar cells degrades quickly as the thickness of ZnO layer increases as shown in Table 7.2.

As shown in Figure 7.6, the sharp pyramidal structures are smoothened out after plasma treatment. As the treatment time is prolonged, the morphology becomes smoother, and the inclination angle \( \alpha \) then becomes smaller. As a result, the inclination angles of the MST substrate is expected to become smaller, which can promote the growth of homogenous high-quality a-Si:H cells on top, as indicated in Table 7.2.

![SEM images of MST-iZ1 subjected to various Ar-plasma treatment durations (0, 4, 8, and 15 min).](image)

**Figure 7.6** SEM images of MST-iZ1 subjected to various Ar-plasma treatment durations (0, 4, 8, and 15 min).
7.3.4 Modulated-surface-textured front electrodes for a-Si:H/nc-Si:H tandem solar cells

To evaluate the performance of the MST front electrode in multijunction solar cells, micromorph tandem (a-Si:H/nc-Si:H) devices were co-deposited on MST-iZ1 4’, on a flat layer stack made of glass/IOH/i-Z1 (denoted as FG-iZ1) and on state-of-the-art LPCVD ZnO on flat glass (referred to as Z2.3 4’ and Z2.3 15’). The corresponding characteristics of the solar cells are presented in Table 7.3 and Figure 7.7. The highest initial efficiency of 13.4% is obtained on MST-iZ1 4’, which represents an absolute gain of 2.0% and 1.1%, respectively, as compared to Z2.3 4’ and Z2.3 15’. The MST substrate also results in an 1.4% absolute efficiency gain compared to FG-iZ1.

Concerning the optical performance, all the substrates provide a high current density in the top cell ($J_{sc,top}>13.5$ mA/cm$^2$) due to the efficient light in-coupling and light trapping provided by the ZnO nano-structures. Z2.3 4’ results in a slightly higher $J_{sc,top}$ than the MST substrate which might be ascribed to the better interplay between the front texture and the n-SiO$_x$:H based intermediate reflector (SOIR) [34]. Note that identical $J_{sc,top}$ values were observed for Z2.3 4’ and MST-iZ1 4’ substrates when using an i-a-Si:H layer as thin as 250 nm and an SOIR layer with a lower refractive index (not shown here).

### Table 7.3 Photovoltaic performance of tandem solar cells deposited on different substrates in the initial and stabilized states. The thicknesses of the i-a-Si:H, SOIR, and i-nc-Si:H are 330 nm, 100 nm, and 2.5 µm, respectively.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$J_{sc}$ top/bottom</th>
<th>FF (%)</th>
<th>Eff (%)</th>
<th>$R_{oc}$ (Ωcm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FG-iZ1</td>
<td>Initial</td>
<td>1.402</td>
<td>11.4</td>
<td>13.6/11.4</td>
<td>75.1</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>Stabilized</td>
<td>1.370</td>
<td>10.9</td>
<td>12.7/10.9</td>
<td>66.2</td>
<td>9.9</td>
</tr>
<tr>
<td>MST-iZ1 4’</td>
<td>Initial</td>
<td>1.401</td>
<td>12.9</td>
<td>13.7/12.9</td>
<td>74.4</td>
<td>13.4</td>
</tr>
<tr>
<td></td>
<td>Stabilized</td>
<td>1.373</td>
<td>12.5</td>
<td>13.0/12.5</td>
<td>67.0</td>
<td>11.5</td>
</tr>
<tr>
<td>Z2.3 4’</td>
<td>Initial</td>
<td>1.371</td>
<td>11.5</td>
<td>14.1/11.5</td>
<td>72.1</td>
<td>11.4</td>
</tr>
<tr>
<td></td>
<td>Stabilized*</td>
<td>1.314</td>
<td>11.8</td>
<td>13.1/11.8</td>
<td>49.3</td>
<td>7.6</td>
</tr>
<tr>
<td>Z2.3 15’</td>
<td>Initial</td>
<td>1.394</td>
<td>11.9</td>
<td>13.5/11.9</td>
<td>74.0</td>
<td>12.3</td>
</tr>
<tr>
<td></td>
<td>Stabilized</td>
<td>1.371</td>
<td>11.9</td>
<td>12.7/11.9</td>
<td>67.9</td>
<td>11.1</td>
</tr>
</tbody>
</table>

*The performance of the cell on Z2.3 4’ is not stable in ambient condition due to the presence of high-density “cracks”, and thus abnormal degradation after light soaking is observed.
Figure 7.7 (a) EQE curves of the top and bottom cells of tandem cells on substrates Z2.3 4’, FG-iZ1, and MST-iZ1 4’, (b) summed EQE curves and 1-R spectra of tandem cells.

Regarding the light trapping in the bottom cell, MST-iZ1 4’ results in a higher EQE than Z2.3 4’ in the wavelength range 650-1100 nm. This improved EQE can be ascribed to the better light-trapping ability and/or higher transparency of the MST substrate, as suggested by the higher summed EQE and slightly lower 1-R. The higher EQE values above 800 nm also indicate that this specific MST substrate exhibits better light-trapping performance than other MST substrates reported previously in the literature [28-29,35]. In particular, the optimized micro-textured glass presented in section 3.1 provides excellent light trapping for the thick bottom nc-Si:H junction and thus a high summed photocurrent. From the cross-sectional SEM images in Figure 7.8, we can clearly see that the micro-textures of the glass are well maintained after the deposition of the ZnO layer and the top a-Si:H junction. The micro-textures are also well-preserved at the interface between Si and the metallic back reflector, which can improve the light-trapping performance. However, for the single-textured ZnO front electrode, the textures are somehow largely smoothened out after the deposition of a thick nc-Si:H layer, which, to some extent, reduces the light-trapping performance [36].
As for the electrical performance in the initial state, the solar cell deposited on the MST substrate has a $V_{oc}$ as high as the cell grown on FG-iZ1, such that it exceeds the $V_{oc}$ of the reference sample Z2.3 4' by 30 mV. It is difficult to directly compare the $FF$ values since they also depend on the current mismatch between the component cells. Even though with a smaller current mismatch, the cell on MST-iZ1 4' has a higher $FF$ than the cell on Z2.3 4'. By further smoothening the surface of Z2.3 (i.e. for Z2.3 15'), the $V_{oc}$ and $FF$ can be improved but still remain slightly below those obtained with MST-iZ1 4'. The high $V_{oc}$ and $FF$ values obtained with the MST substrate, even with a high deposition rate of the nc-Si:H absorber layer, clearly indicate that the MST front electrode here provides a suitable morphology for the growth of high-quality nc-Si:H layers. As seen in Figure 7.8, the small textures of Z1 on flat glass and on micro-textured glass are somehow smoothened out by the top a-Si:H junction and the SOIR, leaving mostly a smooth modulation at the surface of the SOIR. Very dense nc-Si:H absorber layers were grown on FG-iZ1 and MST-iZ1 4’ substrates without the formation of any obvious porous defective filaments. However, for the cell grown on Z2.3 4’ a high density of porous defective filaments is formed in the nc-Si:H layer, especially above the sharp V-shaped valleys. Those porous zones act as shunt paths and recombination sites for the charge carriers, which severely reduces the $V_{oc}$ and $FF$ of solar cells. Especially for high deposition rates, it was reported that a higher density of defective areas forms on sharp features as compared to the case of low deposition rates [15,23,24].
Figure 7.9 J-V curve of a tandem solar cell with the best initial efficiency achieved so far. The thicknesses of i-a-Si:H and i-nc-Si:H are 350 nm and 3 µm, respectively. A moth-eye nanostructured anti-reflective foil was attached directly on the glass to reduce the reflection at the air/glass interface.

By tuning the bandgap of the top cell absorber layer and the thickness of the SOIR and by optimizing the nc-Si:H bottom junction, we were able to further improve the initial efficiency up to 14.8% for tandem cells deposited on the MST substrates, as shown in Figure 7.9. The solar cell has a high $V_{oc}$ of 1.424 V, a $J_{sc}$ of 14 mA/cm$^2$ (with $J_{sc,top}$=14.0 mA/cm$^2$, and $J_{sc,bottom}$=14.4 mA/cm$^2$), and a high FF of 74.4%. The high efficiency is a result of the excellent combination of the highly efficient light management and the growth of high-quality TF-Si layers on the MST front electrode.

7.3.5 Toward high-stabilized-efficiency tandem solar cells with modulated-surface-textured front electrodes

The stabilized performance of solar cells is of crucial importance for practical applications. In Table 7.3 the stabilized performance of solar cells deposited on different substrates is presented. Overall, the cell on the MST substrate has the highest stabilized efficiency of 11.5% among all the samples. The $V_{oc}$ values after light soaking are similar among all cells other than the one deposited on Z2.3 4’. A similar degradation in $J_{sc}$ of the a-Si:H top cells ($J_{sc,top}$) is observed for all substrates. The $J_{sc}$ of the nc-Si:H bottom cells ($J_{sc,bottom}$) slightly degrades with FG-iZ1 and MST-iZ1 4’, but no degradation is observed with Z2.3 4’ and Z2.3 15’. The reasons for the degradation of $J_{sc,bottom}$ on FG-iZ1 and MST-iZ1 4’ substrates are not clear yet. Possible reasons are the decreased transparency of IOH and the non-doped ZnO layers under illumination in humid ambient condition and/or light-induced degradation in the nc-Si:H absorber layer. The cell on Z2.3 4’ substrate degrades beyond normal level, not only because of the light-induced degradation but also because of the high density of porous cracks in the nc-Si:H layer [37].

To obtain a higher stabilized efficiency, following additional modifications have been adapted with respect to the solar cells presented in Figure 7.9:
1. The thickness of the $i$-a-Si:H layer is reduced from 350 nm to 300 nm. An a-Si:H absorber layer with a lower bandgap and a thicker SOIR layer with a lower refractive index were used to ensure a high top cell current.

2. A high aspect ratio concave micro-lens structure (pitch of 9 µm and crater depth of 5 µm) [38] was replicated on the glass by UV nanoimprinting lithography (UV-NIL) to function as an effective anti-reflection coating (ARC). The micro-structured ARC can promote light trapping in the top cell. The preferential enhancement for the top cell, as indicated in Table 7.4, is helpful to obtain a higher stabilized efficiency due to a less top-cell limited device.

Finally, a high stable efficiency of 12.5% (cell area 1.1 cm$^2$) is achieved, as shown in Table 7.4 and Figure 7.10. The cell exhibits a very high summed current density value (28.6 mA/cm$^2$ and 27.8 mA/cm$^2$ before and after light soaking, respectively). The stabilized $J_{sc}$ of 13.9 mA/cm$^2$ is one of the highest reported values for a-Si:H/nc-Si:H tandem solar cells with a total absorber layers’ thickness below 3 µm.

![Figure 7.10](image-url) (a) $J$-$V$ and (b) EQE curves of tandem solar cells deposited on MST substrate before and after 1000h light soaking. The thicknesses of the $i$-a-Si:H, SOIR, and $i$-nc-Si:H layers are 300 nm, 100 nm, and 2.5 µm, respectively.


**Table 7.4** Photovoltaic performance of tandem solar cells deposited on an MST substrate in different states: with and without ARC before light soaking, and with ARC after 1000h light soaking. The $J_{sc}$ and Eff values in parentheses are directly obtained from the $J$-$V$ measurements.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$J_{sc}$ top/bottom</th>
<th>FF (%)</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o ARC</td>
<td>1.399</td>
<td>13.8 (14.0)</td>
<td>13.8/13.9</td>
<td>72.9</td>
<td>14.1 (14.3)</td>
</tr>
<tr>
<td>MST-iZ1 4'</td>
<td>ARC</td>
<td>1.399</td>
<td>14.1 (14.3)</td>
<td>72.1</td>
<td>14.2 (14.4)</td>
</tr>
<tr>
<td></td>
<td>Stabilized</td>
<td>1.377</td>
<td>13.9 (14.0)</td>
<td>65.5</td>
<td>12.5 (12.6)</td>
</tr>
</tbody>
</table>

### 7.3.6 Modulated-surface-textured front electrode for triple-junction solar cells

Similar to the application to tandem solar cells, modulated surface textures can also be superior to single-scale textures for triple-junction solar cells, due to a better trade-off between light management and electrical performance. In contrast to tandem solar cells, triple-junction devices commonly have a thinner high-bandgap a-Si:H absorber layer in the top cell. The “shunt” quenching SOIR is not used between the top and middle cells in triple-junction devices. The absorber layer in the top a-Si:H cell (as thin as around 100 nm) is much thinner than that in the tandem solar cell, making the triple-junction device more prone to generate shunt paths. Furthermore, the performance of high-bandgap a-Si:H solar cells is more sensitive to the substrate morphology than the low-bandgap a-Si:H solar cells used in tandem devices [7]. Therefore, the MST front electrodes optimized for tandem solar cells should be modified further when applied to triple-junction solar cells.

**Table 7.5** shows the performance of a-Si:H solar cells with a thin (140-nm-thick) high-bandgap absorber layer deposited on different substrates. The smooth single-scale textures of E-AZO and Z2.3 15' result in high $V_{oc}$ and FF values. However, for MST-iZ1 4', both $V_{oc}$ and FF drop significantly compared to the case of E-AZO. The optimized MST-iZ1 4' for tandem solar cells are thus not suitable anymore for triple-junction solar cells. If we increase the plasma treatment time up to 8 min, the sharp pyramidal structures can be etched further and become smoother than MST-iZ4, as shown in Figure 7.6. Correspondingly, the $V_{oc}$ and FF are improved significantly and are comparable to Z2.3 15'. Further increasing the treatment time can make the surface morphology even smoother but the light-trapping performance will decline.

To evaluate the performance of MST substrates, a-Si:H/nc-Si:H/nc-Si:H triple-junction solar cells were co-deposited on MST-iZ1 8' and on a state-of-the-art single textured LPCVD ZnO substrate (Z2.3 15', as detailed in Ref. [19]). Table 7.6 and Figure 7.11 present the photovoltaic performance and EQE spectra of solar cells on these two types of substrate. The MST substrate improves the efficiency by 0.5% absolutely as compared to Z2.3 15'. The cells on the two types of substrate have almost the same $V_{oc}$
Table 7.5 Photovoltaic performance of a-Si:H solar cells with a high-bandgap absorber layer deposited on different substrates. The device structure is $p$-SiO$_x$:H (16 nm)/$i$-a-Si:H (140 nm)/$n$-a-Si:H (20 nm)/Ag-Cr-Al.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>Effi (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-AZO</td>
<td>0.982</td>
<td>10.8</td>
<td>73.3</td>
<td>7.8</td>
</tr>
<tr>
<td>FG-iZ1</td>
<td>0.955</td>
<td>10.7</td>
<td>69.4</td>
<td>7.1</td>
</tr>
<tr>
<td>MST-iZ1 4’</td>
<td>0.862</td>
<td>10.7</td>
<td>50.6</td>
<td>4.7</td>
</tr>
<tr>
<td>MST-iZ1 8’</td>
<td>0.966</td>
<td>10.8</td>
<td>71.2</td>
<td>7.4</td>
</tr>
<tr>
<td>Z2.3 15’</td>
<td>0.972</td>
<td>10.9</td>
<td>74.1</td>
<td>7.8</td>
</tr>
</tbody>
</table>

values, while the FF of the solar cell deposited on MST is higher than that on Z2.3. The higher FF can be ascribed to a higher current mismatch and/or better material quality of the nc-Si:H absorber layers grown on the MST substrate. Concerning the optical performance, the MST substrate gives rise to a gain of 1.2 mA/cm$^2$ in summed photocurrent compared to the reference sample Z2.3 15’, indicating a superior light-trapping capability of MST substrates in triple-junction solar cells. The improvement in spectral response is mainly observed in the bottom junction, although a slight improvement in the top and middle junctions is measured as well. We also observe that the triple cells have a substantial loss in EQE at short wavelengths (400-600 nm) compared to other tandem devices shown in Figure 7.9 and 7.10, due to the additional optical losses in the doped layers ($n$-a-Si:H/$n$-nc-Si:H/$p$-SiO$_x$:H) between the top and middle junctions. Replacement of the $n$-a-Si:H/$n$-nc-Si:H layers with more transparent $n$-SiO$_x$:H might significantly reduce the parasitic loss in the doped layers. The results here indicate that MST front electrodes have a high potential to obtain high-efficiency triple-junction solar cells by further optimizing the current matching and silicon deposition conditions.

Table 7.6 Photovoltaic performance of a-Si:H/$n$-Si:H/$n$-Si:H triple-junction solar cells deposited on an MST substrate and a state-of-the-art LPCVD ZnO substrate. No ARC was applied on glass for devices here.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$J_{sc}$ top/middle/bottom</th>
<th>$J_{sc,total}$</th>
<th>FF (%)</th>
<th>Effi (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MST-iZ1 8’</td>
<td>1.869</td>
<td>8.7</td>
<td>9.53/8.73/9.84</td>
<td>28.10</td>
<td>74.8</td>
<td>12.2</td>
</tr>
</tbody>
</table>
Chapter 7 Highly transparent MST for multijunction solar cells

Figure 7.11 EQE curves of a-Si:H/nc-Si:H/nc-Si:H triple-junction solar cells deposited on MST substrate and state-of-the-art LPCVD ZnO substrate (Z2.3 15').

7.4 Conclusions

We proposed highly transparent front electrodes with modulated surface textures for superstrate multijunction TF-Si solar cells. The MST substrates comprise a micro-textured glass, a thin layer of highly transparent and conductive oxide IOH, and a thin layer of nano-textured ZnO. The superposition of small nano-textures from ZnO on the micro-textured glass forms the modulated surface textures. The crater-shaped micro-textured glass with feature size comparable to the thickness of solar cells can both provide efficient light trapping and enable the growth of high-quality Si materials in nc-Si:H solar cells. For application of MST substrates in multijunction solar cells, the surface morphology of as-grown ZnO should be modified to obtain high-performance a-Si:H solar cells deposited on top, according to the thickness and the bandgap of the absorber layer. The MST substrates result in a higher summed photocurrent than state-of-the-art LPCVD ZnO substrates in both tandem and triple-junction solar cells, due to the better transparency of the front electrodes and/or better light-trapping performance. Overall, multijunction solar cells deposited on the MST substrates have a higher efficiency than those on LPCVD-ZnO substrates, due to the superior light trapping and suitable morphology for the growth of high-quality silicon layers. A remarkable initial efficiency of 14.8% and a stabilized efficiency of 12.5% have been achieved in a-Si:H/nc-Si:H tandem solar cells with the highly transparent MST front electrodes, which indicates a high potential of these substrates for high-efficiency multijunction TF-Si solar cells in the future.
Appendix

Table 7.7 Details of the sample name for the front electrodes used in this chapter. FG: flat glass; EG: wet-etched textured glass. The front electrode has a structure of glass/ZnO (doped) or glass/IOH/ZnO (non-doped).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>glass type</th>
<th>IOH</th>
<th>ZnO doping</th>
<th>ZnO thickness (µm)</th>
<th>Ar treatment time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z2.3</td>
<td>FG</td>
<td>No</td>
<td>doped</td>
<td>2.3</td>
<td>0</td>
</tr>
<tr>
<td>Z2.3 4'</td>
<td>FG</td>
<td>No</td>
<td>doped</td>
<td>2.3</td>
<td>4</td>
</tr>
<tr>
<td>Z2.3 15'</td>
<td>FG</td>
<td>No</td>
<td>doped</td>
<td>2.3</td>
<td>15</td>
</tr>
<tr>
<td>Z5 45'</td>
<td>FG</td>
<td>NO</td>
<td>doped</td>
<td>4.5</td>
<td>45</td>
</tr>
<tr>
<td>FG-iZ1</td>
<td>FG</td>
<td>Yes</td>
<td>non-doped</td>
<td>1.0</td>
<td>0</td>
</tr>
<tr>
<td>FG-iZ1 4'</td>
<td>FG</td>
<td>Yes</td>
<td>non-doped</td>
<td>1.0</td>
<td>4</td>
</tr>
<tr>
<td>MST-iZ0.5</td>
<td>EG</td>
<td>Yes</td>
<td>non-doped</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>MST-iZ1</td>
<td>EG</td>
<td>Yes</td>
<td>non-doped</td>
<td>1.0</td>
<td>0</td>
</tr>
<tr>
<td>MST-iZ1 4'</td>
<td>EG</td>
<td>Yes</td>
<td>non-doped</td>
<td>1.0</td>
<td>4</td>
</tr>
<tr>
<td>MST-iZ1 8'</td>
<td>EG</td>
<td>Yes</td>
<td>non-doped</td>
<td>1.0</td>
<td>8</td>
</tr>
<tr>
<td>MST-iZ2.3</td>
<td>EG</td>
<td>Yes</td>
<td>non-doped</td>
<td>2.3</td>
<td>0</td>
</tr>
</tbody>
</table>

References


Chapter 8

Conclusions and perspectives of the thesis

8.1 Conclusions

The integration of effective light-trapping structure is of crucial importance to fabricate high-efficiency thin-film silicon solar cells. The light scattering leads to an increased photon-path length in the absorber layer of the solar cells and thus increases light absorption. Two types of light-trapping structures which can efficiently scatter the incident light have been investigated and fabricated in this thesis: plasmonic back reflectors and surface textured front electrodes. In addition, functional materials such as p-SiO$_x$ window layer, a-Si:H absorbers with tunable bandgap, and highly transparent conductive oxides have been developed. The combination of advanced materials and light management finally resulted in high-performance thin-film silicon solar cells, with a well-balanced trade-off between the light-trapping performance and the electrical performance of solar cells. The major conclusions of this thesis work are:

1. It has been experimentally demonstrated that plasmonic BRs based on self-assembled Ag NPs can provide light trapping performance comparable to state-of-the-art random textures in both a-Si:H and nc-Si:H single-junction solar cells as discussed in chapters 2-4. The conclusion is based on the comparison to high performance n-i-p solar cells. The plasmonic BR has a high haze in reflection in the wavelength range 520-1100 nm, providing efficient light trapping over broad spectral range. By self-assembling of Ag NPs at 400 °C, the high surface coverage and the formation of small and irregular particles can be avoided. The light trapping performance is improved by using a plasmonic BR with a broader angular scattering and a lower parasitic absorption loss. However, the unavoidable parasitic absorption in the plasmonic nanostructures hinders the practical application of plasmonic light trapping in thin-film silicon solar cell at the end. It is also challenging to integrated the plasmonic light-trapping structures in p-i-n superstrate-type thin-film silicon solar cells.

2. For the first time micro-textures obtained from wet-etched glass were investigated to mitigate the trade-offs between light-trapping and electrical performance in nc-Si:H solar cells in chapter 5. The micro-textures lead to higher $V_{oc}$ and FF than commonly used nano-textures in nc-Si:H solar cells. The $V_{oc}$ only drops from 564 to 541 mV as the i-layer thickness increases from 1 to 5 μm. The better electrical performance of nc-Si:H solar cells grown on micro-textures are attributed to the improved material quality. The smooth U-shaped craters and large opening angels are advantageous for the growth of dense nc-Si:H layers free from defective filaments. The well-designed
micro-textured substrates, which can provide both efficient light trapping and high $V_{oc}*FF$ product even in thick nc-Si:H solar cells, pave the road to very high efficiency multijunction solar cells.

3. High efficiency thin-film silicon multijunction solar cells require both high open-circuit voltage and high blue spectral response in the a-Si:H top cell. In chapter 6, mixed-phase p-SiO$_x$ films with varied oxygen content have been developed for the window layer in high $V_{oc}$ a-Si:H solar cells. The microstructure, optical and electrical properties are closely related to the oxygen content, which can be tuned through the CO$_2$/SiH$_4$ gas flux ratio. The p-SiO$_x$ films have strong phase separation and perpendicular growth character as revealed by the TEM measurements, enabling the adequate transverse conductivity despite of the very low planar conductivity. Compared to the standard p-SiC layer as window layer, p-SiO$_x$ improves both the $V_{oc}$ and $J_{sc}$ due to the higher bandgap and lower parasitic absorption loss in the p-layer. Finally, p-SiO$_x$ window layer was successfully applied to high performance multijunction TF-Si solar cells, leading to higher $V_{oc}$ and better blue spectral response than conventional p-SiC based window layer.

4. To further increase the efficiency of multijunction thin-film silicon (TF-Si) solar cells, highly transparent modulated-surface-textured (MST) front electrodes have been developed as light-trapping structures for TF-Si multijunction solar cells in chapter 7. The superposition of small nano-textures from LPCVD ZnO on the micro-textured glass forms the modulated surface textures. For application of MST substrates in multijunction solar cells, the surface morphology of as-grown ZnO should be modified to obtain high-performance a-Si:H solar cells deposited on top, according to the thickness and the bandgap of the absorber layer. The MST substrates result in a higher summed photocurrent than state-of-the-art LPCVD ZnO substrates in both tandem and triple-junction solar cells, due to the better transparency of the front electrodes and/or better light-trapping performance. Multijunction solar cells deposited on the MST substrates have a higher efficiency than those on state-of-the-art LPCVD-ZnO:B substrates, due to the superior light trapping and suitable morphology for the growth of high-quality silicon layers. Combining the high-performance a-Si:H solar cells developed in Chapter 6, a record high initial efficiency of 14.8% and a high stabilized efficiency of 12.5% have been achieved in a-Si:H/nc-Si:H tandem solar cells with the highly transparent MST front electrodes. The results here indicate a high potential of the MST substrates for high-efficiency multijunction TF-Si solar cells in the future.
8.2 Perspectives from the thesis

The aim of this thesis is to investigate and develop novel materials and light-trapping structures for thin-film silicon solar cells. In addition to the results and conclusions discussed in chapters 2-7, many ideas related to the thesis project came out. Here a short description on the perspectives from this thesis is given.

8.2.1 Flat light-scattering substrates based on plasmonic nanoparticles

In chapters 2-4, we have discussed that the light trapping in solar cells deposited on the plasmonic back reflectors is mainly ascribed to the light scattering by the Ag nanoparticles, not by the surface textures of such back reflectors. One method to experimentally verify this is to make the plasmonic back reflectors flat on surface, as shown in Figure 8.1. Here we refer this flat plasmonic back reflector to as plasmonic FLiSS (flat light-scattering substrate). In this structure, light scattering by the textured Si/TCO interfaces is excluded. Table 8.1 shows the performance of nc-Si:H solar cells co-deposited on the flat Ag/ZnO BR and the plasmonic FLiSS. There are indeed light trapping effects with the plasmonic FLiSS. However, the light-trapping performance is not as good as the textured Ag/ZnO BR. We should also note that here the coupling of plasmonic scattering into the absorber layer is less efficient than the case of rough plasmonic BR. Optical measurements in air show that the haze value and angular scattering of the plasmonic FLiSS are close to the non-polished plasmonic BR. The plasmonic FLiSS has a high haze value between 650 and 1200 nm, and it can scatter light into a broad angular distribution which is close to the Lambertian distribution. Further investigation on how to improve the light-trapping performance of plasmonic FLiSS in solar cells is needed.

<table>
<thead>
<tr>
<th>BR</th>
<th>Absorber thickness (µm)</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA/cm^2)</th>
<th>FF (%)</th>
<th>Effi (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat Ag</td>
<td>2.8</td>
<td>0.526</td>
<td>23.3</td>
<td>69.3</td>
<td>8.5</td>
</tr>
<tr>
<td>plasmonic FLiSS</td>
<td>2.8</td>
<td>0.528</td>
<td>25.0</td>
<td>71.9</td>
<td>9.5</td>
</tr>
<tr>
<td>Textured Ag</td>
<td>1.5</td>
<td>0.503</td>
<td>25.8</td>
<td>69.5</td>
<td>9.0</td>
</tr>
</tbody>
</table>
Chapter 8 Conclusions and perspectives

Figure 8.1 Schematic structure of plasmonic light-scattering reflector and light scattering coupled into the absorber layer in nc-Si:H solar cell deposited on top.

Flat light-scattering substrate is of great interest for high-efficiency TF-Si solar cells since it can give high-performance light trapping without sacrificing the electrical performance. Currently the conventional FLiSS is usually fabricated by filling the highly textured low-index ZnO substrate with high-index a-Si:H material, then polishing the layers stack to be flat. The light scattering is mediated through the rough ZnO/a-Si:H interfaces. However, such a conventional FLiSS has several disadvantages from the view of material cost and optical loss. Firstly, the deposition of a thick a-Si:H layer to entirely cover the textured ZnO structure will result in a considerably higher cost in materials and processing. Secondly, the thick dead a-Si:H layer can result in a considerable optical loss (at wavelengths between 600-800 nm) if the substrate is applied to TF-Si solar cells. The plasmonic FLiSS shown here avoids the high materials cost and optical loss of the dead a-Si:H layer in conventional FLiSS, while efficient light trapping can be realized through the strong scattering by metal nanoparticles.

8.2.2 Modulated-surface-textured front electrode for very high efficiency thin-film silicon solar cells with improved absorber layers

The absorber layers and silicon oxide intermediate reflector (SOIR) were not fully optimized for the multijunction solar cells shown in chapter 7, and the standard processing recipes in PVMD group were used. In the past year, enormous progresses have been made on more stable a-Si:H materials and high-quality dense nc-Si:H absorber layers. In addition, high-performance SOIR layers with a refractive index below 1.7 have been realized. Furthermore, the light-trapping performance of modulated-surface-textured (MST) front electrodes can be further improved by replacing the wet-etched glass with honeycomb textures, without sacrificing electrical performance of solar cells.
Such honeycomb textures are also feasible to apply to superstrate configuration by the mature UV-nanoimprinting (UV-NIL) technique as shown in Figure 8.2a. After coating with an IOH/iZ1 stack, the replica of honeycomb textures on glass forms the MST front electrode (denoted as HC-iZ1). As presented in Figure 8.2b, a high summed $J_{sc}$ of 29.1 mA/cm$^2$ in a-Si:H/nc-Si:H tandem cells was obtained with a nc-Si absorber layer of only 2.5 µm (co-deposited with the cells shown in Table 7.4 and Figure 7.10). By optimizing the honeycomb structures and by applying an ARC at the glass/TCO and TCO/Si interfaces, a summed $J_{sc}$ above 30 mA/cm$^2$ can be expected while keeping the absorber layers below 3 µm in tandem solar cells. The HC-iZ1 8’ substrate also resulted in a better performance and a higher summed $J_{sc}$ value in a-Si:H/nc-Si:H/nc-Si:H triple-junction solar cell, as indicated in Table 8.2.

![Figure 8.2](image_url)

**Figure 8.2** (a) AFM image of the replica of the honeycomb structures on glass (with a pitch of 2.5 µm and an aspect ratio of 0.22) and SEM image of the MST front electrode based on honeycomb structure (HC-iZ1). (b) EQE spectra of an a-Si:H/nc-Si:H tandem solar cell deposited on HC-iZ1 4’. The solar cells were co-deposited with the devices shown in Figure 7.10.
Table 8.2 Photovoltaic performance of a-Si:H/nc-Si:H/nc-Si:H triple-junction solar cells deposited on an HC-iZ1 8’ substrate and a state-of-the-art LPCVD ZnO substrate. All the cells were deposited in PVLAB at EPFL. An pyramidal-structured ARC was applied on glass for devices here. The absorber layer thicknesses in the middle and bottom junctions are 1.4 and 2.6 µm, respectively. Data in the first two rows was obtained after the equipments moving to the Microcity. After moving, performance of the a-Si:H and nc-Si:H solar cells were not as good as before the moving. For an indication, data of triple cell deposited on Z2.3 7’ substrate before the moving is also included here.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$J_{sc}$,top/middle/bottom</th>
<th>$J_{sc,total}$</th>
<th>FF (%)</th>
<th>Effi (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC-iZ1 8’</td>
<td>1.947</td>
<td>9.5</td>
<td>10.5/9.7/9.50</td>
<td>29.7</td>
<td>73.3</td>
<td>13.6</td>
</tr>
<tr>
<td>Z2.3 7’</td>
<td>1.940</td>
<td>8.5</td>
<td>10.6/9.4/8.5</td>
<td>28.5</td>
<td>74.9</td>
<td>12.3</td>
</tr>
<tr>
<td>Z2.3 7’</td>
<td>1.870</td>
<td>9.8</td>
<td>10.1/9.8/10.1</td>
<td>30.0</td>
<td>73.6</td>
<td>13.5</td>
</tr>
</tbody>
</table>

Combining with the high-quality a-Si:H and nc-Si:H absorber layers as demonstrated by AIST and Tel Solar, the high-performance SOIR and the MST front electrodes, a stabilized efficiency above 14% can be expected for tandem devices in the future (assuming $V_{oc}=1.41$ V, $J_{sc}=14.5$ mA/cm$^2$, and FF=70%). Note that higher stabilized $V_{oc}$ and FF values have already been achieved by AIST and Tel Solar for tandem cells deposited on very rough single-textured LPCVD ZnO substrates. It is also shown that a high $J_{sc,top}>15.5$ mA/cm$^2$ is achievable with a high-performance SOIR. For a-Si:H/nc-Si:H/nc-Si:H triple-junction solar cells, a high stabilized efficiency above 15% can also be expected with improvements in reference to the 13.4% record triple cell reported by LG (assuming $V_{oc}=2.04$ V, $J_{sc}=10.5$ mA/cm$^2$, and FF=72%). The $V_{oc}$ of 2.04 V in a triple-junction cell is realizable by considering a $V_{oc}$ of 1 V for the top a-Si:H cell and a $V_{oc}$ of 0.52V for each nc-Si:H subcell. A high $J_{sc}$ value of 33 mA/cm$^2$ has been reported for the nc-Si:H solar cells with a 4-µm-thick absorber layer, thus a $J_{sc}$ of 10.5 mA/cm$^2$ is a realistic objective. Considering a loss of ~7% from lab-to-fab (as the case for the record module of Tel Solar), module efficiencies of 13% and 14% can be expected for the tandem and triple-junction configurations, respectively.
8.2.3 The a-Si:H/organic hybrid solar cells: an approach for ultrathin high-efficiency thin-film solar cells

Since nc-Si:H is an indirect bandgap material, even with an effective light trapping a few micrometers in thickness is required for the nc-Si:H junction(s) to achieve high matched current density in a-Si:H/nc-Si:H and a-Si:H/nc-Si:H/nc-Si:H multijunction solar cells. The deposition time of the nc-Si:H subcells is a few times longer than the a-Si:H subcells, limiting the high throughput manufacturing. Moreover, the rather thick nc-Si:H layers also increases the materials cost, compared to the thin a-Si:H layers. One solution to reduce the cost and deposition time is to replace the nc-Si:H junctions with solution-processable low bandgap polymer solar cells, as shown in Figure 8.3. This approach combines the well-established a-Si:H technology and the solution-based processing of polymer solar cells. Due to the high absorption coefficient of both a-Si:H and polymer materials, the total absorber layers stack can be less than 1µm. One crucial advantage of this concept is that both types of solar cell can be processed on flexible substrates with the low cost roll-to-roll deposition technology. As presented in Figure 8.4, a high efficiency of 11.6% has been achieved in the hybrid tandem configuration with a total absorber layer thickness being less than 500 nm. By deploying the triple junction structure, a high efficiency of 13.2% has been obtained while the absorber layers stack is below 1µm. With further efforts on this technology, performance comparable to the traditional devices based on a-Si:H and nc-Si:H can be achieved while the total processing time is much shorter and the cost of manufacturing and materials is lower.
Figure 8.4 Dark and illuminated J-V curves of hybrid a-Si/OPV tandem and a-Si/a-Si/OPV triple-junction solar cells.
Summary

Direct conversion of sunlight into electricity is one of the most promising approaches to provide sufficient renewable energy for humankind. Solar cells are such devices which can efficiently generate electricity from sunlight through the photovoltaic effect. Thin-film silicon solar cells, a type of photovoltaic (PV) devices which deploy the chemical-vapor-deposited hydrogenated amorphous silicon (a-Si:H) and nanocrystalline silicon (nc-Si:H) and their alloys as the absorber layers and doped layers, are one of the promising PV technologies. Compared to other PV technologies, thin-film silicon solar cells have several important advantages such as the use of abundant and non-toxic materials, low processing temperature, short energy payback time and mature large-area manufacturing techniques. Despite the many advantages, thin-film silicon (TF-Si) technology is suffering from the drop in the PV market share due to the relatively low efficiency compared to c-Si, CIGS, and CdTe solar cells. This thesis is devoted to the development of advanced materials and novel light-trapping structures to increase the power conversion efficiency of thin-film silicon solar cells.

To achieve maximal light absorption in the absorber layers, implementation of light-trapping structures is crucial for thin-film silicon solar cells. The status of light-trapping techniques is briefly summarized in chapter 1, together with the background knowledge for thin-film silicon solar cells. To design an effective light-trapping scheme for solar cells, both the optical performance and the influence on the electrical performance of solar cells have to be considered. The light-trapping structure itself should not give additional parasitic absorption losses, or this loss should be minimized. The morphology of the light-trapping substrate should be suitable for the growth of high-quality materials. Meanwhile, absorption losses in the supporting layers such as front electrodes, doped layers, and back reflectors should be minimized.

In chapter 2, the fabrication of plasmonic back reflectors (BRs) based on self-assembled Ag nanoparticles and their application in a-Si:H solar cells are presented. It has been experimentally demonstrated that the optimized plasmonic back reflector can provide light trapping performance comparable to state-of-the-art random textures, without obvious deterioration of open-circuit voltage ($V_{oc}$) and/or fill factor ($FF$). This conclusion is based on the fair comparison with high performance $n$-$i$-$p$ solar cells and state-of-the-art $p$-$i$-$n$ solar cells deposited on Asahi-VU substrates.

The combined optical and electrical design of plasmonic back reflectors follows in chapter 3. The design rules of plasmonic back reflectors based on self-assembled Ag nanoparticles are discussed in detail. The shape of Ag NPs, the thickness of ZnO:Al spacer layers, materials on top of Ag NPs, and nanoparticle size are crucial for the performance of plasmonic BRs. By following the design rules, an 8.4% efficiency plasmonic a-Si:H solar cell has been achieved.

The application of the plasmonic back reflector in low bandgap nc-Si:H solar cells is discussed in chapter 4. The light trapping performance in nc-Si:H solar cells is improved
by using the plasmonic BRs with a broad angular scattering and low parasitic absorption loss through tuning the size of silver nanoparticles. The nc-Si:H solar cells deposited on the improved plasmonic BRs demonstrate a high photocurrent comparable to the one achieved by the state-of-the-art textured Ag/ZnO BR. The commonly observed deterioration of fill factor is avoided by using nc-SiOx:H as the n-layer for solar cells deposited on plasmonic BRs.

In chapter 5, micro-textures on glass with large opening angles and smooth U-shape morphology are proposed and applied to nc-Si:H solar cells for the first time. The micro-textures can provide both efficient light trapping and suitable morphology for the growth of high-quality nc-Si:H materials under a high deposition rate. A higher $V_{oc}$ and $FF$ can be achieved in reference to the cells using nano-textured substrates. For thick solar cells (i-layer thicker than 2 μm), high $V_{oc}$ and $FF$ values are maintained. Particularly, the $V_{oc}$ only drops from 564 to 541 mV as solar cell thickness increases from 1 to 5 μm. The use of micro-textures paves the road to develop multijunction solar cells with a higher efficiency as will be shown in chapter 7.

High-efficiency multijunction thin-film silicon solar cells require both high $V_{oc}$ and high blue spectral response in the top a-Si:H cell. In chapter 6, the mixed-phase p-SiOx films are investigated and used as window layer in high $V_{oc}$ a-Si:H p-i-n solar cells. The use of p-SiOx as window layer results in a higher $V_{oc}$ and a better spectral response than the standard p-SiC based window layer. Consequently, a-Si:H solar cells with $V_{oc} > 1$ V and $FF > 70\%$ have been obtained. A high initial efficiency of 14.4% has been achieved in a-Si:H/nc-Si:H tandem solar cells deposited on the Asahi-VU substrates.

Chapter 7 presents the implementation of highly transparent modulated-surface-textured (MST) front electrodes as light-trapping structures in multijunction TF-Si solar cells. The MST substrates comprise a micro-textured glass as developed in chapter 5, a thin layer of hydrogenated indium oxide (IOH), and a sub-micron nano-textured ZnO layer grown by low-pressure chemical vapor deposition (LPCVD ZnO). The MST front electrode has a good transparency and conductance, can provide efficient light trapping for each subcell and a suitable morphology for the growth of high-quality silicon layers. Efficiencies of 14.8% (initial) and 12.5% (stable) have been achieved for a-Si:H/nc-Si:H tandem solar cells with the MST front electrode and the high-performance a-Si:H top cells as developed in chapter 6, surpassing efficiencies obtained on state-of-the-art LPCVD ZnO.

A short summary of this thesis is given in chapter 8. Perspectives to further improve the performance of thin-film silicon solar cells are suggested and discussed. The light-trapping performance of modulated-surface-textured front electrodes can be further improved by replacing the wet-etched glass with honeycomb textures, without sacrifice in electrical performance of solar cells. The honeycomb textures can be easily applied to superstrate configuration by mature UV-NIL technique. In the end, the hybrid a-Si:H/organic multijunction device configuration is proposed to avoid the use of thick nc-Si:H solar cells. A high efficiency of 11.6% has been achieved in the hybrid tandem configuration with a total absorber layer thickness less than 500 nm. By deploying the triple-junction structure, a high efficiency of 13.2% has been obtained while the thickness of absorber layers stack is below 1μm. With further efforts on this concept, performance
comparable to the traditional devices based on a-Si:H and nc-Si:H can be expected while the total processing time is much shorter and the cost for manufacturing and materials is lower.
Samenvatting

De directe omzetting van zonlicht naar elektriciteit is één van de meest veelbelovende manieren om de mensheid van duurzame energie te voorzien. Zonnecellen gebruiken het fotovoltaïsche effect om op efficiënte wijze elektriciteit uit zonlicht te winnen. De dunne-film silicium zonnecel, waarvan de absorberende en gedoteerde lagen bestaan uit gehydrogeneerd amorf silicium (a-Si:H), nano-kristallijn silicium (nc-Si:H) of legeringen hiervan, is één van de meest veelbelovende PV technologieën. Het voordeel ten opzichte van de meeste andere PV technologieën is dat de materialen niet schaars of giftig zijn, geen hoge verwerkingstemperatuur nodig is, het een korte energie-terugverdientijd heeft en dat de benodigde techniek voor depositie op grote oppervlakken ver ontwikkeld is. Ondanks deze voordelen daalt het marktaandeel van dunne-film silicium zonnecellen door het relatief lage rendement ten opzichte van c-Si, CIGS en CdTe zonnecellen. Dit proefschrift behandelt de ontwikkeling van geavanceerde materialen en nieuwe structuren voor licht-opsluiting, die als doel hebben het rendement van dunne-film silicium zonnecellen te verhogen.

Om voldoende zonlicht te absorberen in de absorptielaag van dunne-film silicium zonnecellen zijn structuren voor licht-opsluiting cruciaal. **Hoofdstuk 1** geeft achtergrondinformatie over de dunne-film silicium zonnecel en vat de huidige stand van technieken voor licht-opsluiting samen. Bij het ontwerpen van een nieuwe methode voor licht-opsluiting moet rekening worden gehouden met zowel de optische prestaties als met de invloed op de elektrische prestaties. De structuur voor lichtopsluiting mag zelf niet of nauwelijks absorberen. De morfologie van de structuur voor lichtopsluiting moet geschikt zijn voor de depositie van hoogwaardige materialen. Tevens moeten de absorptieverliezen in de contacten, gedoteerde lagen en de achterzijde-reflecter, geminimaliseerd worden.

**Hoofdstuk 2** behandelt de fabricage van plasmonische achterzijde-reflectoren, gebaseerd op zelf-geassembleerde Ag nanodeeltjes, en de toepassing hiervan in a-Si:H zonnecellen. Experimenten tonen aan dat de geoptimaliseerde plasmonische achterzijde-reflectoren een niveau van licht-opsluiting bereikt die vergelijkbaar is met de beste willekeurige texturen. Hierbij treedt geen significante verslechtering op van de openklemspanning ($V_{oc}$) of fill factor (FF). Deze conclusie is gebaseerd op een eerlijke vergelijking van een efficiënte n-i-p zonnecel en de beste p-i-n zonnecel, gedeponeerd op een Asahi-VU substraat.

**Hoofdstuk 3** gaat dieper in op het gecombineerde optische en elektrische ontwerp van plasmonische achterzijde-reflectoren. Het ontwerptrject van plasmonische achterzijde-reflectoren, gebaseerd op zelf-geassembleerde Ag nanodeeltjes, wordt in detail besproken. De vorm en grootte van de Ag nanodeeltjes, de dikte van de ZnO:Al scheidingslaag en de materialen boven de Ag nanodeeltjes zijn cruciaal voor een goede prestatie van de plasmonische achterzijde-reflecter. Door dit ontwerptrject te volgen is een plasmonische zonnecel met een rendement van 8.4% verkregen.
De toepassing van de plasmonische achterzijde-reflector in nc-Si:H zonnecellen, met een lage bandgap, wordt in hoofdstuk 4 besproken. Door de grootte van de Ag nanodeeltjes aan te passen werd een plasmonische achterzijde-reflector verkregen met een bredere verstrooiing, lagere parasitaire absorptieverliezen en een betere lichtopsluiting. De nc-Si:H zonnecellen gedeponerd op deze verbeterde plasmonisch achterzijde-reflector leveren, vergeleken met de beste getextureerde Ag/ZnO reflector, een hoge stroom. Een verlaging van de fill factor kan worden voorkomen door een n-laag van nc-SiOx:H op de plasmonische achterzijde-reflector te deponeren.

In hoofdstuk 5 worden micro-texturen op glas met een grote openingshoek en U-vormige morfologie voorgesteld en voor het eerst toegepast in nc-Si:H zonnecellen. Deze micro-texturen bieden een efficiënte licht-opsluiting in combinatie met een morfologie die geschikt is voor de depositie van hoogwaardig nc-Si:H bij een hoge depositiesnelheid. In vergelijking met de conventionele nano-texturen levert dit een hogere $V_{oc}$ en FF op. Voor dikkere zonnecellen (> 2 μm), blijft deze hoge $V_{oc}$ en FF behouden. Wanneer de dikte van 1 naar 5 μm toeneemt daalt de $V_{oc}$ slechts van 564 naar 541 mV. Het gebruik van deze micro-texturen maakt de weg vrij voor multi-junctie zonnecellen met een hoger rendement, zoals hoofdstuk 7 laat zien.

Voor multi-junctie zonnecellen met een hoog rendement is een a-Si:H topcel nodig met zowel een hoge $V_{oc}$ als een hoge blauwrespons. In hoofdstuk 6 worden p-SiOx films onderzocht en gebruikt als vensterlaag voor a-Si:H zonnecellen. Vergeleken met het conventionele p-SiC geeft p-SiOx als vensterlaag een hogere $V_{oc}$ en een betere spectrale respons. Dit resulteert in a-Si:H zonnecellen met $V_{oc} > 1$ V en FF > 70%. Hierdoor bereikt een a-Si:H/nc-Si tandemzonneel, gedeponerd op een Asahi-VU substraat, een hoog initieel rendement van 14.4%.

Hoofdstuk 7 behandelt de implementatie van een hoog-transparant voorzijdecontact met een gemoduleerde oppervlakte textuur (MST) voor licht-opsluiting in multi-junctie dunne-film silicium zonnecellen. Dit MST voorzijde-contact bestaat uit glas met een micro-textuur, zoals beschreven in hoofdstuk 5, een dunne laag gehydrogeneerd indiumoxide (IOH) en een LPCVD ZnO laag met een nano-textuur. Dit MST voorzijdecontact is erg transparant en elektrisch geleidend. Tevens biedt het een efficiënte licht-opsluiting in iedere subcel en heeft het een morfologie die geschikt is voor de depositie van hoogwaardige silicium lagen. Door dit MST voorzijde-contact te combineren met de a-Si:H zonnecellen uit hoofdstuk 6 zijn a-Si:H/nc-Si:H tandem zonnecellen gemaakt met een rendement van 14.8% (initieel) en 12.5% (stabiel). Dit is hoger dan het rendement behaald met het beste LPCVD ZnO substraten.

Hoofdstuk 8 geeft een korte samenvatting van dit proefschrift. Ook worden perspectieven voor het verder verbeteren van dunne-film silicium zonnecellen besproken. Door het nat-geëtste glas te vervangen door een honingraattextuur kan de licht-opsluiting door het MST voorzijde-contact verder worden verbeterd zonder daarbij elektrische prestaties op te offeren. Met behulp van de bestaande UV-NIL techniek kan deze honingraattextuur eenvoudig worden toegepast in een superstraat configuratie. Tenslotte wordt er een hybride a-Si:H/organische multi-junctie configuratie voorgesteld die het gebruik van een dikke nc-Si subcel overbodig maakt. Deze hybride tandem-configuratie heeft een hoog rendement van 11.6% behaald met een totale absorptielaag-
dikte van minder dan 500 nm. Door drie juncties te gebruiken is zelfs een rendement van 13,2% behaald met een totale absorptielaa-dikte van minder dan 1 μm. Het ligt in de lijn der verwachting dat met verdere ontwikkeling dit concept een rendement bereikt dat vergelijkbaar is met dat van de traditionele op a-Si:H en nc-Si:H gebaseerde zonnecellen, bij een lagere kosten, fabricagetijd en materiaalverbruik.

(Translated by Dr. Rudi Santbergen)
List of publications

Journal publications related to the thesis


Co-authored journal papers


Selected publications prior to the PhD study


Oral presentations on international conferences


efficiency multijunction thin-film silicon solar cells, *The 6th World Conference on Photovoltaic Energy Conversion*, 2014, Kyoto, Japan. (*Young Researcher Award*)


**Other contribution to conferences**


**Invited lectures**

12/2014 “Advanced light management schemes for high-efficiency thin-film silicon solar cells”, *PVTEC-AIST*, Tsukuba, Japan

11/2014 “Modulated textured front electrodes for high-efficiency multijunction thin-film silicon solar cells”, *R&D of Kaneka Solar Energy company*, Osaka, Japan

11/2012 “Plasmonic light trapping for thin-film silicon solar cells”, *Nankai University*, Tianjin, China
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Hairen,  27th August, 2015
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**Curriculum Vitae**

Hairen Tan was born in JiangXi, China on 23rd of August 1986. From 2004 to 2008 he studied Materials Engineering at Central South University in Changsha, Hunan Province. In the final year of his BSc study, he became interested in semiconductor materials and devices. With this motivation, he continued the MSc study on semiconductor physics and devices in Institute of Semiconductors, Chinese Academy of Sciences from September 2008 and obtained the MSc degree in July 2011. There he developed the keen interest in solar cells and carried out the MSc project on solution-processed polymer solar cells.

In July 2011, Hairen started working as a PhD student in the Photovoltaic Materials and Devices group at Delft University of Technology in the Netherlands, under the supervision of Prof. Miro Zeman and Dr. Arno Smets. His PhD project was focused on developing advanced materials and novel light trapping structures for high-efficiency thin-film silicon solar cells. From September to November 2014, Hairen had a three-month research visit to the PVLAB group led by Prof. Christophe Ballif at EPFL, Neuchâtel, Switzerland.

In 2014, Hairen has been honored the **Young Researcher Award** on the 6th World Conference on Photovoltaic Energy Conversion to credit his contribution to the development of high-efficiency thin-film silicon tandem solar cells. Hairen has also received the 2013 **Chinese Government Award** for Outstanding Self-financed Students Abroad. In the past two years, Hairen has been active as reviewer for journals *Nano Letters*, *ACS Nano*, *Advanced Energy Materials*, *Solar Energy Materials and Solar Cells*, *Progress in Photovoltaics, Applied Physics Letters, Journal of Applied Physics, Nanoscales, Nano Energy, Optics Express*, etc. From October 2015, Hairen will continue his postdoctoral research in the group of Prof. Edward Sargent at the University of Toronto in Canada.